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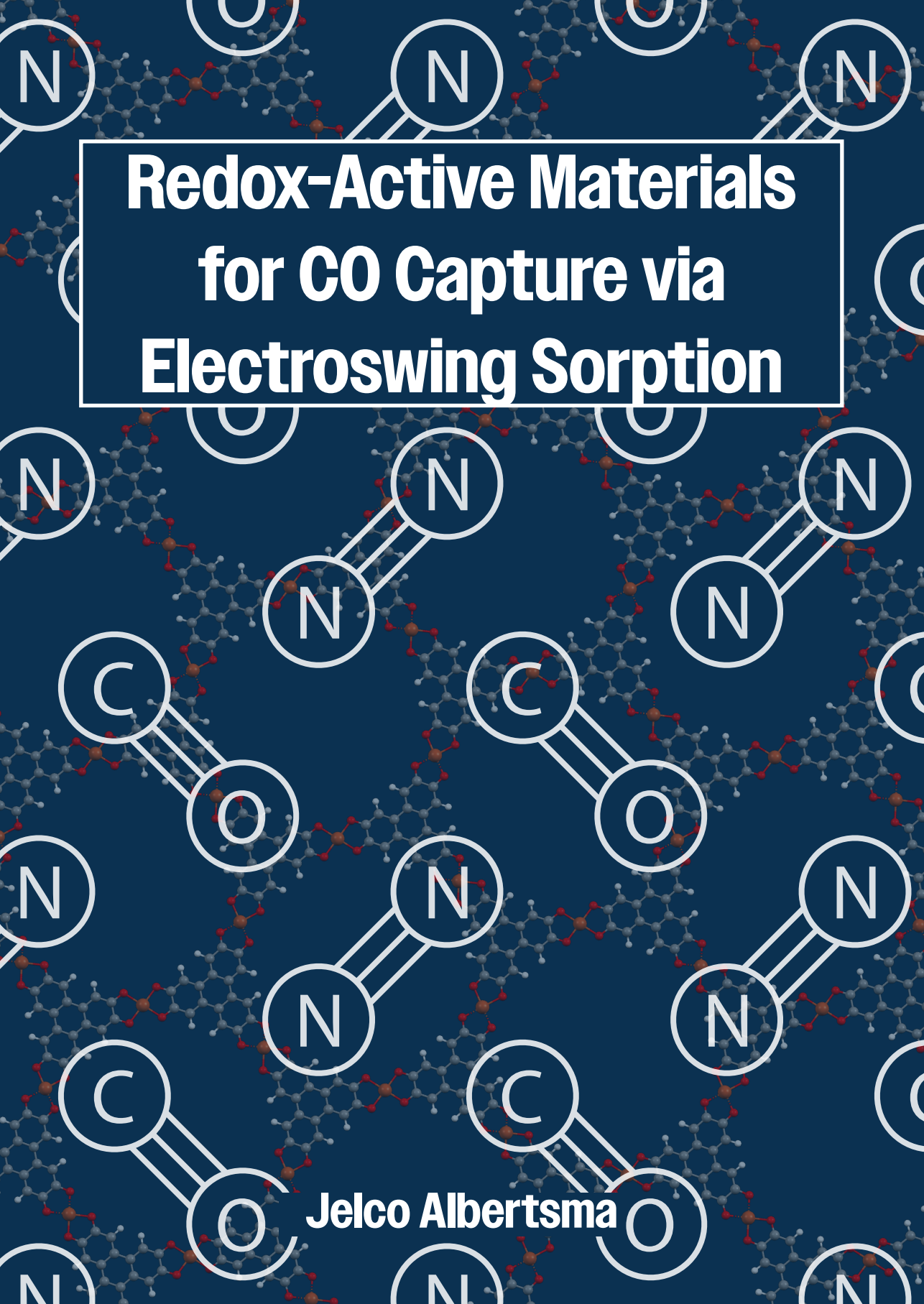
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The background is a dark blue field filled with a repeating pattern of molecular structures. These include ball-and-stick models of organic molecules with grey, red, and white atoms. Overlaid on these are numerous white circles containing the chemical symbols 'N' (Nitrogen) and 'C' (Carbon). Some of these circles are connected by double white lines, suggesting chemical bonds. The overall theme is chemistry and molecular science.

Redox-Active Materials for CO Capture via Electroswing Sorption

Jelco Albertsma

REDOX-ACTIVE MATERIALS FOR CO CAPTURE VIA ELECTROSWING SORPTION

REDOX-ACTIVE MATERIALS FOR CO CAPTURE VIA ELECTROSWING SORPTION

Dissertation

for the purpose of obtaining the degree of doctor
at Delft University of Technology
by the authority of the Rector Magnificus,
Prof. dr. ir. H. Bijl,
chair of the Board for Doctorates
to be defended publicly on
Thursday, 10 September 2026 at 10:00 o'clock

by

Jelco ALBERTSMA

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Contents

Summary	vii
Samenvatting	ix
1 Introduction	1
1.1 Relevance of carbon monoxide	2
1.2 Carbon monoxide and the metal-carbonyl bond	3
1.3 Electroswing sorption	4
1.4 Characterisation	5
1.5 Materials for CO electroswing sorption	8
1.6 Outline of thesis	8
2 Carbon Monoxide Separation	13
2.1 Introduction	14
2.2 Background (Industrial technologies for CO separation)	15
2.2.1 Physico-chemical properties of CO	15
2.2.2 The mechanisms of CO absorption and adsorption	17
2.2.3 Heme binding of CO and the influence of water on CO adsorption	19
2.2.4 Industrial technologies	20
2.3 Current developments in CO separation	35
2.3.1 Key factors that control the adsorption performance	36
2.3.2 Different types of solid adsorbents for CO adsorption	41
2.3.3 Progress in absorption and membranes for CO-separation	64
2.4 Traditional versus emerging CO sources	67
2.4.1 Traditional CO sources from industrial processes	67
2.4.2 Emerging non-traditional CO sources	69
2.4.3 CO capture after electrochemical reduction of CO ₂	71
2.5 Conclusions and outlook	73
3 Activation of Prussian Blue Analogues	95
3.1 Introduction	96
3.2 Experimental section	98
3.2.1 Materials	98
3.2.2 Synthesis of PBAs	98
3.2.3 Methods	98
3.3 Results and discussion	100
3.4 Discussion	110
3.5 Conclusion	111
3.A Appendix - Chapter 3	113

4	Redox-Switchable CO Affinity in Macrocyclic Complexes	129
4.1	Introduction	130
4.2	Methods	132
4.2.1	Computational details	132
4.2.2	Experimental details	133
4.3	Results & Discussion	133
4.4	Conclusion	145
4.A	Appendix - Chapter 4	146
5	Liquid Phase Exfoliation of CoHHTP and CuHHTP	153
5.1	Introduction	154
5.2	Theory	155
5.2.1	Liquid phase exfoliation	155
5.2.2	Mechanism of LPE	157
5.2.3	Parameter optimisation	157
5.2.4	Size separation	158
5.2.5	CoHHTP and CuHHTP	158
5.3	Experimental	159
5.3.1	Materials	159
5.3.2	Synthesis of CoHHTP	160
5.3.3	Synthesis of CuHHTP	160
5.3.4	Exfoliation of MHHTP MOFs	160
5.3.5	Characterisation	161
5.4	Results	161
5.5	Discussion	165
5.6	Conclusion	167
5.A	Appendix - Chapter 5	168
6	Conclusion & Outlook	181
	Acknowledgements	189
	Curriculum Vitæ	193
	List of Publications	195

Summary

Carbon monoxide (CO) is a ubiquitous byproduct from the chemical, steel, and energy industry, which is currently mainly burned for its heat of combustion or for safety reasons. This leads not only to a large emission of CO_2 , but is additionally wasteful, as CO is a valuable starting chemical for C1 chemical processes. Utilising this CO from waste streams would, therefore, make strides towards reducing anthropogenic CO_2 emissions and working towards a circular economy. The main reason why CO is currently not recycled in other chemical processes is the difficulty in separating it from N_2 , which is almost always present in these waste gas streams.

In Chapter 1 and 2, we discuss the current state-of-the-art in CO separation, both from an academic and industrial perspective. We show the achievements and limitations of using traditional swing sorptions based on temperature or pressure for CO as well as the materials developed for these processes. We conclude from this review that traditional methods and materials have shortcomings in selectivity and/or working capacity and are often sensitive to process-relevant conditions such as humidity. Thus, a novel separation method is necessary to make the CO/N_2 separation feasible with sufficient resulting CO purity and in a way that is economically viable.

To this end, we propose the usage of CO electroswing sorption. The swing sorption method uses electrochemistry to manipulate the binding affinity between CO and metal ions in coordination complexes. This method directly targets the electronic structure of the metal-carbonyl bond by changing the π -backbonding interaction strength through oxidation and reduction of the metal, unlike traditional methods based on temperature or pressure swings. However, for this technique to function, new materials are needed which have redox-active unsaturated metal sites which are capable of forming metal-carbonyl bonds.

One of the materials that could be used for this application is Prussian blue analogues, which are typically used in battery or electrocatalysis research. Chapter 3 discusses this class of materials in the context of in gas separation applications. Specifically, we show the process of synthesising and activating Prussian blue analogues in order to utilise the open metal sites dispersed within the material without compromising the crystallinity and (micro)porosity. This chapter highlights the difficulties in using microporous adsorbents with open metal sites in the presence of water, especially those caused by the competition for the open metal sites between water and CO as well as the overall difficulty of removing water from open metal sites.

In Chapter 4, a combined computational and experimental approach to investigate

the interaction of CO with Fe- and Co-based tetraphenylporphyrin and phthalocyanine complexes at various oxidation states is discussed. This chapter shows that the simple π -backbonding model cannot fully explain the switches in affinity in these complexes. It also shows that DFT screening is capable of predicting viable redox couples for CO electroswing absorption, while experiments are still required to verify the model and address any shortcomings therein.

Chapter 5 addresses the problem of accessing open-metal sites in 2-dimensional, semiconductive metal-organic frameworks (MOFs). In this chapter, attempts to exfoliate two hexahydroxytriphenylene-based MOFs are made using ultrasonication to allow access to the open-metal sites. It highlights the practical difficulties in obtaining thin 2-dimensional MOF sheets and discusses potential requirements for exfoliation in these materials to succeed.

Finally, Chapter 6 discusses the overall results presented in the thesis and offers an outlook for further research avenues, both in material development and other separations that could be achieved through electroswing sorption.

Samenvatting

Koolstofmonoxide (CO) is een alomtegenwoordig bijproduct uit de chemische, staal- en energie-industrie, dat momenteel voornamelijk verbrand wordt voor zijn verbrandingswarmte of om veiligheidsredenen. Dit leidt niet alleen tot een grote emissie van CO₂, maar ook tot verspilling, aangezien CO een waardevol reactant is voor C1 chemische processen. Het gebruikmaken van deze CO uit afvalstromen zou dus stappen zetten richting het reduceren van anthropogene CO₂ emissies en het verkrijgen van een circulaire economie. De hoofdreden waarom CO nu nog niet recycled wordt in andere chemische processen is de moeizame scheiding van N₂ die bijna altijd aanwezig is deze afvalgasstromen.

In Hoofdstuk 1 en 2 bediscussiëren we de huidige state-of-the-art in CO scheiding, zowel uit academisch als industrieel perspectief. We laten de prestaties en beperkingen van het gebruik van traditionele druk- en temperatuurwisselsorpties voor CO zien, alsmede de daarvoor ontwikkelde materialen. Wij concluderen uit deze evaluatie dat deze traditionele methodes en materialen tekortschieten in selectiviteit en/of werkcapaciteit en vaak gevoelig zijn voor procesrelevante condities zoals luchtvochtigheid. Een nieuwe scheidingsmethode is dus noodzakelijk om de CO/N₂ scheiding mogelijk te maken met voldoende CO zuiverheid als resultaat en op een manier die economisch haalbaar is.

Om dit te bewerkstelligen stellen wij het gebruik van CO elektrowisselsorptie voor. Deze wisselsorptiemethode maakt gebruik van elektrochemie om de bindingsaffiniteit tussen CO en metaalionen in coördinatiecomplexen te manipuleren. Deze methode richt zich direct op de elektronische structuur van de metaalcarbonylbinding door de interactiesterkte van de π -backbonding te veranderen door middel van oxidatie en reductie van het metaal. Dit is in tegenstelling tot traditionele methodes die gebaseerd zijn op druk- of temperatuurwissels. Voor deze techniek zijn, daarentegen, nieuwe materialen nodig met redoxactieve onverzadigde open metaalsites die in staat zijn metaalcarbonylbindingen te vormen.

Een van de materialen die gebruikt zou kunnen worden voor deze toepassing zijn de Pruisisch blauw analogen die normaal gesproken voor batterij- of elektrokatalyse-onderzoek worden gebruikt. Hoofdstuk 3 bediscussieert deze klasse van materialen in de context van gasscheidingstoepassingen. In het bijzonder laten we het proces van het synthetiseren en activeren van Pruisisch blauw analogen zien om gebruik te kunnen maken van de open metaalsites verspreid in dit materiaal zonder de kristalliniteit en (micro)porositeit aan te tasten. Dit hoofdstuk brengt de moeilijkheden van het gebruik van microporeuze adsorbentia met open metaalsites in het bijzijn van wa-

ter aan het licht. In het bijzonder worden de competitieve adsorptie tussen water en CO en de algemene moeilijkheid van het verwijderen van water van open metaalsites aangestipt.

In Hoofdstuk 4 wordt een gecombineerde computationele en experimentele aanpak gebruikt om de interactie van CO met Fe- en Co-gebaseerd tetraphenylporfyrine- en ftalocyaninecomplexen in verscheidene oxidatiestaten te bestuderen. Dit hoofdstuk laat zien dat het simpele π -backbondingmodel niet volstaat om de affiniteitsverandering in deze complexen uit te leggen. Het laat ook zien dat DFT doorlichting in staat is om potentiële redoxkoppels voor CO elektrowisselabsorptie te voorspellen, hoewel experimenten nog steeds nodig zijn om het model te verifiëren en eventuele tekortkomingen te adresseren.

Hoofdstuk 5 adresseert het probleem van toegang tot open metaalsites in tweedimensionale halfgeleidende metaal-organische roosters (MOFs). In dit hoofdstuk worden pogingen gedaan om twee hexahydroxytrifenyleen-gebaseerde MOFs te exfoliëren door middel van ultrasonication om toegang tot de open metaalsites te verkrijgen. Het benadrukt de praktische obstakels in het verkrijgen van dunne tweedimensionale MOF-vellen en behandelt de randvoorwaarden om exfoliatie in deze materialen te laten slagen.

Tenslotte wordt in Hoofdstuk 6 een discussie over de getoonde resultaten in het proefschrift behandeld evenals een vooruitblik op vervolgonderzoek zowel in de materiaalontwikkeling als in andere chemische scheidingen die met elektrowisselabsorptie zouden kunnen worden gerealiseerd.

Chapter 1

Introduction

1.1. Relevance of carbon monoxide

Carbon monoxide (CO) is commonly seen as a byproduct from heavy industry such as steel manufacturing, energy generation, or the petrochemical industry. [1–3] As a feedstock it is highly valuable and used in many industrially relevant processes such as the Fischer-Tropsch and water-gas shift reactions as well as being the starting point for a significant amount of C1 chemistry. [4]

However, most of the produced CO is not used as a feedstock, but rather burned for energy or to simply emit CO₂, which is less toxic, instead of CO. This way, 2.7% of the global CO₂ emissions are produced by the burning of CO from the steel industry alone. [5] The reason why this happens is the need for high purity CO for the aforementioned processes, [6] which currently cannot be achieved in recycling CO from mixed gases, mainly due to difficulty in separating CO from N₂. [4]

CO and N₂ are physically similar in size, density, and boiling point, meaning that typical large-scale separation methods, such as distillation or size-selective membrane separation, are not selective enough to yield high purity CO that is economically viable to produce. [4, 5] To achieve more selective separation, the use of affinity-based separation, which targets the electronic structure differences between CO and N₂, is required. Traditionally, this is done through absorption [7] or adsorption [2, 8, 9] using metal-carbonyl bonds, where swings in temperature and/or pressure lead to the binding and release of CO.

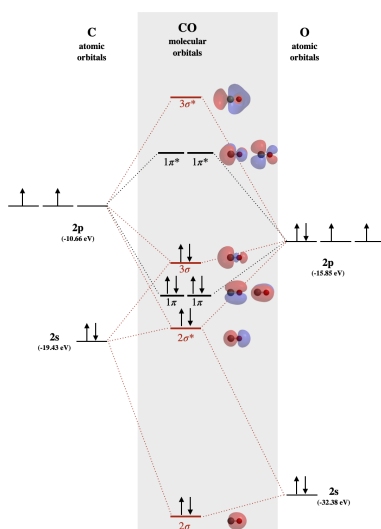


Figure 1.1 Molecular orbital diagram of carbon monoxide [10], CC BY-SA 4.0

1.2. Carbon monoxide and the metal-carbonyl bond

CO is a diatomic molecule of carbon and oxygen, which, at standard temperature and pressure, is a colourless, odourless gas. The carbon and oxygen in the molecule contribute 2 and 4 electrons, respectively, leading to the creation of a triple bond and the molecular orbitals as shown in Figure 1.1.

While CO is isoelectric with N_2 , which is inert under most circumstances, the unequal distribution of electrons donated to the triple bond cause a polarisation in the CO molecule. This causes the electron density to be more localised in the carbon atom as seen in the 3σ HOMO of CO, which also causes a slight negative charge in the carbon. This electron density on the carbon then allows for σ -donation to transition metals allowing for metal-carbonyl bonds.

However, the σ -donation is not the only mechanism that constitutes the metal-carbonyl bond. A second mechanism, the π -backbonding from the d-orbital of the metal into the $1\pi^*$ -orbital strengthens the metal-carbon bond, leading to the overall mechanism shown in Figure 1.2.

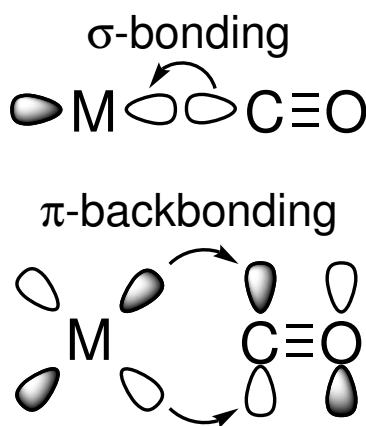


Figure 1.2 Schematic overview of the σ -bonding and π -backbonding interactions between a metal and CO.

The combined mechanism is synergistic in nature: the σ -donation enhances the π -backbonding and vice-versa. This synergism makes this bond attractive to modulate via electrochemical means due to the dependence on the π -backbonding of which the strength can easily be changed through the oxidation state of the metal ion.

1.3. Electroswing sorption

Electroswing sorption is a relatively new separation method, which relies on swings between binding and non-binding conditions using electrochemistry. Currently, electroswing adsorption is mostly researched in the context of CO₂ sorption. [11–13] In the case of CO₂, electroswing sorption functions by using the redox switchable affinity of CO₂ towards 1,4-anthraquinone [11–13] or related molecules. [14] Through reduction of the quinone, it is able to bind CO₂, while the oxidation again releases it (Figure 1.3). This process is highly selective towards CO₂ and has a high working capacity due to the binary binding mechanism. Additionally, the energy required for capture and release can directly be applied to the active site leading to a 30–80 kJ mol^{−1} CO₂ energy cost for this separation, [11] far lower than typical TSA and PSA energies which can still cost up to 200 kJ mol^{−1} CO₂ in optimised systems. [15] Furthermore, the electrochemical process is fast, with cycle times of 30 minutes, unlike typical temperature or pressure swing systems which can take hours to days to cool or depressurise.

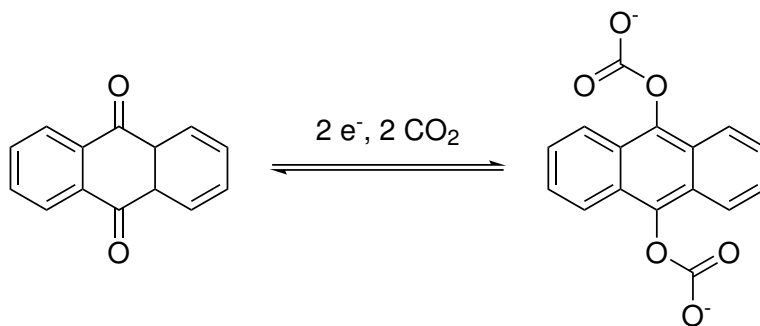


Figure 1.3 Overall two electron reduction reaction of 1,4-anthraquinone in the presence of CO₂

Due to the difficulties that currently exist in the separation of CO, especially separation from N₂, electroswing sorption is an attractive target technology. However, the mechanism is rather different from that of CO₂ electroswing, since CO generally does not undergo reversible electrochemical reactions with organic molecules. It is, however, possible to target metal-carbonyl species and their π -backbonding interaction since the strength of this interaction, and thus the overall binding strength, depends on the metal and its oxidation state. [16]

An early example of this interaction, was given by Terry et al. who produced a predecessor to electroswing sorption already in 1995. [17] Using the Cu⁺/Cu²⁺ redox couple in an acidic aqueous solution with a high Cl[−] concentration, they were able to concentrate CO from two gas bottles at 0.61 and 0.81 atm to a single bottle at 1.24 atm, leaving the other bottle at 0.07 atm, while maintaining the N₂ pressure in both bottles. This is an indication that electroswing sorption is an

interesting technique worthy of further investigation for separating CO from N₂.

1.4. Characterisation

After confirming the successful synthesis of a target compound with the desired properties (Section 1.5), a method is required to show the efficacy of electroswing sorption using this material under process relevant conditions. While the separation of CO/N₂ is the final goal of the electroswing sorption process, this process is lengthy to optimise and requires long measurements to assess the stability of the system. To validate if a material has potential for electroswing sorption, we need a simple measurement that shows whether the chosen material is redox active and shows changes in affinity towards CO.

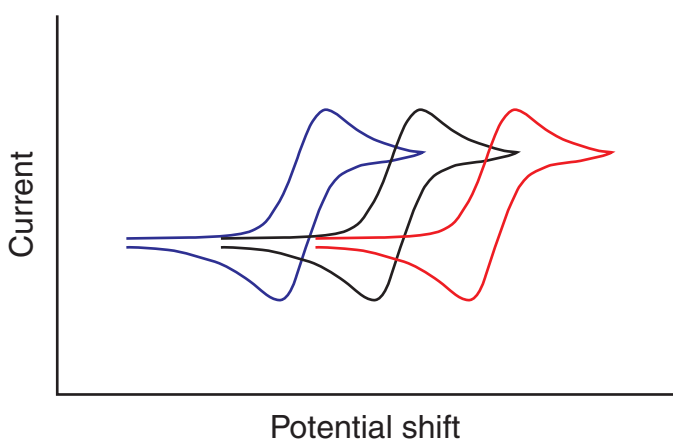
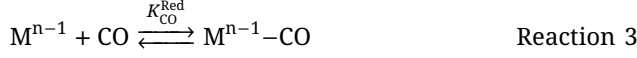


Figure 1.4 Schematic overview of the effect of the CO atmosphere on the shift of redox couples compared to the same redox couples under a N₂ atmosphere. Black line: redox couple has no interaction with CO. Red line: lower oxidation state binds more strongly to CO. Blue line: higher oxidation state binds more strongly to CO.

Fortunately, whether a material is capable of electroswing sorption with CO is easily proven through cyclic voltammetry using a N₂ and a CO atmosphere. The change in atmosphere can induce a shift in the location of the redox couple if the material interacts with CO. The direction of the shift to more positive or negative potentials depends on the oxidation state that binds more favourably, while the amount of the shift gives an indication of the ratio of equilibrium constants and, therefore, the binding energies with the complex. [18, 19] Schematically this difference is shown in Figure 1.4.

This behaviour can be thermodynamically deduced based on 4 governing equilibria, 2 chemical and 2 electrochemical:



Here, Reaction 1 shows the electrochemical equilibrium under standard conditions, Reactions 2 and 3 are the chemical equilibria between the metal and metal-carbonyl complex for the oxidised and reduced metal species, respectively, and Reaction 4 is the electrochemical equilibrium under CO.

For these equilibria the general equations for the Gibbs energy hold which lead to the Nernst equation.

$$\Delta G = \Delta G^0 + RT \ln(Q) \quad (1.1)$$

$$\Delta G^0 = -RT \ln(K_{eq}) \quad (1.2)$$

$$\Delta G^0 = -nFE^0 \quad (1.3)$$

$$E = E^0 - \frac{RT}{nF} \ln(Q) \quad (1.4)$$

Where ΔG and ΔG^0 are the Gibbs free energy of reaction and Gibbs free energy of reaction under standard conditions, respectively. Q is the reaction quotient and K_{eq} is the equilibrium constant. E and E^0 are the electrode potential and standard electrode potential, respectively. T and n are the temperature and number electrons, while R and F are the gas and Faraday constants, respectively.

We can then rewrite the Gibbs free energy for Reaction 4, using the respective ΔG^0 values, as

$$\Delta G_4^0 = \Delta G_1^0 - \Delta G_2^0 + \Delta G_3^0 \quad (1.5)$$

Which can be rewritten using Equation 1.2 as

$$\Delta G_4^0 = \Delta G_1^0 + RT \ln \left(K_{CO}^{Ox} \right) - RT \ln \left(K_{CO}^{Red} \right) \quad (1.6)$$

$$\Delta G_4^0 = \Delta G_1^0 + RT \ln \left(\frac{K_{CO}^{Ox}}{K_{CO}^{Red}} \right) \quad (1.7)$$

Combining Equation 1.3 and 1.7, we arrive at the equation for the standard electrode potential under CO.

$$E_4^0 = E_1^0 + \frac{RT}{nF} \ln \left(\frac{K_{\text{CO}}^{\text{Red}}}{K_{\text{CO}}^{\text{Ox}}} \right) \quad (1.8)$$

From Equation 1.8 we can clearly see that the electrode potential of the metal under CO changes depending on the ratio between the equilibrium constants of the oxidised and reduced metal with CO. In case these are equal, $E_4^0 = E_1^0$ follows, meaning no shift occurs. If $K_{\text{CO}}^{\text{Ox}} > K_{\text{CO}}^{\text{Red}}$, meaning the binding between CO and the oxidised species is stronger, this results in $E_4^0 < E_1^0$, meaning the potential shifts to lower values. If $K_{\text{CO}}^{\text{Ox}} < K_{\text{CO}}^{\text{Red}}$, the opposite is true, resulting in a shift to higher values of the electrode potential. This relatively simple measurement thus allows for the identification of redox couples of interest for the CO electroswing sorption process.

This derivation, however, only holds for reactions under standard conditions and does not necessarily lead to the same equation when converting to non-standard conditions due to different reaction quotients in Equation 1.1. This issue can, however, be resolved by starting from the Nernst equation with the standard formal electrode potential $E^{0'}$ for Reaction 1 and 4 and the equilibrium constants for the binding of CO to the ions in different oxidation states. [20]

$$E_{\text{M}^n/\text{M}^{n-1}} = E_{\text{M}^n/\text{M}^{n-1}}^{0'} + \frac{RT}{nF} \ln \left(\frac{[\text{M}^n]}{[\text{M}^{n-1}]} \right) \quad (1.9)$$

$$E_{\text{M}^n\text{-CO}/\text{M}^{n-1}\text{-CO}} = E_{\text{M}^n\text{-CO}/\text{M}^{n-1}\text{-CO}}^{0'} + \frac{RT}{nF} \ln \left(\frac{[\text{M}^n\text{-CO}]}{[\text{M}^{n-1}\text{-CO}]} \right) \quad (1.10)$$

$$K_{\text{CO}}^{\text{Ox}} = \frac{[\text{M}^n\text{-CO}]}{[\text{M}^n][\text{CO}]} \quad (1.11)$$

$$K_{\text{CO}}^{\text{Red}} = \frac{[\text{M}^{n-1}\text{-CO}]}{[\text{M}^{n-1}][\text{CO}]} \quad (1.12)$$

By rearranging Equations 1.11 and 1.12 in terms of $[\text{M}^n]$ and $[\text{M}^{n-1}]$, respectively, and plugging these into Equation 1.9, we obtain a Nernst expression for M-CO complexes:

$$E_{\text{M}^n\text{CO}/\text{M}^{n-1}\text{CO}} = E_{\text{M}^n/\text{M}^{n-1}}^{0'} + \frac{RT}{nF} \ln \left(\frac{\frac{[\text{M}^n\text{-CO}]}{K_{\text{CO}}^{\text{Ox}}[\text{CO}]}}{\frac{[\text{M}^{n-1}\text{-CO}]}{K_{\text{CO}}^{\text{Red}}[\text{CO}]}} \right) \quad (1.13)$$

$$= E_{\text{M}^n/\text{M}^{n-1}}^{0'} + \frac{RT}{nF} \ln \left(\frac{K_{\text{CO}}^{\text{Red}}}{K_{\text{CO}}^{\text{Ox}}} \right) + \frac{RT}{nF} \ln \left(\frac{[\text{M}^n\text{-CO}]}{[\text{M}^{n-1}\text{-CO}]} \right) \quad (1.14)$$

Comparing Equations 1.10 and 1.14, we find

$$E_{M^nCO/M^{n-1}CO}^{0'} = E_{M^n/M^{n-1}}^{0'} + \frac{RT}{nF} \ln \left(\frac{K_{CO}^{Red}}{K_{CO}^{Ox}} \right) \quad (1.15)$$

This is similar to the result obtained in Equation 1.8 without the stringent requirements of standard conditions, either through the standard formal potential itself or Equation 1.9.

1.5. Materials for CO electroswing sorption

In order to be able to use electroswing sorption for CO separation, materials with specific properties are needed. In particular, the materials should have, at the very least, redox active, unsaturated metal sites with a change in affinity towards CO in the different oxidation states. Typically, the streams in which CO is present are also humid, such as water-cooled blast furnace gas, meaning stability in the presence of water is required. Similarly, to simplify handling, the material should preferably be air stable. For adsorption, there is also the additional need for some electrical conductivity in the material to reduce Ohmic losses and achieve the redox chemistry on the active sites.

This is a difficult list of properties to satisfy simultaneously. In the case of electroswing adsorption, the need for electrical conductivity as well as air and water stability immediately invalidates all current state-of-the-art materials used in CO separation since most are based on insulating metal-oxides or metal-organic frameworks (MOFs) and/or impregnation with air and water sensitive CuCl (Table 2.3). This necessitates the search for either more exotic new materials or older materials that can satisfy the required properties with some modification, such as those developed for other applications, e.g., batteries or electrocatalysis.

For absorption, there are some known candidate complexes which show redox switchable binding with CO: CuCl [17], Ni(cyclam)Cl₂ [21, 22], and metal-porphyrins [23, 24]. However, the list of materials is limited and it is unclear why certain complexes do show redox-switchable affinity while others do not, highlighting the need for more theoretical investigation of the underlying causes as well as expansion of the material space.

1.6. Outline of thesis

The aim of this thesis is to study materials which can be used for the separation of CO using electrochemically modulatable metal-carbonyl bonds. To achieve this, we review the state-of-art in CO separation in **Chapter 2**. It shows the need of having selective CO separation, specifically from inert gases such as N₂, to allow for feasible conversion of CO into useful chemicals. Typical mechanisms used to

bind CO selectively over N_2 as well as problems with classical separation methods are highlighted using examples from both industrial and academic sources. Lastly, we offer some potential future applications which will benefit from more effective CO separation as well as showing some of the shortcomings in current research.

Chapter 3 deals with the application of Prussian blue analogues, a porous material typically used in electrochemistry, in gas separation applications. Specifically, it entails the process of synthesising and activating Prussian blue analogues in order to utilise the open metal sites dispersed within the material without compromising the crystallinity and (micro)porosity. This chapter shows the difficulties in using microporous adsorbents with open metal sites in the presence of water caused by the competition for the open metal sites between water and CO as well as the overall difficulty of removing water from open metal sites.

Chapter 4 shows the combined computational and experimental approach to investigate the interaction of CO with Fe- and Co-based tetraphenylporphyrin and phthalocyanine complexes at various oxidation states. This chapter shows that the simple π -backbonding model cannot fully explain the switches in affinity in these complexes. It also shows that the computational screening is capable of predicting viable redox couples for CO electroswing absorption, while experiments are still required to verify the model and address any shortcomings therein.

Chapter 5 tackles the problem of accessing open-metal sites in 2-dimensional, semiconductive metal-organic frameworks (MOFs). In this chapter, attempts to exfoliate two hexahydroxytriphenylene-based MOFs are made using ultrasonication to allow access to the open-metal sites. It highlights the practical difficulties in obtaining thin 2-dimensional MOF sheets and discusses potential requirements for exfoliation in these materials to succeed.

Finally, **Chapter 6** discusses the overall results presented in the thesis and offers an outlook for further research avenues, both in material development and other electrochemically targettable separations.

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Chapter 2

Carbon Monoxide Separation: Past, Present, and Future

Large amounts of carbon monoxide are produced by industrial processes such as biomass gasification and steel manufacturing. The CO present in vent streams is often burnt, this produces a large amount of CO₂, e.g., oxidation of CO from metallurgic flue gases is solely responsible for 2.7 % of manmade CO₂ emissions. The separation of N₂ from CO due to their very similar physical properties is very challenging, meaning that numerous energy-intensive steps are required for CO separation, making the CO separation from many process streams uneconomical in spite of CO being a valuable building block in the production of major chemicals through C1 chemistry and the production of linear hydrocarbons by the Fischer-Tropsch process. The development of suitable processes for the separation of carbon monoxide has both industrial and environmental significance. Especially since CO is a main product of electrocatalytic CO₂ reduction, an emerging sustainable technology to enable carbon neutrality. This technology also requires an energy-efficient separation process. Therefore, there is a great need to develop energy efficient CO separation processes adequate for these different process streams. As such the urgency of separating carbon monoxide is gaining greater recognition, with research in the field becoming more and more crucial. This review details the principles on which CO separation is based and provides an overview of currently commercialised CO separation processes and their limitations. Adsorption is identified as a technology with the potential for CO separation with high selectivity and energy efficiency. We review the research efforts, mainly seen in the last decades, in developing new materials for CO separation via adsorption and membrane technology. We have geared our review to both traditional CO sources and emerging CO sources, including CO production from CO₂ conversion. To that end, a variety of emerging processes as potential CO₂-to-CO technologies are discussed and, specifically, the need for CO capture after electrochemical CO₂ reduction is highlighted, which is still underexposed in the available literature. Altogether, we aim to highlight the knowledge gaps that could guide future research to improve CO separation performance for industrial implementation.

This chapter is based on: Ma, X.*; **Albertsma, J.***; Gabriels, D.; Horst, R.; Polat, S.; Snoeks, C.; Kapteijn, F.; Eral, H. B.; Vermaas, D. A.; Mei, B.; de Beer, S.; van der Veen, M. A., Chemical Society Reviews, 2023, **52**, 3741-3777.

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2.1. Introduction

Carbon monoxide (CO) is an important component for chemical reactions such as the water-gas shift, Fischer-Tropsch, methanol synthesis, steel making in blast furnaces and the Koch reaction. Additionally, it is a key reactant for the synthesis of various organic chemicals (Figure 2.1), e.g., light hydrocarbons fuels, methanol, acetic acid, metal carbonyls, phosgene and oxo-alcohols) [1]. Besides the use of CO as feedstock for the chemical industry, CO can be employed as direct product as well. For example, in food packaging [2] and as a therapeutic agent in clinical applications [3, 4]. For these applications, a CO gas stream of either high purity (>99 mol%) or in a well-defined ratio with other gases is needed. These CO gas streams are currently produced by energy intensive processes such as steam methane reforming or autothermal reforming of methane, and consecutive purification.

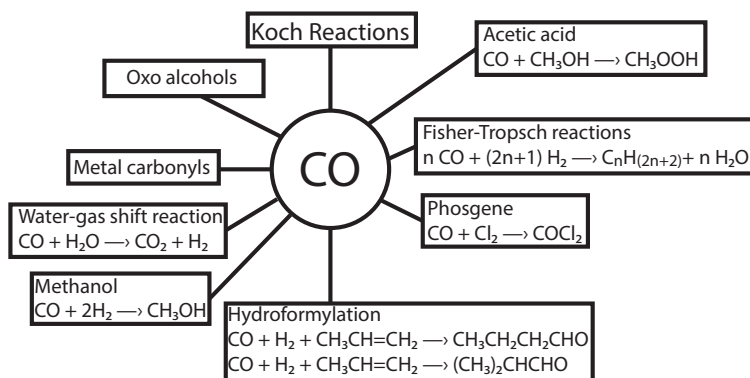


Figure 2.1 The utilisation of CO in chemical industry.

Next to being an important feedstock, CO is a common by-product. Large amounts of CO are produced during steel manufacturing, petroleum refining or fossil fuel combustion. When captured, this CO could be a copious resource. However, the manufactured CO is usually present in a complex mixture with other gases (e.g., CO_2 , CH_4 , N_2 , H_2 , H_2S and other sulfur compounds, etc.), which makes the separation of CO energy and cost intensive. Especially the separation of N_2 and CO is not straightforward, due to the very similar physical properties of these molecules regarding molecular mass, size and boiling point, such that classical separation technologies cannot be utilised. This has hampered the reuse of CO as a resource material [5]. Instead, the CO-containing mixtures are currently burnt for their caloric value, while producing significant quantities of CO_2 . Thus, by developing economically viable separation technologies that allow for reuse of the CO byproduct, important feedstock is generated, and CO_2 emissions are reduced. The development of these separation technologies is, however, challenging.

Given the intrinsic limitations for separating CO based on weight, size or

boiling point, researchers are designing new materials and processes that enable separation by affinity-based adsorption [6–8]. The development of adsorption-based CO separation technologies will not only be key in the transition to a circular economy, it can be utilised in other applications as well, such as in sensing [9] or in emerging technologies such as electrocatalytic and photocatalytic reduction of CO_2 . In the latter, the continuous separation of CO will likely contribute to the yield and overall efficiency of the process, which in-turn will further promote establishing a carbon neutral society [10]. Recently NASA developed a new instrument, called the MOXIE, which can convert carbon dioxide into oxygen and carbon monoxide to provide enough breathable oxygen on Mars and to make fuel for the return journey to earth [11]. For safety reasons, these products need to be carefully separated and CO adsorbents can capture the last traces of CO. Thus, all in all, the separation of CO has a profound significance.

The present article aims to give a holistic review on the current state-of-the-art of different technologies for CO separation. Although a great deal of research has been conducted, an in-depth overview of the current progress in the field is still missing. Previous reviews concerning CO adsorption have either covered numerous related adsorbates (e.g., different types of gases to separate) [6] or only focused on a single type of solid adsorbent (e.g., metal-organic frameworks) [7, 8] or more comprehensive, but with a large focus on dispersion of CuCl on porous support. [12]. Our review aims to take a rounded analysis and systematic comparison of the different separation techniques for CO, comparing the different types of commercialised CO separation techniques (Section 2) with the current state-of-the-art is research on CO separation via absorption, adsorption and membrane separations (Section 3). Via this comparison and by discussing the separation needs of existing CO-containing streams, as well as emerging CO streams (e.g., via electrocatalytic reduction of CO_2), we can pinpoint current research gaps, and make recommendations. We anticipate that this review will provide inspiration for future discoveries of solid CO adsorbents, with a focus on the needs of future technologies.

2.2. Background (Industrial technologies for CO separation)

2.2.1. Physico-chemical properties of CO

Separation methodologies are primarily based on differences in physico-chemical properties between components. Common industrial examples for gas separations include differences in relative volatility seen in distillation, the interaction strength or binding energy in adsorption, and solubility in absorption and membrane separation. For CO, these separation processes can incur significant costs as some gases are difficult to separate from CO. To understand the nature of this difficulty, some physical and chemical properties of CO in relation to other gas molecules are illustrated below.

Under normal atmospheric conditions, CO is a colourless, tasteless and odourless gas. The CO molecule consisting of one carbon atom and one oxygen atom, yielding a total of 10 valence electrons. Those electrons are distributed as defined by the octet rule, where four shared electrons originate from the oxygen atom and two from the carbon atom. The resulting triple bond consists of 2 π -bonds and 1 σ -bond that is *sp*-hybridised, with a length of 112.82 pm [13] and a bond association energy of 1.070 MJ/mol [14]. Two electrons derived from the oxygen atom in one of the bonding orbitals form a dipolar bond, causing polarisation within the molecule. Moreover, the difference in electronegativity between the carbon and oxygen atom, 2.55 and 3.44 respectively on the Pauling scale [15], leads to an unequal charge distribution within the molecule. These two characteristics and the asymmetrical geometrical nature of the CO molecule, together, give rise to a relatively small electric dipole moment. The solubility of CO in water is very poor and becomes almost negligible above 340K. It is, however, easily soluble in compounds like chloroform, ammonium, hydroxide, benzene and ethanol.

Table 2.1 provides an overview of the physical property data of CO and components commonly found in CO containing gas mixtures. It follows from the data that separation of CO from H₂ and CO₂ should be feasible based on significant differences in boiling point or the kinetic diameter. However, the separation of CO from N₂ will be more challenging as their boiling points (81.6 K vs. 77.4 K) and kinetic diameter (3.76 Å vs. 3.64 Å) hardly differ. Separating these two gases based on physical principles would require extreme process conditions to reach the desired gas purity, though separations based on the difference in dipole and quadrupole moment are feasible, as well as on their difference in electronic structure (see Section 2.2.2). The choice of separation principle is clearly constrained by the gas composition.

Table 2.1 Physical property data [16–18]

Compound	Molecular weight [g/mol]	Kinetic diameter [Å]	Normal boiling point [K]	Density (298 K, 1 atm) [kg/m ³]	Polarizability [10 ²⁵ cm ³]	Dipole moment [D]/[10 ³³ C·m]	Quadrupole moment [10 ²⁰ C·m ²]
CO	28.02	3.69	81.66	1.145	19.5	36.6	8.35
CO ₂	44.01	3.30	216.55	1.808	26.5	0	14.4
H ₂ O	18.01	2.65	373.15	997	14.5	556	-
H ₂	2.02	2.827-2.89	20.27	0.089	8.042	0	2.2
N ₂	28.01	3.64-3.80	77.35	1.1606	17.407	0	5.08
CH ₄	16.04	3.758	111.66	0.657	25.93	0	0
H ₂ S	34.08	3.623	212.84	1.36	37.82-39.5	293	-

2.2.2. The mechanisms of CO absorption and adsorption

Adsorption and absorption separation processes are based on the difference in interaction energy or binding energy on a surface or in a solvent. Commonly two types are distinguished: physical and chemical absorption, and for adsorption, physisorption and chemisorption.

Physical absorption and physisorption.

Physical absorption and physisorption are the ab/adsorption processes defined by weak physical interactions which only slightly perturb the electronic structure of the ab/adsorbate, which means there is no chemical bonding [19]. Examples of these weak non-covalent interactions are Van der Waals forces and π - π interactions. Both of these interactions are possible with CO: Van der Waals forces are universal and CO is known to interact with aromatic rings through π - π interactions [20]. The heats of physisorption and physical absorption range from -10 to -40 kJ/mol. These processes usually follow Henry's law, meaning that the temperature dependent equilibrium concentration is proportional to the partial pressure, and the ab/adsorbate does not react with the solvent or adsorbents. Because uptake is higher at high partial pressures, pressurising of the feed is the main source of energy consumption, making physical absorption or physisorption generally uneconomical when ab/adsorbate feed concentration is under 15% [21]. To regenerate the loaded ab/adsorbent, heat is provided, pressure is reduced or a combination of both.

Chemical absorption and chemisorption.

Chemical absorption and chemisorption are characterised by changes in the electronic structure of bonding atoms or molecules and results in a chemical interaction between the ab/adsorbent and the ab/adsorbate. The bonds can be covalent, coordinative or ionic in character. The heats of chemisorption range from -80 to -400 kJ/mol. These processes are preferred when the ab/adsorbate concentration or partial pressure in the feed is low. For chemical absorption, the liquid phase is chosen in a way that the equilibrium favours the formation of the intermediate complex. Two types of chemical absorption are distinguished: reversible and irreversible absorption. In reversible absorption the solvent can be regenerated using heat or pressure changes, in the second case the bonded intermediate is essentially irreversible and is commonly applied for trace amounts to be absorbed and where marginal exit concentrations are required. In chemisorption and chemical absorption, the ad/absorption rate can be slow, leading to a long time to reach the uptake equilibrium. The rate increases with an increase in temperature, but often disfavours the equilibrium uptake.

Chemisorption and chemical absorption are based on the chemical interaction of the target molecule and the ad/absorbent determined by the electronic structure of both. Therefore, the electronic structure of CO is essential for its binding

mechanism to metals and metal ions [22] (Figure 2.2). In CO, the oxygen atom supplies four electrons to the C-O triple bond, causing an uneven electron density distribution in the molecular orbitals. The oxygen becomes slightly positively charged, and the carbon slightly negatively charged. The HOMO-1 molecular π bonding orbitals of CO (π_x and π_y) are concentrated on the oxygen atom, while the HOMO bonding σ_C orbital as well as the LUMO antibonding π^* orbitals (π_x^* and π_y^*) are concentrated on the carbon atom. The electronic structure causes the preference of binding through the carbon atom onto metals, as the σ_C orbital can form a σ -bond with one of the empty d -subshell orbitals of the metal through electron donation. Furthermore, the metal can also back-donate electrons from its d -orbital to the π^* antibonding orbitals of CO perpendicular to the bond axis. This back-donation weakens the internal C-O bond, due to the filling of the antibonding π^* orbitals, but strengthens the bond between the metal and CO.

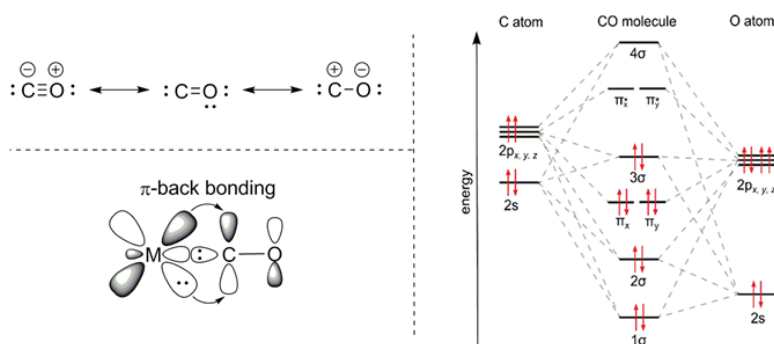


Figure 2.2 Electronic structure of CO and its binding scheme with transition metals. The π -backbonding occurs due to the donation of d -orbital electrons to the π^* -orbitals of CO, π_x^* and π_y^* . Reprinted from [23], Copyright (2019) with permission from Elsevier.

Spin crossover. An effect that can be utilised to influence the chemisorption of CO is spin crossover (Figure 2.3). When ligands are bound to metal atoms, the symmetry of the d -orbitals is broken due to interaction with said ligands. This symmetry breaking causes a change in the energy of the individual d -orbitals, resulting in a splitting of the levels. Depending on the number of ligands and the symmetry of the ligands around the metal several level splittings can occur, such as octahedral and tetrahedral level splitting. If a metal contains four to seven electrons in its d -subshell multiple spin states can exist due to the allocation of electrons to the various levels. The metal can either be in a low spin state in which the total spin of the complex is minimised or in a high spin state in which the total spin is maximised. Which spin state is the most stable depends on the magnitude of the splitting parameter and the energy penalty for pairing two electrons in the same d -orbital. The splitting parameter itself depends on the type of metal and its charge, as well as the ligands surrounding the metal. A crowded

metal ion will generally favour a high spin configuration as indicated by high spin metal ions having longer metal-ligand bond lengths [24]. When the difference in energy between the splitting energy and the pairing energy is small, spin crossover can occur wherein the complex can change between spin states. Generally, such spin crossover effects are observed in octahedral complexes as therein the splitting parameter is larger, allowing for a more accessible low spin state.

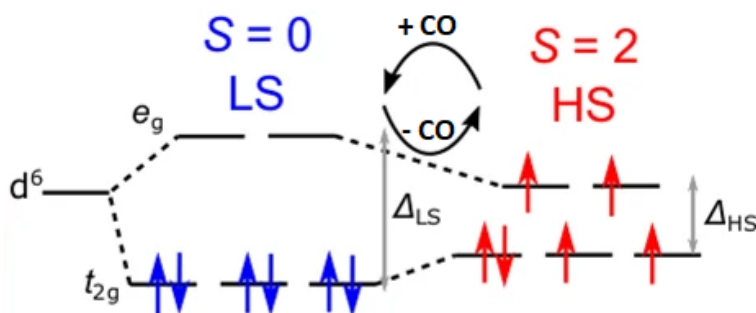


Figure 2.3 Schematic of the spin crossover effect caused by the adsorption of CO onto unsaturated octahedral d^6 metal sites. Figure reprinted from [25] with modifications with permission from Springer Nature, copyright 2015.

This spin crossover can be utilised to influence the chemisorption of CO. CO can accept electrons through its π^* antibonding orbitals which are higher in energy than the d -orbitals of the metal. This electron accepting character of CO will increase the splitting parameter if it chemisorbs to a metal. This increase in the splitting parameter can lead to a change from the high spin state to the low spin state resulting in a stronger CO bond.

2.2.3. Heme binding of CO and the influence of water on CO adsorption

Many of the process streams from which CO is to be separated are humid streams. Especially in the case of chemisorption and chemical absorption, water can cause instability of the CO-metal ion complex (see Section 2.4.1), meaning this humidity needs to be removed before the separation process, which is economically unfavourable. In this regard, the binding of CO to hemoproteins, which happens in aqueous conditions, deserves consideration.

The high toxicity of CO, causing the dysfunction of hemoproteins (e.g., hemoglobin, myoglobin and cytochrome c oxidase) that are indispensable for carrying or consuming O_2 , is due to the formation of a stable complex called

carboxyhemoglobin. This complex is over 200 times stronger than the hemoglobin complex with oxygen [26], which causes a deficit of oxygen in the tissue of the exposed organism over time.

2

In the carboxyhemoglobin complex, the binding with CO distorts the d orbitals of the Fe^{2+} . The CO binds to a site in line with the z -axis. The original t_{2g} orbitals, d_{xy} , d_{xz} , and d_{yz} , are split in energy due to the stabilising of the d_{xz} and d_{yz} orbitals, while the e_g orbitals remain at the same energy level. These new levels are all concentrated on the metal centre, while the π^* orbitals increase in energy and are concentrated on the CO ligand. As already established, the σ_c molecular orbital forms a bond with a d -orbital from the metal, d_{z^2} in the example with the CO in line with the z -axis, which is called a donation interaction. However, the metal can also back-donate electrons to CO into the empty π^* orbitals. These π -interactions strengthen the M-C bond while simultaneously weakening the C-O bond due to the filling of the antibonding orbitals. Due to π -back bonding, the carbon atom of CO interacts strongly with Fe(II) in hemoproteins with high stability. What is even more interesting is that the reversible CO binding in hemoproteins can hardly be impacted by the presence of water, which is rarely seen in CO adsorbents. The reason is that the native hemoproteins protect the heme site with apolar amino acids which form a solvent penetration barrier, reduce the size of the cavity, and form a hydrophobic pocket which reduces the occurrence of the water-catalyzed autoxidation of the Fe(II) to Fe(III) porphyrins [27]. On top of these protection mechanisms, it was also found that the binding energy of water with Fe-porphyrin-imidazole, a complex which is used as a simple model for the heme site, was found to be more than 20 kJ/mol lower than that the binding of the same complex with CO [28], making CO the statistically more likely adsorbate. Perhaps development of new CO capture approaches can take a clue from nature. For instance, haemoglobin utilises a strategy called allostery to optimise its CO_2 binding capacity by going through significant conformational changes [29]. The overarching idea of leveraging stereochemistry of cooperative effects in allostery, higher efficiency CO binding can also be achieved. Notably, a synthetic supramolecular compound composed of an Fe(II)porphyrin and a cyclodextrin dimer has been demonstrated to reversibly bind to CO at ambient temperatures [30].

2.2.4. Industrial technologies

In this Section current commercial separation strategies are evaluated and discussed for their application for carbon monoxide capture at industrial scale. Technologies that are discussed are based on cryogenic distillation, absorption, membrane separation and adsorption [31]. The most suitable technique is very often dependent on feed conditions and compositions and on the required end-product specifications. The advantages and disadvantages of each technology are introduced and compared.

Cryogenic distillation.

Cryogenic distillation is the dominant industrial technology used to obtain pure gas species from gaseous mixtures. The separation process is based on the relative volatilities of the components in the mixture using the effective vapour pressures to extract one or several components from the mixture [32]. The cryogenic range begins when so-called permanent gases (N_2 , O_2 etc.) start to liquefy around -150°C . The reason to chill gases to these low temperatures is that phase changes start occurring, and separation can be performed based on differences in condensation and sublimation point. Based on this principle, high purity oxygen and nitrogen ($> 99.9\%$) are obtained in air separation [33] and, in a similar manner, CO_2 can be captured from flue gases with 99.99% purity and recovery [34]. These examples indicate the possibilities to obtain a high quality product by cryogenic processes.

There are two types of cryogenic process used in commercial industry to separate carbon monoxide from gas mixtures containing H_2 : low-temperature partial condensation cycle and liquid methane wash [35]. For both cases, traces of contaminants such as water and CO_2 that could freeze in the unit can cause clogging problems. Hence, they must be eliminated from the feed gas by a pretreatment procedure: the process gas is initially dried in a molecular sieve adsorber station. Separation of CO and N_2 using a cryogenic distillation process is not performed since these two gases have a close boiling temperature (CO: 81.55 K; N_2 : 77.35 K at atmospheric pressure) [36].

The low-temperature partial condensation process. Partial condensation cycle operates with gas mixtures (e.g., from partial oxidation) supplied at high pressure, with high CO, H_2 and low CH_4 concentration [35]. This process utilises the difference in the boiling points of the main components of the feed gas. In the separation procedure (Figure 2.4) the feed gas first enters a warm exchanger and is cooled against the cold product stream. It is further cooled down by using its heat to reboil the CO/ CH_4 splitter. In the warm separator, the liquefied CO and CH_4 are separated from the hydrogen vapour. The separated hydrogen vapour is cooled down in the cold exchanger and enters a cold separator. In this separator most of the remaining CO in the hydrogen vapour will be condensed and separated from the vapour. The CO liquid flow is used as a reflux in the CO/ CH_4 splitter. The H_2 vapour collected overhead from this cold separator flows through the cold exchanger to be heated up. After that it is cooled down by expansion and then warmed up in both the cold and warm exchanger by absorbing the heat. The hydrogen vapour product recovered from the process has a purity of 98%. The CO and CH_4 containing liquid from the bottom of the warm separator are reduced in pressure and dropped in temperature by a throttle valve. Hereafter, some remaining hydrogen gas is further removed from the CO and CH_4 liquid stream in the flash separator. The hydrogen vapour from the flash separator is rewarmed, compressed, and recycled back to the incoming feed to recover more CO from the stream. The liquid from the flash separator containing mostly carbon monoxide

and methane flows into the CO/CH₄ splitter, which acts as a distillation column, and is rewarmed. Carbon monoxide vapour flows out of the splitter and warmed up in both exchangers with a purity of 98-99%. In order to use CO in a downstream process, compression of the CO product stream is necessary. The remaining liquid containing methane and carbon monoxide leaves the splitter through the bottom, whereafter it is heated up and exit the process as a reformer fuel.

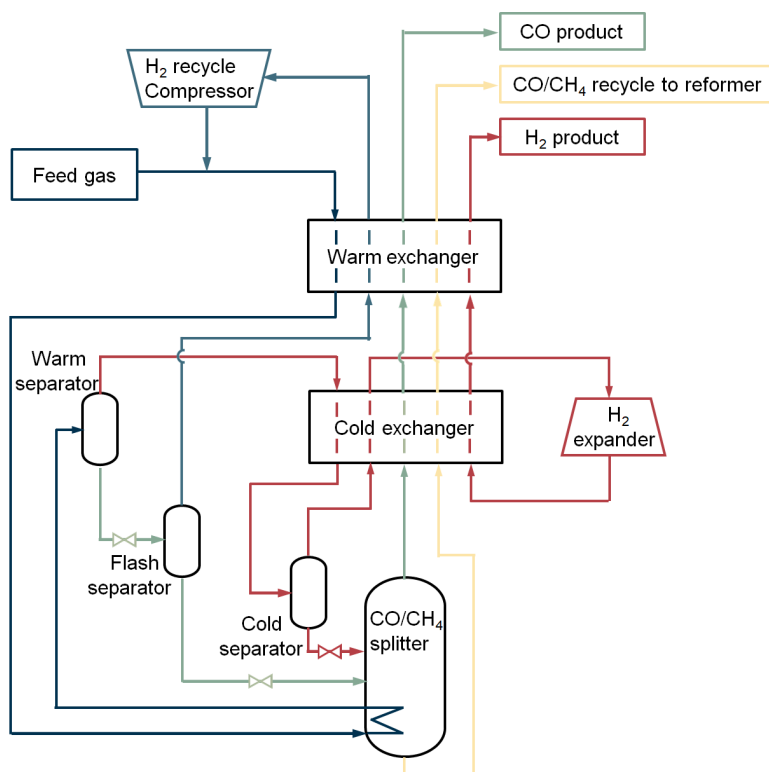


Figure 2.4 Low-temperature partial condensation process. Figure based on process scheme from Dutta et al. [31].

The partial condensation cycle process has a carbon monoxide recovery of 75-80%. Due to uncondensed carbon monoxide in hydrogen vapour and leftovers in the methane flow, a 100% yield is not reached. The total capacity of the system is 55000 Nm³/h product CO. The operating expenditures (OPEX) to keep the process running is 18-100 kWh/tonne CO product. Most energy is consumed by the pretreatment, pressurisation of the feed, H₂ recycle compressor and the H₂ expander. In addition, it may be assumed that some energy is used to provide extra cooling in case the refrigeration system falls short. Other costs are dependent on the quality of the feed gas, the required purity and pressure of the CO product.

The liquid methane wash process. Liquid methane wash process operates with low pressure feed gases, for instance gas mixtures from steam reforming. The feed gas usually contains a low CH_4/CO ratio and a high CH_4 concentration. The feed gas is pretreated by removing residual water and CO_2 before entering the system with a pressure of approximately 1.5-3.5 MPa [32].

Figure 2.5 is a representation of a liquid methane wash process. The feed gas is cooled down through the main exchanger to a temperature of 93 K and enters the wash column at the bottom. CO and CH_4 are liquefied through this process, while the hydrogen remains as vapour. To prevent losses of carbon monoxide in the hydrogen vapour, the rising hydrogen gas is washed with a cooled methane refluxing in the wash column. This liquid methane reflux enters the column via the top and washes the carbon monoxide out of the hydrogen gas. The hydrogen vapour is heated up in the main exchanger and leaves the system as a product with a purity of 99% (with small amount of methane (1-1.5%)). The liquid containing mostly CO and CH_4 flows out of the wash column, whereafter it is preheated immediately followed by cooling down the dissolved gas through expansion in the flash column. The generated vapour leaving this column, consisting of hydrogen dissolved in methane, is rewarmed and recovered as a fuel product. Similarly, a cooled methane reflux enters into the flash column and washes the gas vapour to reduce the carbon monoxide loss. The liquid from the flash column, which is free of hydrogen, is heated and flashed into the warmed CO/ CH_4 splitter. Carbon monoxide vapour flows out of the splitter at the top. After this it is rewarmed and compressed. A part of the stream will leave the system as a CO product with a purity of 99%, the other part will be cooled and flows back as a recycle stream. This recycle stream firstly reboils the CO/ CH_4 splitter and warms up the heaters, secondly it is cooled down by expansion in a throttle valve. The carbon monoxide condensate is used as a reflux in the splitter. The methane liquid in the splitter is pumped into the wash and flash column to serve partly as cooled reflux stream. The remaining methane liquid is heated up and leaves the system as fuel gas.

The liquid methane wash cycle has a high carbon monoxide recovery of 99%. The total capacity of the system is 34000 Nm^3/h product CO. The OPEX in this process is 300-600 kWh/tonne. The energy is consumed by the pretreatment, pressurisation of the feed, preheaters, the CO product compressor, methane pump and extra cooling for the system if the refrigeration system falls short. Quality of the feed gas, purity and pressure of the CO product determine the other economic costs.

Concluding remarks. The advantages of cryogenic distillation are well-known, some include high maturity of the process, no need to introduce additional components and the ability to produce high purity products combined with minimal losses of product [37].

Although this technology has the advantage of economy of scale, capital and

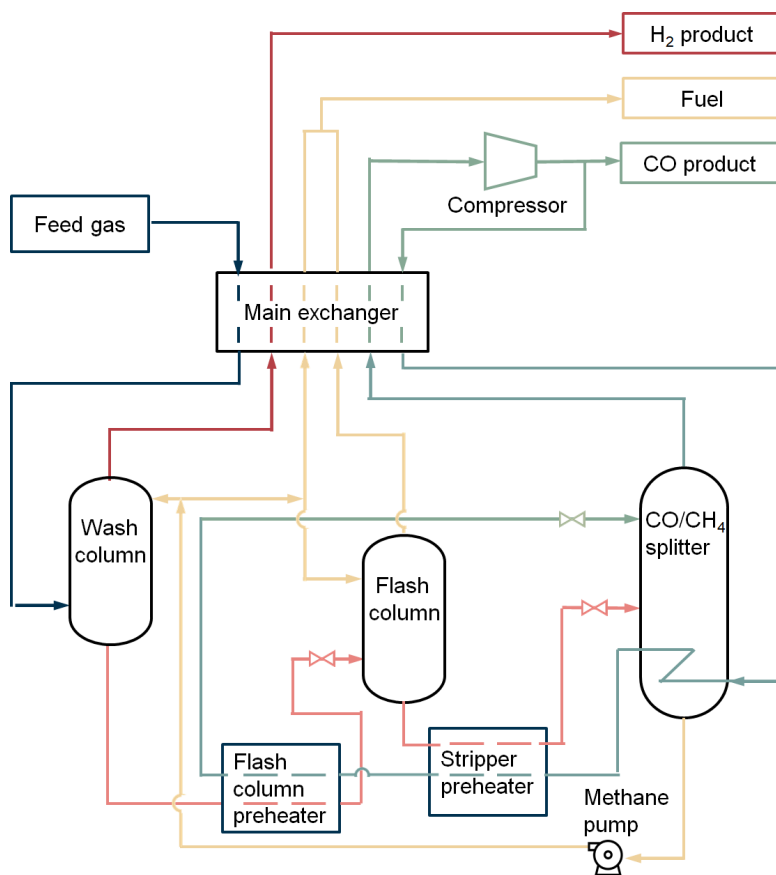


Figure 2.5 The liquid methane wash process. Figure based on process scheme from Dutta et al. [31].

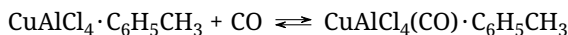
energy costs associated with cryogenic distillation for CO separation are significant. The need to operate at very low temperatures lead to the inherent need for cooling, incurring additional compression power costs for refrigeration compressors. An expensive external cooling utility, such as liquid nitrogen is also required to satisfy the process cooling demands, further increasing operating costs. In addition, to meet the requirement of operating at harsh conditions, the investment of constructing the distillation columns and auxiliary units is much higher than those operated at ambient temperature and low pressures. Finally, it is important to note that, due to the close boiling points of CO and N₂, it is impossible to recover pure CO from gas-mixtures that contain N₂ using a cryogenic distillation process.

Absorption.

Absorption separation is based on relative solubilities of individual components in the mixture in liquid phase, meaning some components get enriched in the bulk aqueous phase, while the remainder stays in the gas phase, leading to a separation of the mixtures.

Only chemical absorption technology is reported for CO absorption, which uses chemical solvents that react reversibly with the gas component [31]. The CO absorption separation processes, such as COSORB, COSORB^{II} or COPureSM, based on CuAlCl₄ complexes in toluene operate with different kinds of feed gases, for example refinery gas, coke oven gas, blast furnace gas from the steel industry, steam reforming gas and a few more. The process can separate CO from feed gases that contain N₂, CO₂, H₂ and CH₄. The gas mixtures need to be pretreated if they contain impurities such as water and gases with sulfur components. Water can degrade CuAlCl₄ into HCl, which leads to the corrosion of the steel columns. H₂S and other sulfur compounds could lead to the precipitation of Cu(I) sulfide. Molecular sieve adsorption and refrigeration are used for removal of water. Activated carbon adsorption is used to remove sulfur components.

COSORB process. The general COSORB process which is developed by Tenneco Chemicals is displayed in Figure 2.6 [38]. In this process, the cuprous aluminium chloride (CuAlCl₄) complex is utilised to selectively capture carbon monoxide over other gases (e.g., CO₂, H₂, N₂ and CH₄) in a toluene solution. The stoichiometric reaction can be described as follows:



The activation energies evaluated for the forward and reverse reactions were -32.93 and -97.42 kJ/mol, respectively [39]. The chemical CO absorption mechanism is based on the interaction between the CO gas molecule and the Cu(I) metal ion. The σ orbital of the carbon site in CO donates electrons to the empty d -orbital of the copper atom and forms a σ bond. Meanwhile, the electrons in a filled d -orbital of the copper move to an empty π^* -orbital of the CO molecule and a strong π -back bonding is formed.

The feed gas [38] flows into the absorber column after the pretreatment. It contacts with the CuAlCl₄ in toluene in counter current flow. A CO complexing compound is formed. In addition, CO₂, H₂ and CH₄ are physically absorbed in toluene. Vaporised toluene is recovered from the overhead gas through compression and adsorption. A part of the physically absorbed gas components in toluene also leaves the process via the top of the absorber column. The liquid, containing chemically absorbed CO and physically dissolved CO₂, H₂ and CH₄, is separated in the flash drum by a drop in pressure. The solution is then

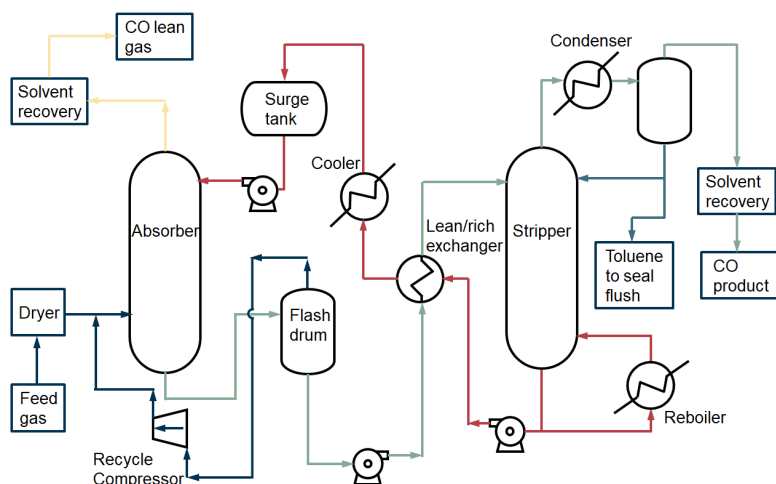


Figure 2.6 The basic COSORB process. Figure based on process scheme presented in Keller et al. [38].

decompressed to release the physically dissolved gases (CO_2 , H_2 and CH_4), which can be recycled back to the absorber column. The $\text{CuAlCl}_4(\text{CO})$ complex solution is heated up in the heat exchanger with the counter current stream which is derived from the bottom of the stripper. The solution enters the stripper, and the carbon monoxide is decomplexed from Cu(I) by heating the solution at high temperature (408 K) and lowering the pressure to ca. 0.15 MPa [5]. The carbon monoxide flows out at the top of the stripper and is cooled. The co-evaporated toluene in the CO stream is separated. The recovered toluene either flows back into the splitter or is sealed and removed from the process. Before the carbon monoxide vapour flows out of the process, the remaining toluene, which is volatile and harmful, is extracted from the product. The CO product stream is compressed in order to be used in a downstream process. A part of the solvent with CuAlCl_4 dissolved in toluene from the bottom of the stripper is reused in the stripper. The remaining part flows back to the absorber column and heat is recovered in the lean/rich heat exchanger. To recover a pure CO product after absorption to the CuAlCl_4 , decomplexation takes place at low pressure and high temperature [40, 41].

The CO product capacity of COSORB absorption separation units ranges from 270 to 5500 Nm^3/h . The final recovery of CO is 98% and typical purity is 99% for CO feed concentrations $>0.16 \text{ kmol/m}^3$ [42]. To run the process the utility consumptions are 392 kWh/tonne product for electrical power (climate-dependent) and 1448 kWh/tonne CO for cooling water and reboiler heat.

COPureSM is the commercial process used today for CO absorption, which is an upgrade of old COSORB and COSORB^{II} techniques and developed by COSTELLO. In

this process, a more effective pretreatment is used and a CO-recovery rate of 98% with a purity of 99% is obtained.

Concluding remarks. High purity and recovery of CO can be achieved in an absorption separation process, although there are several disadvantages of the technology: the CuAlCl_4 complex can be easily poisoned by H_2O , H_2S , SO_2 and oxides of nitrogen, so a pretreatment procedure is required to remove these components. While the energy consumption is very steep: e.g., for COSORB circa 400 kW/tonne product for electrical power and circa 1400 kWh/tonne CO for cooling water and reboiler heat is required [43], absorption is capable of separating N_2 and CO. On top of that, it has an advantage in capital investment (48% less cost) compared to cryogenic distillation of the most favourable separation of CO and H_2 , and in contrast to cryogenic distillation, CO_2 does not have to be removed prior to the CO separation [44]. Meanwhile, the solvent degradation and the precipitation of solids need to be considered. Some environmental and safety issues arise during the absorption process, such as the disposal of spent solvent and handling of the corrosive or volatile solvent. The absorbent degradation is the reason that the COSORB process is relatively seldom used [31].

Membrane separation.

The third technology that is considered is the membrane separation of carbon monoxide. A membrane can be seen as a selective barrier; under influence of a pressure difference as a driving force it allows some species in the gas and liquid phase to pass through, but rejects or retards others. For the separation of CO, only gas membrane separation is relevant. Gas membrane separation is based on the relative permeability of an individual gas through a membrane based on the physical or chemical properties of the gas. The main driving force in the separation is the pressure difference across the membrane and based on the gaseous solubility and permeability, the permeable molecules (permeate) diffuse through and the non-permeable molecules (retentate) stay on the feed stream side. The specific kind of membrane (glassy or rubbery polymers) that is used, is of great importance in the design of a membrane-separation unit as it will hugely affect the performance. Although a lot of research is carried out to develop novel membrane materials, only polymeric membranes are used commercially for CO separation at industrial scale. Here, the higher the solubility of a gas component in the polymer matrix, and the higher its diffusion coefficient in the matrix, the higher its permeability [45].

The commercial application of membranes in CO purification is mainly focused on the separation and purification of CO from syngas, based on the high permeation rate of hydrogen versus CO. Also components like CH_4 , CO_2 and N_2 have lower permeation rates in polymeric membranes compared to hydrogen, so it is a priori difficult to separate them from carbon monoxide using this method. In industrial processes, syngas ($\text{H}_2 + \text{CO}$) is required to make a variety

of products, with each product type demanding a specific, optimal ratio of H_2 to CO in the feed syngas. However, as the H_2 /CO ratio produced depends on the syngas generation process and the hydrocarbon feed, this primary ratio may not be optimal for downstream products, and some H_2 /CO ratio adjustment is needed. Membrane technology is perfectly suited for this, based on the different permeability of the two gases through the membrane. The gas mixture is fed at high pressure to one side of a thin polymer film or hollow fiber membrane unit, yielding a high pressure CO enriched retentate and a low pressure H_2 -rich permeate. Ramírez-Santos et al. [46] compared process designs for blast furnace gas (BFG) treatment based on a H_2 selective glassy polymer membrane from UBE industries (B-H) with one based on a CO_2 selective rubbery polymer membrane from MTR (Polaris). For both systems CO recovery can reach 80-90% but purity is limited to ca. 30%, indicating the trade-off in membrane separation.

PRISM membrane systems. The PRISM membrane separator (based on polysulfone and developed by Air products) can be utilised not only to purify CO from feed streams containing hydrogen and water vapour, but also to change the H_2 /CO ratio in oxo-alcohol synthesis gas to meet the real application requirements [47].

The separator consists of polymeric hollow fibers that act as a molecular filter. The feed gas (e.g., 48% H_2 , 51% CO, <1% N_2 and saturated H_2O) flows into the system with a pressure of 6 MPa. The pressure at the end of the separation system is 150 kPa, which creates a driving force for the separation. The permeated gas molecules (H_2 , water), which have higher permeation rates compared to carbon monoxide, permeate across the thin skin of the hollow fiber wall driven by a partial pressure difference and are channeled into the permeate stream. The retentate leaves the system with a CO product purity of 85 mol% and a recovery of 85 mol% [48]. A two-stage system and a recycle compressor can be used to improve the separation and the CO purity can be increased to ≥ 95 mol%.

Cellulose acetate membrane. Toshiba Corporation developed a cellulose acetate membrane separation technique to change the H_2 /CO ratio of syngas. This membrane can also be used to produce a CO product stream of 2200 Nm^3/h from synthesis gas [49].

The separation process consists of a two-stage membrane system. In the first stage, the feed enters the system at a pressure of 2.8 MPa and a temperature of 313 K. The hydrogen gas permeates the membrane and flows out of the system with a pressure of 70 kPa. The residue gas leaves the first membrane and enters to the second one with a pressure of 2.7 MPa. The permeate from the second membrane is recycled in order to obtain a high recovery of CO. The non-permeated CO product has a purity of 98%. The cellulose acetate membrane has a high permeability, so less surface area is needed for separation. The

sheet-like membrane is configured into spiral wound elements, which is less expensive than hollow fiber modules. Compared to the polysulfone membrane, the cellulose acetate was found to provide higher selectivity and permeability at the same operation conditions for both syngas ratio adjustment and CO production [31].

Concluding remarks. The general advantages of membrane processes include its simple operation and easy (linear) up or down scaling. Meanwhile, since it operates under milder conditions, it can offer cost advantages over cryogenic separation, although it has not the economy of scale advantage. It also reduces the environmental impact due to the absence of any chemicals. Weaknesses of this technology are its sensitivity to fouling by impurities, plasticization by feed components, and compaction caused by pressure or temperature effects. Moreover, the technology is mainly used for separating H_2 from syngas to adjust the H_2 :CO ratio. Separation of CO from gases like CO_2 , CH_4 , N_2 , which have similar solubility and diffusivity properties in common polymers, remains challenging. Therefore, thorough pretreatment or multistage separation is often needed in order to achieve sufficient high purity and recovery of CO, which is expensive for some applications [50].

Adsorption.

Adsorptive separation is based on differences in gas adsorption on a solid adsorbent, adsorption selectivity [51]. Depending on the binding strengths of gas molecules with the adsorbent physisorption and chemisorption are distinguished (Section 2.2.2). Adsorption technology is a cyclic process: firstly, uptake of gas components upon contact with the solid adsorbents occurs under controlled temperature (temperature swing adsorption: TSA), pressure (pressure swing adsorption: PSA; vacuum swing adsorption: VSA), or electric potential (electric swing adsorption: ESA) conditions. In the second step, the adsorbed gas is released, regenerating the laden adsorbent. In TSA, PSA, VSA or ESA processes, the adsorbents are regenerated by heating, reducing the pressure, under vacuum or in a low-voltage electric current condition, respectively. Three commercial PSA plants that are operated for CO separation are discussed in this section. The setup of adsorption processes can differ in numbers of stages and columns depending on the size of the process.

COPISA process (physisorption). Kawasaki Steel Corporation and Osaka Oxygen Industries LTD developed the first commercial process for CO separation using the PSA technology named COPISA (CO pressure induces selective adsorption). This is a process in which carbon monoxide is recovered from basic oxygen furnace gas (BOF), which is a mixture of CO, CO_2 and N_2 (CO: 71%, N_2 : 14%, CO_2 : 13%, O_2+H_2 : 2%). The process consists of (Figure 2.7): (1) Pretreatment process; (2) CO_2 separation process (De- CO_2 -PSA); (3) N_2 separation process (De- N_2 -PSA); (4)

Refining process (De-O₂ and De-H₂O). Before the adsorption operation, the feed gas is pre-treated at high pressure to remove the dust followed by compression to 5-15 kPa at 298 K [52].

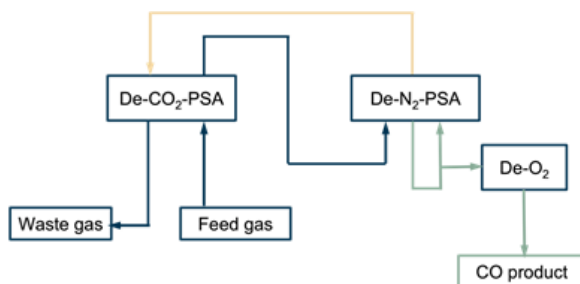


Figure 2.7 General overview of the COPISA process.

In the first section (De-CO₂-PSA) of the adsorption operation, CO₂ is removed from the feed gas by an activated carbon adsorbent. De-CO₂-PSA requires two or three adsorption columns following the process cycles of: adsorption, depressurisation, evacuation, and purge. The CO₂ is adsorbed whereafter the effluent (mainly CO and N₂) flows to the next section. The adsorption ends before the CO₂-breakthrough point at which CO₂ saturation is reached, to avoid CO₂ leaking into the effluent gases. For the purge step, a CO₂-free waste gas from the next section (De-N₂-PSA) is used. In this section the purge step acts to further desorb and regenerate CO₂. After evacuation the feed gas slowly pressurises the column up to the required adsorption pressure. After removing CO₂, the gas effluent leaves the first section and flows to the second section (De-N₂-PSA). It contains a mixture of 82% CO, 16% N₂, 2% of H₂ and O₂.

In this process a zeolite based adsorbent (Na-MOR) is used). Carbon monoxide physisorbs at a pressure of 150-250 kPa through Van der Waals forces with an adsorption capacity of approximately 1 mmol/g adsorbent (298 K and 1 atm). The CO/N₂ adsorption selectivity is about 2.5-3.0. The effluent gas originating from the adsorption step, which mainly consist of N₂ and a small residual amount of CO, is used as a waste gas purge in the De-CO₂-PSA unit. In the process the vacuum pressure to evacuate CO is set at 6.6-13.3 kPa.

After the adsorption steps, oxygen and water are removed to ensure the utilisation of CO as a raw material in chemical industry. The oxygen is removed by converting it catalytically with CO into CO₂. Moisture is removed using molecular sieves. The moderate CO/N₂ ideal selectivity of 2.5-3.0 means that achievement of a high purity of 98% CO, comes at the expense of a lower recovery ratio (45% for a feed with 71% CO, and 60% for a feed with 80-85% CO). Thus, this process is only appropriate for CO-separation from feeds with very high CO concentrations. Unrecovered CO exits the process as waste gas purge. The capacity of the reported

process is 410 Nm³/h of CO product. No energy consumption and cost information are disclosed.

Activated alumina coated with carbon and impregnated with copper compound (chemisorption). Kobe Steel Ltd has developed a commercial plant for pressure swing adsorption of CO from Linze-Donawitz converter exhaust gas (LDG: 68% CO, 16% CO₂, 13% N₂, 2% H₂, 1% O₂+Ar), however other feed would also be usable as well [53]. A porous activated alumina coated with a surface carbon layer constitutes the support of the adsorbent. Copper compounds (CuCl, CuCl₂) dispersed on the support surface provide the active chemisorption sites. The carbon layer serves to prevent the oxidation of Cu(I) and reaction with the alumina, and to reduce Cu(II) to Cu(I), while the alumina provides the particle texture. Before the gas mixture is fed into the PSA process, it is pretreated in a thermal-swing process over activated carbon to remove sulfur compounds and water. Sulfurous compounds cause the deactivation of the CO adsorbent and water adsorbs strongly to the adsorbent. The PSA process has four adsorption columns, each cycling through four sequential process steps (adsorption, purging, desorption (ca. 13 kPa), and repressurisation). In principle, the relatively strong interaction of CO with CuCl already facilitates production of high purity CO (> 99%) in a single stage PSA. This is caused by the close to ideal selectivities of ca. 25 for CO/N₂ and 7.5 CO/CO₂ (as estimated from the single component adsorption isotherms) at 20 °C. The latter also means that a PSA-stage for the removal of CO₂ prior to the CO-separation is not necessary. The adsorption capacity for CO at 20 °C is ca. 1 mmol/g. Due to the high selectivity for CO a very high purity with high recovery can be achieved: for LDG 99% purity with 90% recovery, and a 99.9% purity with 75-80% recovery. The pilot produces 150 Nm³/h of CO product. Two years of operation showed no deterioration of the adsorbent. Based on the positive result of this plant, Kobe built another plant with a CO product flow of 2000 Nm³/h.

PU-1 (chemisorption). The VPSA-CO (VPSA: vacuum pressure swing adsorption) plant, which is developed by Peking University Pioneer Technology Co in recent years, has a CO product flow that varies from 1700 to 20000 Nm³/h. This technology is suitable for any CO-rich feed gas. The separation process consists of two units (VPSA-1 and VPSA-2;). In the first unit, H₂O, CO₂ and trace heavy components such as sulfur-containing compounds are removed. This unit contains three adsorption columns, which have low adsorption capacity for CO but high adsorption for CO₂ and H₂O. The compressed feed gas enters the VPSA-1 at 801 kPa and room temperature. Each adsorption column undergoes the same PSA steps: adsorption, pressure-equalisation, counter depressurisation, purge and regeneration, partial pressurisation, re-pressurisation. The purge step is done with effluent gas from the VPSA-2 section. The VPSA-2 section provides further purification to obtain a CO product with a purity of 99%. The feed gas enters the VPSA-2 section at 343 K and a pressure of 750 kPa and operates according to the

PSA process steps as described before. A vacuum pressure of 13-20 kPa is used in the regeneration step. This section contains four adsorption columns filled with CuCl/zeolite adsorbent, also known as PU-1. It has a CO adsorption capacity of (>50 ml/g equivalent to 2.03 mmol/g adsorbent at 1 atm and ambient temperature) and an ideal CO/N₂ selectivity at 20 °C of ca. 20, with similar values for CO versus H₂ and CH₄, while the ideal selectivity of CO/CO₂ is only around 2-2.5. This rationalises why CO₂ needs to be removed in a first PSA unit (VPSA-1), and why very high purities combined with very high recoveries of CO can be reached. The CO product feed flows out of the process with a purity >99% and a recovery >85% from a syngas gas containing about 30% CO and rich in H₂ (41%), N₂ (17%), CO₂ (8%) and CH₄ (2%). To keep the process running it requires 340 kWh/tonne CO electricity. [54–56]

Concluding remarks. Adsorptive separation of CO, in contrast to cryogenic distillation, does not rely on phase changes and volatility differences to achieve separation. It can be seen as a good candidate for the separation of close-boiling gas mixtures, such as CO and N₂. It is energy-efficient and has the advantages of low installation and operating costs, low water and electricity consumption, easy operation and maintenance, high production capacity and CO purity, no equipment corrosion and environmental pollution. However, its downsides are: (1) high requirement for raw gas quality: H₂O or sulfur compounds impurities that reduce capacity need to be removed first; (2) for raw gases with a low CO concentration, the CO recovery rate decreases, especially for the COPISA process based on physisorption; (3) the scale of PSA devices is limited to a certain extent. If the gas volume is large, multiple parallel operation units are required. Meanwhile, the performance of adsorptive separation strongly relies on the adsorption mechanism. Chemisorption performs much better than physisorption in terms of recovery and purity. Yet a chemisorption process has the disadvantage that the energy required for desorption will be larger due to the higher adsorption enthalpies involved. Yet, the PU-1 chemisorption process requires far less energy input than the COSORB process based on chemical absorption (ca. 340 versus ca. 1400 kWh/tonne CO, respectively), but with some loss in recovery (85% for PU-1 versus 98% for COSORB). The choice of a proper sorbent has a significant influence on the CO adsorption performance and process design. With thousands of known adsorbents and novel adsorbents being constantly developed, identifying a suitable adsorbent and separation scheme for a given separation problem remains a challenging task.

Table 2.2 A comparison of existing industrial CO purification technologies

Separation mechanism	Separation technology	CO product stream		Energy needs [kwh/tonne CO]		Advantages	Limitations
		Purity [%]	Recovery [%]	Throughput [Nm ³ /h]			
Cryogenic distillation	Partial condensation process	98-99	75-80	55000	18-100	Mature technique High CO purity	High capital and operating costs Unable to separate CO and N ₂ due to the similar boiling points
	Liquid methane wash process	99	99	34000	300-600		Pretreatment removal of H ₂ O and CO ₂ necessary
	COSORB	99	99	270-5500	1446 (cooling/reboiler) 392 (kW electrical power/tonne CO)	High purity and recovery of CO product Can separate CO/N ₂	The CuAlCl ₄ complex can easily be poisoned The solvent degradation and the precipitation of solids need to be concerned
Membrane separation	Copure SM	99	99	Not known	Not known		Environmental and safety issues
	Prism	97	89	Not known	Not known	The process can be operated in the presence of H ₂ O and CO ₂ Can achieve desired H ₂ /CO syngas ratio	Poor stability of the material Multistage separation is often needed in order to achieve high purity and recovery
	Cellulose acetate	98	88	2200	Not known	Reduce the environmental impact due to the absence of chemical systems	Cannot separate CO/N ₂
Adsorption	COPISA	98	45	450	Not known	Easy operation	A pretreatment is needed to remove H ₂ O and sulfur components
	Activated Al with impregnated C & Cu compound	>99	>80	≥150	Not known	Low cost and relatively energy-efficient for the separation of CO/N ₂	Only for high CO concentration feeds
	PU-1	>99	>85	1700-20000	340	High CO product purity, with modest to relatively high recovery	

Evaluative notes.

At present, several technologies are already being used for CO separation. Each of them has pros and cons related to the separation performance (see Table 2.2). For the purification of syngas and composition adjustment most of the technology is focused on the intrinsic differences in the physical properties between H_2 and CO. In this case cryogenic distillation, pressure swing adsorption and membrane separation can be readily employed. Cryogenic distillation here has the advantages of being a very established technology that operates favourably at very large scale. Membrane separation on the other hand has the advantages that pretreatment for the removal of H_2O and CO_2 is not necessary, and that less energy is required compared to cryogenic distillation. However, there is no economy of scale, which limits the capacity. In fact, all other current CO separation processes require removal of H_2O via pretreatment. Moreover, beyond membrane separation, the only processes that do not require removal of CO_2 , are based on chemical absorption and on chemisorption.

Flue gas streams often also contain large amounts of CH_4 and N_2 , which are hard to separate from CO based on conventional separation principles like boiling point (cryogenic distillation) and kinetic diameter (membrane separation). Design of such N_2/CO separation unit results in expensive and energy intensive solutions to reach required purities of 98-99%. This explains the preference for reactive separation in both absorption and adsorption processes exploiting the affinity differences of CO and N_2 towards binding in *d*-metal complexes to selectively extract CO. The exception being the COPISA process based on a sodium-type-mordenite. Most likely the higher quadrupole moment and polarisability of CO compared to those of N_2 lead to a stronger interaction with sodium. Yet, the CO/N_2 selectivity of 2.5-3 is only modest, hence, the desired high purity (98%) can only be achieved via a lower recovery (ca. 45%). The other commercialised absorption and adsorption processes are based on cuprous complexes. The Cu(I)-CO π -complexation bonds are stronger than the Van der Waals interactions in the COPISA process. This means that high purity (99%) can be achieved with high recovery (80-99%). So, chemisorption based processes are needed to achieve high purity at high yield, even when the CO concentrations in the feed are high. The formed Cu(I)-CO bonds are still weak enough to be broken by traditional engineering means such as decreasing pressure and/or increasing temperature. This reliance on heating for cyclic operation, i.e., switching between ab/adsorption and desorption operation modes is a disadvantage of the ab/adsorption process, especially as heating and cooling stages are typically more time-consuming compared to changes in pressure. Moreover, the low solubility of the metal complexes in the hydrocarbon solvents limits the uptake capacity, resulting in energy intensive heating and cooling stages of the process (1446 kWh needed per tonne CO). Additionally, solvent degradation may cause environmental issues.

Overall, relatively adequate solutions seem to exist for the separation of CO and H_2 . They can be lean in energy use, e.g., cryogenic distilla-

tion based on the partial condensation process, and probably – though no information is present in literature – membrane separation. The latter has the additional advantage that no preconditioning to remove H_2O and CO_2 is needed.

For the separation of CO and N_2 , the options for high purity solutions are far more limited. Absorption processes can yield high purity with high recovery, but at a high energy cost and with environmental concerns related to the use of solvents. Adsorption processes, on the other hand, are more energy efficient. A techno-economical analysis comparing the COSORB absorption process and the Kobe steel adsorptive Linde-Donawitz gas (LDG) treatment revealed the favourable economic performance of the adsorption process [57]. The environmental concerns are lower, as no solvents are used. However, the CO recovery is lower (45-85%) and the process is only sensible for separating flue gas streams with a high CO content. A real impact can be made by a process for flue gas separation of CO from N_2 with high recovery and purity, even if the stream only contains a few percent of CO. Especially if such a process would not require the need a pretreatment to remove CO_2 and H_2O .

2.3. Current developments in CO separation

The vast plethora of new materials identified the last decade as capable of separation CO concerns adsorbents, which is perhaps not surprising considering the advantages of CO separation via adsorption (simple equipment, process operation at moderate conditions and low energy requirements) and the limitations of current separation technologies (Section 2.2.4). It has been reported that many solid materials, such as activated carbons, zeolites, and metal-organic frameworks (MOFs), are capable of adsorbing CO to a certain extent. Therefore, we provide a comprehensive overview of these adsorbents (Section 2.3.2), pointing out essential further development of suitable CO adsorbents. We note a lack of criteria on the evaluation of adsorption performance, which are, however, critical to assess the large-scale viability of the adsorption process. Therefore, in Section 2.3.1, evaluation criteria for the CO adsorption performance are suggested. Using these criteria, the performance of each type of adsorbent from the last decade under different adsorption conditions (e.g., concentration, pressure, temperature, etc.), and the relation with structure is discussed. Meanwhile, the benefits and limitations of each type of adsorbent will be highlighted. Most importantly, we will summarise the key factors that control the CO adsorption performance of different materials and point out the most promising application. Also, the literature on emerging adsorbents and membranes for CO separation is discussed (Section 2.3.3), and their performance contrasted with that of the adsorbents. This evaluation of materials provides a wish list of desirable properties for future materials designed for this specific application.

2.3.1. Key factors that control the adsorption performance

Ideal adsorbent for CO adsorption.

The advent of material science and approaches borrowing from inorganic-organic chemistry opened new opportunities to develop novel adsorbents. Over the past decade, the research conducted to identify solid adsorbents for carbon monoxide (CO) capture has rapidly expanded. Several solid adsorbent materials, such as activated carbon, zeolites, silica gel, mesoporous alumina, and metal-organic frameworks, have exhibited favourable properties for CO adsorption, each with its own set of thermodynamic and structural characteristics, such as adsorption/desorption isotherms, number of active sites per area, surface area per mass of adsorbent, pore structure, and porosity [12]. However, identifying the ideal adsorbent for CO in an industrial process is not a straightforward task as it requires optimisation of thermodynamic and structural characteristics along with relevant transport phenomena while considering process requirements [51, 58]. The thermodynamic properties of an adsorbent such as adsorption/desorption isotherms and selectivity are characterised and correlated to nano/mesoscopic structure characterisation on lab scale [59]. These thermodynamic and structural characteristics enable process engineers to estimate the extent of achievable separation and the amount of CO adsorbed per weight of CO adsorbent under ideal conditions. As industrial operations occur under dynamic conditions, determination of breakthrough profiles under conditions mimicking cyclic processes are essential in providing information of coupled mass and heat transport phenomena. In literature, very few materials are tested with benchtop pre-pilot experiments, even fewer reach pilot scale where harsh process conditions can quickly alter adsorption performance. Any proposed adsorbent for CO separation should be tested in humid conditions as well as in the presence of N_2 , due to their ubiquitous nature and the challenges these compounds cause in current industrial processes (Section 2.2.4). Moreover, practical considerations such as adsorbent stability under process conditions, especially regeneration, resistance against attrition, materials cost and availability are important. Together with process design specifications and heat integration possibilities these collectively shape what an ideal adsorbent is for a given process. These considerations are discussed in subsequent sections.

Thermodynamics and selectivity.

In CO adsorption, the nature of interaction with an adsorbent is the key factor directly determining the thermodynamics, the adsorption/desorption isotherm and, hence, the maximum achievable separation performance. Depending on the strength of this interaction, the adsorption process is classified as physical or chemical in nature, the later possessing stronger interactions (see Section 2.2.2). Assessment of thermodynamics of a new CO adsorbent, such as standard Gibbs free-energy change (ΔG°) and the enthalpy change (ΔH°), provides information about the nature of adsorbent–adsorbate interactions [60–62] and the kind of sorption, i.e., the presence of various forces, including Van der

Waals, hydrophobic/hydrophilic interactions, hydrogen bonds, ligand exchange and dipole–dipole interactions. In general, the magnitude of $-\Delta H^\circ$ for absolute physical adsorption is <20 kJ/mol, while it is within the range of 80–200 kJ/mol for chemisorption [63, 64]. Noticeably, an exothermic adsorption process ($\Delta H^\circ < 0$), releases energy in the form of heat to its surroundings, and includes either physisorption, chemisorption, or a mixture of both (comprehensive adsorption). By contrast, an endothermic process ($\Delta H^\circ > 0$), in which heat is absorbed from the surroundings, is unequivocally attributable to chemisorption [65–68]. For any proposed material CO adsorption should happen spontaneously, i.e., $\Delta G^\circ < 0$. When $\Delta G^\circ > 0$, the process will be neither feasible nor spontaneous [69, 70].

In addition to desirable thermodynamics, selectivity has to be a key feature of CO adsorbents, particularly for complex gas streams commonly encountered in industrial practice. In physical separation processes, the difference between CO and N₂ is small causing problems separating the two as shown in Section 2.2.4, 2.2.4, and 2.2.4. Physisorption suffers from a similar problem. Due to the physical similarities between CO and N₂, N₂ tends to occupy the same physisorption sites, strongly reducing both the adsorption capacity of CO and selectivity towards CO when N₂ is present. Chemisorption can solve the issue of separating CO and N₂ due to its increased selectivity towards CO, but most CO sources also have a considerable humidity. Water will also compete for adsorption sites and may cause issues in stability of the adsorbents. Therefore, either water must be removed prior to adsorption process with a separate dehumidification step, as outlined in Section 2.2.4, or robust adsorbents capable of operating under humid conditions should be developed [58].

Structure, adsorption capacity, and mechanical properties.

As adsorption is a process that takes place on the surface of the adsorbent, structural characteristics such as available surface area, porosity, and the number of sorption sites per adsorbent mass determines the maximum amount of CO that can be adsorbed per unit mass, i.e., the capacity [71]. In other words, the adsorbent capacity is the characteristic collectively dictated by thermodynamics and texture. As a general rule, a larger specific surface area of an adsorbent results in more sorption sites and a higher capacity to adsorb another material [72]. Moreover, the pore size, shape, and size distribution, i.e., texture, dictates the gas transport properties, so the dynamic adsorption rate [65].

Pores in adsorbents are classified in three categories according to IUPAC [73]. Macropores with diameter, d_{pore} , less than 50 nm ($d_{\text{pore}} < 50$ nm) and mesopores ($2 \text{ nm} \leq d_{\text{pore}} \leq 50 \text{ nm}$) are primarily relevant for mass transport into the interior of the adsorbent particles; whereas, micropores ($d_{\text{pore}} < 2 \text{ nm}$) constitute the largest portion of the internal surface of an adsorbent and contribute most to total pore volume and capacity [71]. The molecules adsorbed are transported through the macropores into the mesopores and finally into the micropores.

In the micropores the attractive forces are dominant and most of the gaseous adsorbates are adsorbed within that region. Industrially implemented processes for CO separation, such as COPISA (Section 2.2.4), use a combination of carbon black particles with a broad pore size distribution along with zeolite with only micropores to separate CO from a mixture of CO, CO₂ and N₂. The most common problem related to pore size is the blockage of pores during operation. These blockages originate from impurities limiting the effective capture of CO [65]. Thus, careful consideration and balance of all the porous characteristics are crucial for determining the ideal adsorbent to capture CO under a given set of conditions.

From a structural perspective, adsorbents are divided into two broad classes: homogeneous and composite adsorbents. Homogeneous adsorbents comprise a similar pore network throughout the particle, whereas composite adsorbents are formed by aggregation of small microporous microparticles. As a result, composite particles have a well-defined bimodal character with micropores within the microparticles connected through macropores within the pellet [72]. The commercialised COPISA process uses a homogeneous zeolite adsorbent while the Kobe steel process uses a heterogeneous adsorbent with activated alumina as the carrier and carbon impregnated with CuCl as the active material.

An ideal CO adsorbent should withstand packed bed weight or resist attrition during moving bed operation. This requirement is often at odds with multiscale porous structure promoting the mass transport of the adsorbates while offering a large surface area. As a rule of thumb, the more porous the structure is, the more fragile it becomes. Resistance to attrition is particularly relevant for moving and circulating bed adsorption designs [72].

Transport phenomena and scaling.

Testing of novel adsorbents in bench-top dynamic breakthrough experiments helps in gaining information about mass transport properties (Section 2.3.1). Particularly, breakthrough time and width are used as a first estimate in scale up calculations. However, these lab-scale experiments cannot entirely replace pilot scale or industrial scale experiments alone. The coupled heat, mass, and momentum transfer phenomena and their corresponding coefficients do not simply scale linearly as the process is scaled up from bench-top to industrial scale. The observed adsorption kinetics in an industrial process is collectively dictated by the mass transfer rate of the species from bulk to the adsorbent active site. In general, the overall rate of physical adsorption is controlled by limitations in mass and heat transport rather than by the actual rate of equilibrium adsorption/desorption inside the adsorbent pores. Chemisorption often introduces slower desorption kinetics due to the higher binding energies. Consequently, physisorption processes are more commonly encountered in industrial CO adsorption when dealing with pre-treated feed streams with high-capacity separations as in the case of the COPISA process (Section 2.2.4). Chemisorption, on the other hand, is preferred

to reach higher selectivity as in the case of the Kobe Steel Ltd process (Section 2.2.4).

In industrial scale processes not only mass transport influences adsorption process design, heat transport can also be a critical factor in a cyclic TSA or (V)PSA. The largest drawback of industrial scale TSA implementations is the large cycle times needed if gas-solid contacting devices are restricted in fixed bed designs. Heating and cooling times in packed bed or pellets are in the order of hours due to poor heat transport in these systems. Consequently, (V)PSA is preferred in fixed bed designs over TSA in industrial systems although thermal effects also interfere strongly due to the exothermicity of adsorption. As a solution to reduce the long heating time in meter sized adsorption processes, circulating fluidised beds or moving beds have been proposed [58]. Despite the fact that circulating fluidised beds or moving beds are more difficult to operate and require higher capital investment costs, they offer a solution to long heating times in fixed bed TSA processes.

Regeneration and stability.

The adsorbents used in CO separations must also be regenerated after extended use. Therefore, this regeneration process must be conducted efficiently and without damage to the adsorbents' mechanical and adsorptive properties. The performance of regeneration step is dictated by the nature of adsorbent-CO interactions as well as mass transfer [74]. The regeneration step is also important in the context of the economic and environmental aspects in the process design. In the current era of sustainable development and circularity, it is imperative that designed adsorbents permit the effective regeneration, recovery, and re-use of the adsorbate, a topic often overlooked in CO adsorption literature [75, 76]. One of the environmental issues associated with adsorption processes is disposal of the adsorbent at the end of its life cycle. Regeneration can reduce the requirement for new adsorbent materials while simultaneously alleviating the problem of adsorbent waste. Furthermore, industrial adsorption processes are usually cyclic, during which the adsorption and regeneration steps of the adsorbent material change periodically; regeneration is often critical, since it determines the length of the cycle and the energy efficiency [77]. Although all the commercial CO adsorption processes described in Section 2.2.4 are cyclic, no information is available on the recycling of the adsorbents. Poisoning of the adsorbents by impurities such as SO_x and NO_x along with attrition due to thermal and mechanical stresses are the most common issues in regeneration [58].

Cost and accessibility.

One of the most critical factors influencing the industrial scale implementation of any adsorption process is the costs involved. Especially, for industrial purposes, this is the key factor in the comparison and selection of adsorbents. An

adsorbent can be considered low cost and accessible if it requires minimal processing and is made of abundantly accessible materials. The cost of the entire process is dictated by capital investment (CAPEX) that is influenced by the design choices shaped by adsorbent and operational costs (OPEX) that include the cost of adsorbents that need to be regularly replaced due to attrition and irreversible adsorption of impurities. The cost of porous adsorbent material will be directly proportional to the quantity required in the process, which in return will be determined by their effectiveness in capturing CO. Therefore, there is a need to develop low-cost and easily available materials that can be used on a large scale in an economically beneficial way [78]. For CO adsorption, commercial processes such as COPISA use a multi-step process with abundant and low-cost activated carbon for CO₂ and a zeolite based adsorbent (sodium-type-mordenite) as CO adsorbent, whereas activated alumina porous materials with a copper impregnated carbon is used at Kobe steel, Japan, for extraction of CO from metallurgic flue gases. These industrial implementations underline the importance of using low-cost and abundant materials for any novel process.

In addition to the direct costs of adsorbent, the heat required for switching between adsorption and desorption also known as swing operation in TSA should be considered as operational costs, while in PSA this is represented by compression costs. The preferred heat of desorption is intimately dictated by the available heat streams available for heat integration at site. For instance, for adsorption from post combustion flue gas, the isotherm of the adsorption must show a strong change in uptake within the temperature range 30–150 °C. This is the range of temperatures at which heat is available in the power plant (e.g., low pressure turbine, flue gas waste heat, CO₂ compression after cooler heat, etc.) and that can be used to contact the adsorbent either directly or indirectly. In addition to direct heating, alternative heating strategies such as indirect heating in fixed beds [79] and even electrical heating systems [80] in structured packings have been proposed.

Criteria for the evaluation of adsorption performance.

A viable industrially implementable CO adsorption process should feature a high adsorption capacity with favourable CO adsorption/desorption isotherms allowing significant changes within a reasonable temperature or pressure range, as well as considerable operational and mechanical sorbent stability over a broad range of process conditions along with low cost. Some of the desired properties are (i) high and sustained CO adsorption capacity even in the presence of impurities such as SO_x, NO_x and occasionally HCl, which may be present in the flue gas; (ii) high selectivity for CO and preferably not adsorbing nitrogen and water; (iii) rapid adsorption kinetics and low energy requirement for swing operation between adsorption and desorption; (iv) high resistance to attrition, particularly for circulating and moving bed process implementations; (v) and low corrosion sensitivity for the feed stream. Considering the commercially available processes any novel adsorbent with high adsorption capacity should comply with these

criteria. In the next section we will consider different materials and evaluate their performance on these aspects.

2.3.2. Different types of solid adsorbents for CO adsorption

Since the performance of the adsorption separation technology highly depends on the adsorbent material, it is of importance to carefully choose or design it. It has been reported that many solid materials, such as activated carbons, zeolites, and metal-organic frameworks (MOFs), etc., are capable of adsorbing CO to a certain extent. Hence, it is necessary to provide a comprehensive guide to the essential development of suitable CO adsorbents at this stage. In this section, we will review and analyze the performance of each type of adsorbents from the last decade under different adsorption conditions (e.g., concentration, pressure, temperature, etc.), as well as the relationships between their structures and the application performances. Meanwhile, the benefits and limitations of each type of adsorbent will be discussed. Most importantly, we will summarise the key factors that control the CO adsorption performance of different materials and point out the most promising technique. An insight into desirable properties to include in future materials designed for this targeted application will be provided.

Activated carbon and other carbon-based porous solids.

Activated carbon (AC) is one of the most widely used adsorbents for gas separation. It is composed of “pores” consisting of different sizes and shapes, which may vary over a large range. Different precursors and the preparation methods determine the internal pore structure and surface characteristics of the AC. It may have a BET surface area ranging from 500 m²/g to 1500 m²/g, which is associated with functional groups on the pore surface. Meanwhile, the total pore volumes can change between 0.3-0.8 cm³/g. These large differences have a significant impact on the adsorptive characteristics of the components of a gas mixture to be separated [81].

Lopes et al. [82] studied the ability of activated carbon for the separation of gas mixtures from steam methane reforming. It is reported that the adsorption capacity of the gases follows the order as CO₂>CH₄>CO>N₂>H₂ with a CO adsorption capacity of 0.4 mmol/g and CO/N₂ selectivity of 1.3 at 1 bar. Therefore, it is difficult to use AC to selectively separate CO from those gas mixtures because of the lower adsorption capacity and selectivity. This is evidenced by the small differences in isosteric heats of adsorption between CO₂ (-29.1 kJ/mol), CH₄ (-22.7 kJ/mol), N₂ (-16.3 kJ/mol) and CO (-22.6 kJ/mol). Additionally, all isosteric heats of adsorption reported are in the range that can be classified as physisorption, which could perhaps explain the unselective nature of activated carbon adsorbents for these gases. Meanwhile, activated carbon is non-polar or slightly polar with a high surface area, which gives it the advantage of adsorbing non-polar or weakly polar

molecules. To use it for CO adsorption/separation purpose, active metal sites (e.g., Cu(I)) are introduced on the surface of the activated carbon with impregnation method.

The formation of strong π -complexation bond between Cu(I) and CO can be a benefit for CO adsorption process showing high selectivity and capacity. The bond will further be broken by raising the temperature or decreasing the pressure of the system. The adsorption/desorption of CO on activated carbon impregnated with metal halides (AgCl, CuCl, CuBr, CuI, FeCl₂, FeCl₃, NiCl₂, PdCl₂ and ZnCl₂) was measured via fixed bed runs (measured at 1 bar, 0.05 mol% CO, 323 K). Only the copper halides and PdCl₂ showed a higher CO uptake in comparison to unimpregnated carbon, with PdCl₂ 20 times and CuCl 8 times that of the unimpregnated activated carbon, and the uptake decrease as CuCl > CuBr > CuI. For the Cu halides, all CO could be desorbed without heating, while for PdCl₂ it was necessary to heat to 423 K [83]. Inspired by this, many works have been done to synthesise adsorbents with monolayer dispersed Cu(I) on the surface of AC to adsorb CO molecules. CuCl is usually chosen instead of bare Cu(I) due to its weakened Cu-CO binding interaction, as the bare Cu(I) does not allow for facile desorption even at pressures as low as 100 Pa at temperatures around 100 °C [84, 85].

The metal sites can be formed on the pore surfaces by direct dispersion and impregnation of CuCl. Hirai et al. [84] used various solvents, such as water, concentrated hydrochloric acid solution, acetonitrile, and toluene, to disperse CuCl and activated carbon as to impregnate the CuCl into the activated carbon. After the impregnation the CuCl/activated carbon was dried under an inert atmosphere creating a uniform distribution of CuCl throughout the activated carbon. The usage of the various solvents leads to a range of CuCl loading (mmol/g AC): 0.84 (water), 1.41 (3 M HCl), 0.92 (acetonitrile), and 0.20 (toluene). These loadings in turn lead to a CO adsorption capacity (mmol/g) of 0.56 (water), 1.24 (3 M HCl), 0.61 (acetonitrile), and 0.13 (toluene) in which the highest CO/CuCl ratio of 0.88 is found from the preparation in 3 M HCl. In a further study, in which the amount of CuCl is changed for a set amount of 3 M HCl and activated carbon, it is observed that higher loading of CuCl in the activated carbon significantly reduces the BET area by up to 50% at a CuCl loading of 4.1 mmol/g AC, which in turn leads to a lower CO/CuCl ratio which decreases strongly after a CuCl loading of 2.5 mmol/g AC.

Another method that was used instead of the drying under an inert atmosphere is the calcination of the activated carbon after impregnation as shown by Huang et al. [86]. CuCl and activated carbon were dispersed in hexane, after which the activated carbon was calcined under argon at 623 °C. A maximum loading of CuCl in the activated carbon of 16.16 mmol/g was observed, while the optimal loading is found to be 12.12 mmol/g with a maximum observed CO adsorption of 1.98 mmol/g at 0.9 P/P₀ and a CO/N₂ selectivity of 100-450 at 0-10 kPa. The maximum adsorption of 1.98 mmol/g means that only 18.6% of the CuCl is utilised

at 0.9 P/P₀ under optimal loading, which is a significant decrease compared to the work of Hirai et al. This underutilisation of impregnated CuCl is caused by reduction of Cu(I) to Cu(0), attributable to carbon acting as a reducing agent in the calcination, clustering of CuCl which is caused by higher loading of CuCl, and oxidation of Cu(I) to Cu(II), which probably occurs during the initial mixing step.

In both the method of Hirai et al. [84] and Huang et al. [86], preparation of the CuCl needs to (partially) be done in a dry, inert atmosphere as to prevent oxidation of the Cu(I) rendering the material useless. The usage of CuCl is, therefore, not suitable for larger scale production. A more suitable alternative to CuCl is the usage of stable CuCl₂ during impregnation which can then later be reduced to CuCl.

Gao et al. [87] proposed such a method in which they ground CuCl₂·H₂O and activated carbon together, after which the CuCl₂ was reduced at 453 K under nitrogen flow to CuCl. CuCl loadings of 4.0, 5.0, 6.0, 7.0, and 8.0 mmol/g AC were produced with an adsorption capacity of 2.44, 2.59, 2.77, 2.95, and 2.95 mmol/g at 1 bar, 303 K. Optimal CuCl loading was, therefore, determined to be 7.0 mmol/g AC, as increasing the CuCl loading did not increase the capacity any further. Selectivity compared to other common gases in industrial streams such as CO₂, CH₄, and N₂ is high, with selectivity values for CO/CO₂, CO/CH₄, and CO/N₂ of 6.28, 16.39, and 42.14, respectively. The material is also stable after multiple uses with a reversible CO adsorption capacity of 2.53 mmol/g at 1 bar and 303 K which remains stable during 6 cycles of ad- and desorption.

In order to utilise this adsorbent in a real PSA process Gao et al. [88] later reported a simulation of a five-bed and 7-step VPSA process with Aspen software. After optimising the operating conditions, a high recovery of 92.9% with 98.1 vol% purity of CO can be achieved from the syngas (32.3 vol% CO, 1.0 vol% CO₂, 2.4 vol% CH₄, 18.3 vol% N₂, 46.0 vol% H₂).

Ma et al. [89] reported a solution impregnation method to disperse Cu metal salts on activated carbon. The activated carbon was added to an aqueous solution containing CuCl₂, CuCl₂ and Cu(CH₃COO)₂, or CuCl₂ and Cu(HCOO)₂. After removing the water and activating the solid at high temperature under a reducing atmosphere, the Cu-based adsorbents were obtained. The most efficient adsorption is found at a loading of Cu(I)-ions of 4 mmol/g AC with an adsorption of 0.98 mol CO/mol Cu(I) using CuCl/Cu(HCOO)₂ in a 1:1 ratio. It is reported that only when the mixture of CuCl₂ and Cu(HCOO)₂ is used as starting material, the Cu(II) salt supported on AC can be reduced completely to highly dispersed CuCl after activation resulting in an adsorption capacity of 2.28 mmol/g at a loading of 4 mmol Cu(I)/g AC which is equal to that obtained by the dry grinding method of CuCl and activated carbon. Meanwhile, the CuCl₂/Cu(CH₃COO)₂, 1:1 ratio, results in a CO adsorption capacity of 1.67 mmol/g at 4 mmol Cu(I)/g AC. Although the introduction of copper causes a decrease in BET surface area

and pore volume in the activated carbon, its CO adsorption capacity increases, meaning that the CO adsorbs onto Cu(I) ions. The stronger interaction between Cu(I) and CO also leads to a relatively high CO adsorption selectivity over CO/CO₂, CO/CH₄ and CO/N₂ of 3.2, 35, and 9, respectively, at 1 bar and 298 K. The adsorbent shows a good adsorption-desorption reversibility thanks to the average adsorption heat of CO (25 kJ/mol). However, the CO adsorption capacity does decrease rapidly when the adsorbent is exposed to air for several hours.

Relvas et al. [90] used a wet impregnation method, first reported by Golden et al. [91], which adds a dispersing agent to the Cu salt solution to make the adsorbent for a PSA system which can be used to produce pure H₂ gas. First, they pretreated the AC at high temperature under air to make its surface more hydrophilic, increasing the distribution of the Cu. After letting the AC cool down slightly, the AC was placed in an aqueous CuCl₂·2H₂O solution in which ammonium citrate was added as the dispersion agent. The AC was then activated under a reducing atmosphere at elevated temperature. 5 different loadings were tested and compared: 0, 0.5, 2, 3.5, 5 mmol Cu/g adsorbent. The highest CO adsorption capacity, CO/CO₂ and CO/H₂ selectivity all belong to the 5 mmol Cu/g adsorbent with values of 2.01 mmol/g, 4.5, and 200, respectively. Taking into account the need to remove both CO and CO₂ they used the 2 mmol Cu/g of adsorbent system to produce a H₂ stream containing only 0.17 ppm CO from an input stream containing 1% CO.

Though the Cu(I) adsorbents can be prepared by impregnating Cu(II) salts into activated carbon and then reducing Cu(II) to Cu(I) using a reducing agent, it is sometimes difficult to control the reduction degree, as Cu(II) is easily overreduced to Cu(0). Based on this consideration, Xue et al. [92] reported a solid-state auto reduction-dispersion method with Cu(II) metal salts to develop Cu(I) dispersed AC adsorbent. The activated carbon was mixed with CuCl₂ and Cu(HCOO)₂ salts in solid state and the Cu(II) salts were transformed into CuCl after activation at 533 K under vacuum. It is found that the CO adsorption capacity increases with increasing CuCl loading from 0 to 4 mmol/g. The highest CO adsorption capacity of 1.85 mmol/g is obtained when CuCl loading in the activated carbon is 4 mmol/g with selectivities towards CO/CO₂, CO/CH₄, and CO/N₂ of 2.6, 8.0, and 34, respectively, at 1 bar. This adsorption capacity remains constant during six adsorption/desorption cycles. Increasing the copper loading above 4 mmol/g AC results in a decrease of the surface area of AC and an agglomeration of Cu(I) on the AC surface. As a result, the active sites decrease as well as the amount of adsorbed CO.

Thanks to the π -complexation bond formed between Cu(I) and CO, which is stronger than the van der Waals force, the Cu(I) doped AC adsorbents show higher adsorption capacity and higher selectivity of CO than AC. Moreover, these bonds can be broken by raising the temperature and/or decreasing the pressure, such as shown in the Aspen simulations done by Gao et al. [88] in which pressure was

changed between 6 bar and 0.14 bar, while keeping the temperature at 303 K for their VPSA, showing that these adsorbents always possess good adsorption and desorption reversibility. However, the disadvantage is that the stability of Cu(I) is very poor in air and the adsorbents need to be protected by a dry, inert atmosphere.

A recent study by Kwon et al. [93] using petroleum based and sulfur doped activated carbon supported Ni showed an exceptionally high CO adsorption capacity in a TSA setup (6.56 mmol/g at standard temperature and pressure) owing to the strong interaction between well-dispersed Ni(0) atoms and CO. The presence of sulfur enhances both the adsorption capacities and the desorption characteristics of the adsorbent. Unfortunately, no IAST (Ideal Adsorbed Solution Theory) selectivities are reported for comparison and the Ni loading was quite high (10 wt%), but a reversible uptake of 3.57 mmol/g could be reproduced for 10 cycles with an overall loss in activity of 4.8%.

Other than Cu and Ni, an activated carbon impregnated with SnO₂ was employed in a pressure swing adsorption system as an adsorbent to remove CO from H₂/CO mixture. The CO adsorption capacity of the SnO₂/AC is 1.43 mmol/g. The species that are responsible for the improvement of the adsorption ability is SnO₂. However, the adsorption capacity of CO with SnO₂ is much lower compared to Cu(I), which is due to the weak physisorption interactions between CO and SnO₂. The mechanism is that CO reacts with O⁻ on the AC-SnO₂ surface at high pressure and ambient temperature and forms a CO-(O-)SnO₂-AC complex. The simulation results show that the adsorbent has a CO recovery and purity of 99.99% and 57.48% at a cyclic time of 600s in PSA process operating between 1 and 10 atmospheres [94].

Yoon et al. [95] proposed a porous organic polymer with chelating N-sites for embedding CuCl. The polymer, SNW-1, was synthesised solvothermally by combining melamine and terephthaldehyde in dimethyl sulfoxide at 180 °C in a teflon liner for 10 hours. After purification of the polymer, SNW-1 was added to a CuCl in acetonitrile solution and stirred for 72 hours at 25 °C under a reflux condenser, yielding nCu(I)@SNW-1 with n depending on the amount of mg CuCl/mg SNW-1. This resulted in an increase in dynamic CO capacity (0.1 to 1 bar) from 0.31 mmol/g with bare SNW-1 up to 0.61 mmol/g at 1.3Cu(I)@SNW-1. The IAST CO/CO₂ selectivity similarly increases from 0.10 on bare SNW-1 to 23.3 on 1.5Cu(I)@SNW-1. Similar materials based on graphitic carbon nitride were also reported as CO-sensor materials [96, 97], however, only their strong interaction with CO is noted.

Zeolites.

Another type of porous materials with an extensive library of high surface area structures that could be used as adsorbents for capturing CO is zeolites. Zeolites are crystalline aluminosilicate structures originally found in nature, but nowadays mass produced to be used as commercial adsorbents. They generally consist of structured cages, which can contain a large number of guest molecules. Negative

charges caused by exchange of Si^{4+} by Al^{3+} are balanced with cations (e.g., Na^+ , K^+ , Ag^+) and the size of the window apertures, which can range from 3 Å to 10 Å, depends on the zeolite crystal structure, as well as the type and number of cations. These cations are loosely bound to the structure and can be exchanged with other cations by contacting the zeolite with a cation-containing solution. It is found that the Si/Al ratio, pore size, chemical composition, and the location of extra framework cations in zeolites greatly influences the adsorption capacity and gas adsorption selectivity. [98]

Zeolites have been investigated as potential materials for CO adsorption and separation. As the Al and Si atoms are present at the centre of tetrahedral units, thus not directly accessible by the gas molecules, the interaction of the gas molecules with the zeolite surface are mainly with the lattice oxygen atoms and accessible extra framework cations. For ZSM-5 [99] with Si/Al ratios varying from 25 to 900, and Na^+ as counter cation. The CO adsorption capacity and CO/N_2 selectivity increases as the Si/Al ratio decreases due to an increase in the sodium cations per unit cell. For example, at 1 bar and 303 K, the CO/N_2 selectivity is 1.8 and the CO capacity is 0.93 mmol/g for Si/Al = 25, while only being 1.4 and 0.27 mmol/g for Si/Al > 400. Thus, the electrostatic interaction between the counter cations and the CO molecules is important. The quadrupole moments, the polarisability, and the dipole moment of the gas molecules determine the magnitude of these electrostatic interactions. A stronger interaction between Na^+ and CO compared to N_2 is observed because of the higher quadrupole moment and polarisability of CO compared to that of N_2 [99]. While ZSM-5 is a medium pore zeolite, it is observed that for narrow-pore zeolites (e.g., Linde Type A (LTA)) the pore size can become limiting for diffusion of CO. In zeolite 3A specifically (LTA with K^+ as counter cations) the effective pore aperture is only 3 Å, while the kinetic diameter of CO is 3.69 Å. Indeed it has been shown that CO can only adsorb on the outer surface of zeolite 3A, in contrast to LTA-zeolites with a slightly larger pore size like zeolite 4A (Na^+ cations) and zeolite 5A (Na^+ and Ca^{2+} cations). [100]. In zeolite 5A the adsorption capacity of CO at 298K and 1 bar is 1.2 mmol/g. [101]

By far the most research has been done on large pore zeolites with a faujasite-type structure (pore aperture ≈ 8 Å), like zeolite X and Y, with zeolite X usually having a Si/Al ratio of 1-1.5 and zeolite Y having a Si/Al ratio above that [102].

Pillai et al. [103] studied the sorption of CO in different alkali metal ions exchanged Zeolite-X materials (Si/Al=1.18) in which it is observed that both the equilibrium adsorption capacity of CO and its adsorption enthalpy decreases as the cation element goes down the period table: $\text{LiX} > \text{NaX} > \text{KX} > \text{RbX} > \text{CsX}$. This is due to the increase of the cation radius from Li^+ to Cs^+ , which again leads to a decrease of the electrostatic interactions between CO and the metal ions. As such, the LiX shows a higher CO adsorption capacity than CsX. The selectivity of CO/N_2 is around 2 for all alkali metal ion exchanges zeolite X materials.

Sethia et al. [104] exchanged the Na^+ in Zeolite X with alkaline earth metal ions (Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+}). Apart from MgX, the CO adsorption capacity of alkaline earth metal ion exchanged Zeolite X is higher than those exchanged with alkali metal ions. The adsorption enthalpy again (excluding Mg^{2+}) decreases with increase of the cation radius: $\text{CaX} > \text{SrX} > \text{BaX}$. Thus the electrostatic interaction between the quadrupole and dipole moment of CO and the earth alkaline ions is enhanced by the increase of charge density of the cation. MgX, the most charge dense ion, has a distinctly lower CO adsorption capacity and adsorption enthalpy. This is due to its very small ionic radius: during activation Mg^{2+} ions migrate from the supercages to the smaller sodalite cages where they are not able to effectively interact with the CO molecules. Among the alkaline earth metal ions Sr^{2+} -exchanged Zeolite X shows the highest CO capacity of 1.90 mmol/g at 303 K and 1 atm.

Ion-exchanged zeolite Y, which has the same crystalline structure as zeolite X, but a higher Si/Al ratio and, thus, fewer counter cations, was also studied both in the proton exchanged form with Si/Al =5 [105] and in the Na^+ form with Si/Al=2.4. [106]. The former shows a CO capacity of 0.21 mmol/g (303K, 1 bar) and the latter 0.48 mmol/g (293K, 0.6 bar). The lower performance compared to zeolite X is probably due to the presence of relatively few counter cations.

The above research shows that although the effect of the bound alkali and earth alkaline cation can improve the CO adsorption capacity of zeolites to some extent due to the electrostatic interactions, the overall capacity of ion-exchanged zeolite-based adsorbents is relatively modest with a maximum value of 1.90 mmol/g observed for Sr-exchanged zeolite X.

Therefore, more effort was put into using zeolites as high surface area supports for transition metal salts, especially Cu(I)-salts, for selective capture of CO [107]. As mentioned in 2.2.4, the commercialised CO adsorbent PU-1 is made by heating a mixture of CuCl and a zeolite at a suitable temperature to disperse the CuCl onto the surface of the zeolite (the type of zeolite is not further specified). The researchers prepared a series of adsorbents by mixing CuCl with different porous supports ($\gamma\text{-Al}_2\text{O}_3$, zeolite 4A, 13X, NaY, Cu(I)Y) and heating the mixtures at 350 °C for four hours under nitrogen [106]. It is found that the CO adsorption capacity of all adsorbents increases after doping with CuCl. Among them, the CuCl/NaY (3.66 mmol/g) and CuCl/Cu(I)Y (4.05 mmol/g) have the highest adsorption capacity of CO at 293 K and 60 kPa, and also simply the highest optimal loading of CuCl in the support. The CuCl optimal loadings are: 0.55 g CuCl/g NaY; 0.50 g CuCl/g Cu(I)Y; 0.35 g CuCl/g 13X; 0.25 g CuCl/g 4A; 0.20 g CuCl/g $\gamma\text{-Al}_2\text{O}_3$. Apparently, the differences in the adsorption capacity originate from the different structure of the support. The $\gamma\text{-Al}_2\text{O}_3$ has the smallest surface area, which has a small dispersion capacity of CuCl, thus it has a low CO adsorption capacity (<1.09 mmol/g, 293 K, 60 kpa). Also the results of Wu et al. [108] fit in this trend, as they found an optimal loading of 0.33 g CuCl/g SAPO-34, corresponding to a CO adsorption capacity of 1.8

mmol/g at 298K and 1 bar. Based on their the results, Xie et al. [106, 107] designed the commercialised adsorbent PU-1. This adsorbent shows a high CO adsorption capacity (>50 ml/g or 2.03 mmol/g at 1 atm and ambient temperature) and a high selectivity for CO over other gases including H₂ (52), N₂ (26), CH₄ (17). The selectivity of CO over CO₂ is modest, namely 1.93, hence CO₂ is removed during the gas pretreatment in the PU-1 process. A large-scale plant has been designed using this adsorbent in a VPSA process and built in China for separation of CO from syngas [54].

Nowadays, Cu(II) salts are more often chosen as starting material due to their chemical stability and cost. Cu(I) is usually obtained by reduction under vacuum or at elevated temperature and a suitable reducing agent. Ma et al. [89] presented a method to impregnate CuCl into zeolite using a CuCl₂-Cu(HCOO)₂ mixture as precursors. The synthetic method is the same as was used for an AC support (Section 2.3.2). The CO adsorption ability of CuCl/Y (2.23 mmol/g; the Cu loading is 4 mmol/g) is as high as that of AC modified with a CuCl monolayer (2.28 mmol/g). The comparison of the isosteric heat of adsorption for CuCl/Y (63.5 kJ/mol) and CuCl/AC (25 kJ/mol) reveals a stronger interaction between the zeolite based adsorbent and CO. As a result, CuCl/AC shows a better adsorption-desorption reversibility of CO (98% of CO desorbed in the first cycle) than CuCl/Y (70% of CO desorbed in the first cycle).

Gao et al. [105] did experiments on materials similar to PU-1. Zeolite HY powder (SiO₂/Al₂O₃ = 5) was mixed together with CuCl₂·2H₂O to prepare the CuCl/Y adsorbent. The sample is activated in CO atmosphere at 663 K to achieve full reduction of Cu(II) to Cu(I). It is found that the amount of adsorbed CO increases greatly when the Cu(I) loading increases and the highest CO adsorption is 2.67 mmol/g (1 bar, 303 K) when the CuCl loading reaches 5.0 mmol/g. The CO adsorption ability decreases when the loading of CuCl into the zeolite is further increased due to the blockage of pore channels and the corresponding decreasing accessibility of Cu(I). The CO/CO₂, CO/CH₄ and CO/N₂ adsorption selectivity factors are 2.83, 24.73 and 68. A high selectivity can be obtained, due to the stronger interaction between the highly dispersed CuCl and CO via the π -complexation and the weaker van der Waals and electrostatic interactions of CO₂, CH₄ and N₂ with the adsorbent.

Not only the available pore volume, also the nature of the counteranions in the zeolite have an effect on the performance of CuCl-doped zeolites. While the above results on CuCl embedded in zeolite Y where performed on either Na⁺ or H⁺ exchanged zeolite Y, Fan et al. [109] studied CO adsorption on zeolite Y, with varying amounts of Na⁺ and H⁺ counteranions. They found that the CO-adsorption capacity is higher; the higher the acidity (higher amount of H⁺) of the framework. The framework hydroxyls provided good sites for exchange of H⁺ with Cu⁺, while the pure Na⁺-Y showed the highest amount of CuCl particles around the zeolite support. Yang et al. [110] compared the performance of CuCl dispersed in zeolite Y

exchanged with Na^+ , La^{3+} and Ce^{3+} . The CO-adsorption capacity at 1 bar and 298 K remained roughly the same (≈ 2.5 mmol/g), but the CO/N_2 selectivity improved from 28 (Na^+), to 47 (Ce^{3+}) and 53 (La^{3+}) for the lanthanide exchanged zeolites due to a decrease in the adsorption of N_2 .

It is intriguing that the PU-1 process is a VPSA process, while several reports show that desorption by reducing the CO pressure at ambient temperature from CuCl-doped zeolites is limited. E.g., the CuCl(5mmol/g)-zeolite Y studied by Gao et al. [105] requires heating to 453K and vacuum for 30 minutes to achieve complete desorption. Fan et al. [109] also observed minimal CO desorption from various CuCl doped zeolite Y samples upon pressure reduction.

Very strong chemisorption was found for Cu^+ present not in the form of CuCl, but as the counteranions in ZSM-5. Rakic et al. [111] exchanged HZSM-5 with Cu^{2+} , Fe^{2+} , Co^{2+} as well as bimetallic forms. They found for CuZSM-5 (230 mmol/g Copper) that CO-adsorption was dominated by irreversibly adsorbed CO, namely 110 $\mu\text{mol/g}$ (adsorbed at a few Pa at 303K) of a total CO-adsorption capacity around 170 $\mu\text{mol/g}$. The heat of adsorption of this irreversibly bound CO has a very high value, namely 125 kJ/mol. It was found that this was due to the presence of Cu^+ , due to reduction of Cu^{2+} during the pretreatment in vacuum. In fact, only in the Cu-containing materials significant irreversibly adsorbed CO was observed. These results may indicate that CO adsorption on Cu^+ exchanged zeolites may simply be too strong, compared to dispersed CuCl, to make this a viable adsorbent for CO separation.

In general, zeolites do show higher CO adsorption results than activated carbon due to favourable electrostatic interactions between the cation ions and CO. However, the best adsorption functionality still comes from *d*-metal salts, especially CuCl dispersed onto a zeolite adsorbent. The adsorption ability of metal salt impregnated zeolites is limited by its dispersion capacity and the degree of reduction of Cu(II) to Cu(I). After reaching the loading threshold value, increasing the loading of Cu(I) further will lead to the accumulation of excessive copper and the blockage of pore channels decreasing the adsorption capacity.

Mesoporous alumina

Mesoporous alumina adsorbents have the characteristics of large specific surface area, high dispersion of active species on the grain surface, and mesopore size with a uniform pore size distribution, which can be considered as a potential porous support for CO adsorption. In the commercialised pressure swing adsorption process developed by Kansai Coke and Chemicals Co. Ltd., the active alumina carrier has an appropriated pore size distribution, which is doped with carbon and CuCl for the chemisorption of CO. The carbon is used to prevent the oxidation of Cu(I) [53]. It is reported in two commercial CO-PSA plants, which recover CO from Linz-Donawitz converter exhaust gas (LDG: 68% CO, 16% CO_2 , 13% N_2 , 2% H_2

and 1% O₂+Ar) from steel-making plants, that the product CO has a high purity of 99% and a high yield of 90% by applying this specific adsorbent. Further studies have continued to feature metal ion-modified alumina for CO adsorption purposes. Wang and Lin [112] prepared CuCl-modified γ -alumina by immersing the sol-gel derived γ -alumina support into the cuprous solution under inert atmosphere. The synthesised sample absorbs CO with an adsorption capacity of 0.78 mmol/g.

As described in Section 2.3.2, γ -Al₂O₃ has a lower surface area compared to zeolites, which result in a low dispersion of CuCl and thus a lower CO adsorption capacity. Cho et al. [113] found that mesoporous boehmite (γ -AlO(OH)), decomposed aluminium hydroxide, shows a larger surface area compared to the conventional γ -alumina. The Cu(I) was introduced into the support by a heat treatment of the CuCl and boehmite mixtures under vacuum. The CO adsorption capacity of Cu(I)/boehmite (1.56 mmol/g) is higher than that of their Cu(I)/ γ -alumina (0.45 mmol/g), which is caused by the higher hydrophilicity of boehmite. Specifically the higher amount of hydroxyl groups on the surface of the boehmite results in a stronger affinity of CuCl, which leads to a better dispersion of CuCl in mesopores of the support. Fan et al. came to a similar conclusion: a higher amount of hydroxyls in zeolite Y led to better dispersion of CuCl in the pores (vide supra) [109]. The CuCl-boehmite showed a high CO/CO₂ selectivity of up to 12.4 and it maintained its CO adsorption capacity even after 70 adsorption-desorption cycles.

Cho et al. [114] then continued their studies using an even further decomposed aluminium oxide, bayerite, as their substrate. The material was prepared by first heat treating the bayerite under N₂ atmosphere, after which CuCl and the treated bayerite were physically mixed at room temperature. The mixture was then heated under vacuum resulting in the adsorbent. Using a loading of 30 wt% CuCl they were able to obtain a CO adsorption capacity of up to 1.97 mmol/g and a CO/CO₂ selectivity of 16.8. Using a higher loading of 36 wt% they were able to increase the CO/CO₂ selectivity even further to 35.5, although the overall CO adsorption capacity decreased to 1.69 mmol/g. Both of these loadings show both a higher capacity and a higher CO/CO₂ selectivity than that of the Cu(I)/ γ -alumina and Cu(I)/boehmite.

Yeom et al. [115] synthesised a mesoporous alumina with a post-hydrolysis method using a chemical template. This mesoporous alumina has a maximum uptake capacity of 0.05 mmol/g at 1 bar and 25 °C. After immobilising Pd-nanodots, the uptake capacity of the adsorbent is enhanced to 0.33 mmol/g at 1 bar and 25 °C. At higher pressures, however, the uptake strongly increases to a capacity of 3.9 mmol/g at 4 bar and 25 °C. Without the Pd-nanodots the capacity at at these conditions is 2.86 mmol/g, only 27% lower. The CO-adsorption isotherms indeed show a type V shape, with the increase in slope starting at 2.5 bar, indicative of the adsorbate-adsorbent interactions being more favourable than the adsorbate-adsorbent interactions. The size of the pores, mesopores of 3.4 nm, is probably instrumental in allowing for a high degree of favourable CO-CO interactions at high filling.

Metal-organic frameworks (MOFs).

Metal-organic frameworks are materials that consist of metal ions or metal clusters linked together by organic ligands forming crystalline structures in 1, 2 or 3 dimensions. Due to the way the metal centers and the ligands connect, MOFs are often highly porous structures with reported BET surfaces of more than 7500 m²/g [116]. The variety of MOFs available, both topologically as well as chemically, is staggering due to the large variety of metal centers and organic ligands available; over 5 million structures are reported in the MOF database published by the Snurr group [117].

The tunable porosity and reactivity in combination with their extremely high surface area make MOFs suitable for gas separation purposes. Size exclusion separation of CO and N₂ with MOFs is not feasible due to their similarity in kinetic diameter. What is interesting in the application of MOFs for CO separation, however, is their ability to incorporate *d*-metals into their structure and correspondingly capture CO via metal carbonyl bonds. These unsaturated metal-ions are either present in the structure of the MOF itself, such as in M-MOF-74 or Cu-BTC, or similarly to the previously discussed materials introduced as a doped π -complexation moiety, such as in CuCl in MIL-100(Fe).

An often heard argument against the usage of MOFs for industrial applications is their high cost and low stability, which would make these types of materials uneconomical and, therefore, prevent their usage in industrial-scale applications. Firstly, the stability of MOFs is highly dependent on the building blocks and their net. While going into the specifics of what constitutes a stable MOF is outside the scope of this review, several reviews have already been written on the overall design of stable MOFs and which design elements improve stability [118–121]. While having to adhere to certain design principles does limit the total scope of possible MOFs, with millions of already known structures and more being discovered every day, this should not pose a problem that cannot be overcome. Secondly, the price of the MOFs is largely determined by the material and, especially, solvent costs associated with solvothermal methods [122]. If aqueous or liquid assisted grinding methods are used, combined with industrial scale production of the required linkers, prices in the order of magnitude of \$10/kg of MOF could be achieved on an industrial scale [122].

Unsaturated transitional metal atoms as CO adsorption sites. In literature, several CO binding mechanisms are described for different MOFs. A frequently described mechanism uses MOFs with coordinatively unsaturated metal sites, examples are MOF-74 (Co²⁺, Fe²⁺, Mg²⁺, Mn²⁺, Ni²⁺, Zn²⁺), HKUST-1 (Cu²⁺), MIL-101 (Cr³⁺, Fe³⁺), MIL-100 (Cr³⁺), and DUT-82 (Rh²⁺).

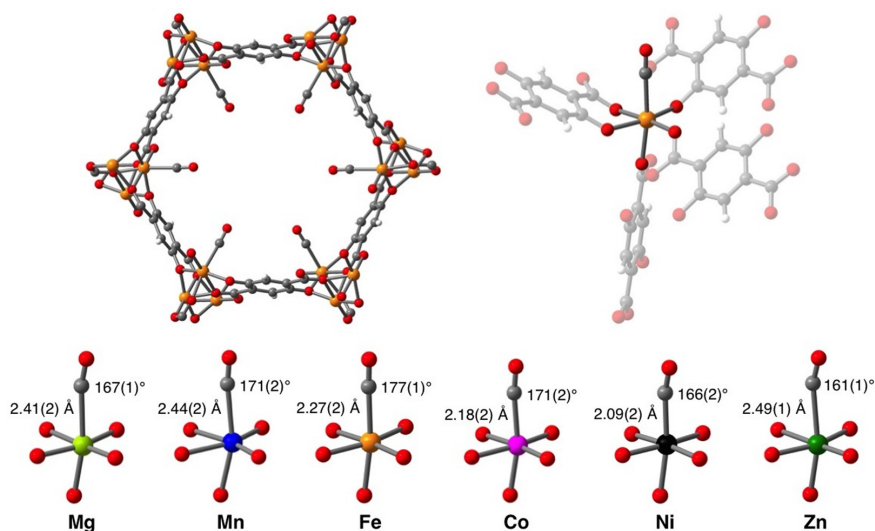


Figure 2.8 Structures of M-MOF-74 determined by neutron diffraction. Top left: View along the c-axis of Fe-MOF-74-1.5 CO, corresponding with 75% loading. Top right: Coordination environment of Fe-MOF-74-1.5 CO. Bottom: First coordination sphere of the M²⁺-ions in M-MOF-74-1.5 CO. M-CO distance and M-C-O angles are indicated. Reprinted with permission from [123]. Copyright 2014 American Chemical Society.

Likely the most studied MOF with unsaturated metal ions, MOF-74 (also termed CPO-27-M or M₂(dobdc), M referring here to the specific metal ion used) consists of 2,5-dioxido-1,4-benzenedicarboxylate (dobdc) linkers coordinated to divalent metal cations (Mg²⁺, Mn²⁺, Fe²⁺, Co²⁺, Ni²⁺ and Zn²⁺). The metal center is coordinated to five oxygen atoms from four dobdc and one H₂O in an octahedral fashion. The extended MOF structure has a network of one-dimensional honeycomb-shaped channels with around 11 Å diameter. By removing the coordinated water molecules with heat or reduced vapour pressure, the unsaturated metal sites can bind to CO via σ - and π -type bonding via the mechanism described in Section 2.2.2. CO adsorption follows the Irving-Williams series with the highest (negative) isosteric heats of adsorption following Ni > Co > Fe > Mg > Mn > Zn, ranging from -52.7 to -27.2 kJ/mol. In line with these values, the M-CO bond length increases from Fe to Zn. The strong Ni(II)-CO bond, and accompanying short Ni-C bond length of 2.148 Å is due to the large charge transfer and the π -back donation effect of Ni(II). Unlike Ni(II) metal sites, the Mg(II) ions do not possess *d*-electrons for π -back-bonding, and Zn(II) ions with a filled *d*-shell cannot receive σ -donation with fully occupied 3*d*-orbitals. Therefore, the M-CO interactions in M-MOF-74 (M = Mg and Zn) are weak, and the Mg-C and Zn-C distances (2.486 and 2.491 Å) are long. The adsorption capacities at 1.2 bar for the three best performing materials are in fact close to 1 CO per M(II), which would be, roughly, 6 mmol/g, namely 5.78 mmol/g for Ni(II), 5.90 mmol/g for Co(II) and 5.95 mmol/g for Fe(II). The reported

IAST selectivity for Ni-MOF-74 of 2000-5000 (CO/H_2) and 155-500 (CO/N_2) are the highest reported values in literature, while the capacity of 5.79 mmol/g at 1.2 bar CO at 298 K is one of the highest reported values for MOFs under these mild conditions [123]. Yet, the dynamic CO-adsorption capacity (defined as difference in amount of adsorbed CO at 1 versus 0.1 bar at 298K), the strongly adsorbing M(II)-MOF-74 are actually outperformed by Mg(II)-MOF-74, which has a dynamic CO adsorption capacity of 3.13 mmol/g.

The dynamics of carbon monoxide adsorbed in M-MOF-74 ($\text{M} = \text{Mg}$ and Zn) is investigated by Lucier et al. [124] using solid state NMR spectroscopy together with a spectral simulation approach. The motion of carbon monoxide adsorbed in open metal sites of MOF-74 are dominated by two different modes: a localised “wobbling” motion of CO at a specific metallic center and a non-localised sixfold (C_6) “hopping” motion of CO transferring between adjacent open metallic centers. It is demonstrated that a larger wobbling and smaller hopping angles lead to weaker CO-metal binding by comparing the heats of adsorption and CO motional angles.

As the most studied MOF with unsaturated metal sites, activated HKUST-1 ($\text{Cu}_3(\text{BTC})_2$; BTC = 1,3,5-benzenetricarboxylate) was also reported by Yin et al. [125] to have a CO adsorption capacity of 0.30 mmol/g and an IAST selectivity in equimolar streams of 8.3 (CO/H_2) and 1.5 (CO/N_2) at 25 °C, 1 bar. HKUST-1 possesses Cu^{2+} - Cu^{2+} paddlewheel units, the general structure of which is shown in Figure 2.9.

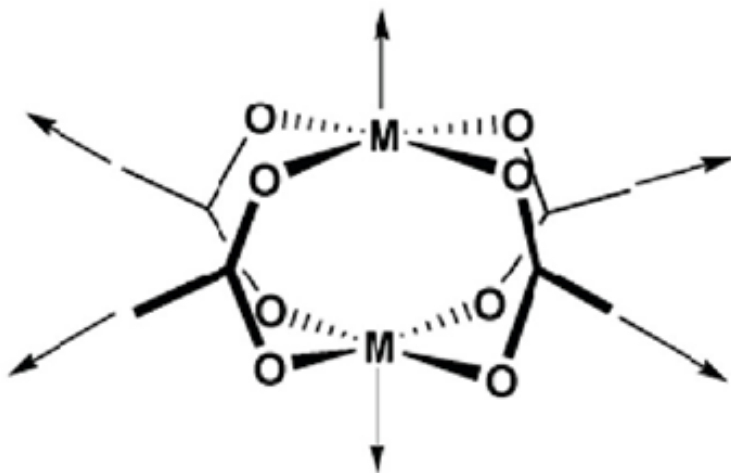


Figure 2.9 General structure of an M^{2+} - M^{2+} paddlewheel. Reprinted with permission from [126]. Copyright 2008 American Chemical Society.

Similar to HKUST-1, the unsaturated metal sites in the Rh^{2+} - Rh^{2+} paddlewheel

units of activated Rh-DUT-82 can also bind to CO molecules. It is reported that this framework has a CO uptake of 2.11 mmol/g at 25 °C and 1 bar, which is higher than the CO adsorption capacities of HKUST-1 under the same conditions [127]. The adsorption enthalpy is also quite high (-50.6 kJ/mol). The CO adsorption has not been compared with other gases.

A study by Sato et al. [128] demonstrated the self-accelerating CO adsorption (7.15 mmol/g at 120 K, 1 bar) in a Cu(II) porous coordination polymer (PCP) (Cu(aip)) as a result of the conformational change of the structure upon adsorption of CO (Figure 2.10). The MOF contains paddlewheel units constructed by Cu²⁺ and 5-azidoisophthalate (AIP). After activation, the bound water molecules were removed from the axial position of the Cu-Cu paddlewheel unit, which narrows the channels of the framework and reduces the accessible pore volume from 38% of the unit cell to 25%. The structure can be changed into a third phase, similar to the as-synthesised crystal structure, by exposing the dry Cu(aip) to enough CO. This phase can be seen in Figure 2.10C and D between points c and h. Water can similarly be used to return to the as-synthesised structure, effectively undoing the drying. The dry Cu-PCP shows a selectivity of 2.24 towards CO in CO/N₂ mixtures at 120 K. When CO diffuses in the small channel of the Cu-PCP, it breaks a coordination bond between Cu and the O atoms of carboxylates and forms a coordination bond with Cu²⁺. N₂, on the other hand, due to its extremely weak coordination ability, cannot diffuse into the channel which is filled by the coordinated CO. The MOF demonstrated a decent capacity for concentrating CO to 84% in one cycle from 1:1 CO/N₂. However, the tests were performed at 120 K, complicating comparison with other materials. However, the low CO/N₂ selectivity of 2.24 is indicative of relatively weak interactions with CO.

The adsorption of CO on MIL-100(Fe) was studied by Yoon et al. [129]. The oxidation states of iron and the amount of open metal sites were quantified using in situ IR spectroscopic analysis under CO atmosphere. At room temperature, CO molecules interact weakly with the Fe³⁺ sites in the network as confirmed by a weak band at 2190 cm⁻¹ and an adsorption enthalpy of -39 to -28 kJ/mol. By increasing the activation temperature, two new bands at 2182 and 2173 cm⁻¹ appeared, which are assigned to the adsorption on the open Fe²⁺ sites. It is demonstrated that uncoordinated Fe²⁺ sites are created at higher temperature due to the loss of an X⁻ ligand and partial reduction of Fe³⁺-X⁻ sites (X⁻ = F⁻ or OH⁻). The reduced sample with both open Fe²⁺ and Fe³⁺ sites shows a higher adsorption enthalpy of -51 to -39 kJ/mol, which validate that the Fe²⁺ sites have a stronger interaction with the CO molecules.

Preferential binding often occurs already at low CO partial pressures (<0.1 bar) evidenced by steep adsorption isotherms. As more metal sites are occupied, the adsorption slows down due to increased scarcity of sites. After all metal sites are occupied the adsorption is limited to physisorption. At high pressures CO adsorption does still occur, but dispersion forces dominate causing a severe drop

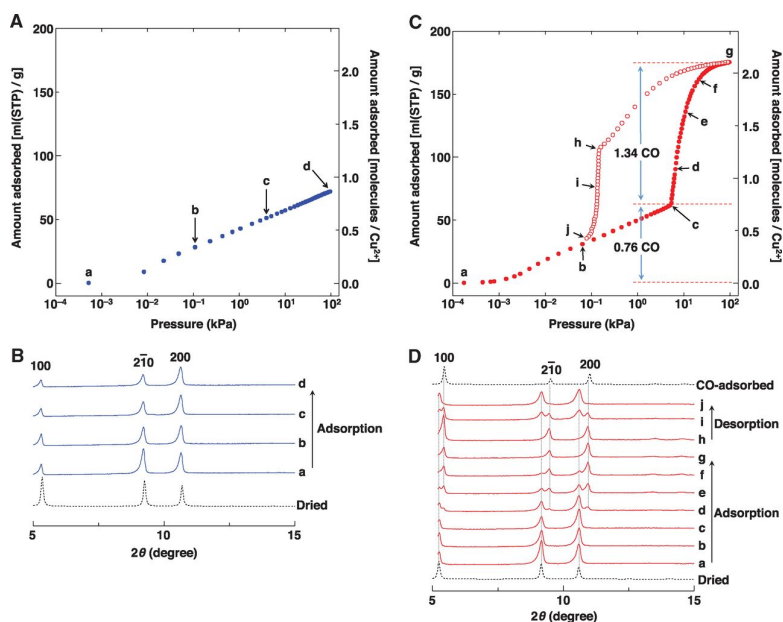


Figure 2.10 N_2 and CO adsorption isotherms and coinciding PXRD measurements. A, N_2 adsorption isotherm at 120 K. B, PXRD patterns of the measurement points indicated in A (a-d), with the simulated pattern of dried Cu-aip on the bottom. C, CO adsorption (●) and desorption (○) isotherms at 120 K. D, PXRD patterns of the measurement points indicated in A (a-j), with the simulated pattern of dried Cu-aip on the bottom and CO adsorbed Cu-aip at the top. From [128]. Reprinted with permission from AAAS.

in CO selectivity.

Spin-crossover. Other CO adsorption mechanisms include binding by spin state transition of the metal in the framework FeBTTri; $(\text{Fe}_3[(\text{Fe}_4\text{Cl})_3(\text{BTTri})_8]_2 \cdot 18 \text{CH}_3\text{OH})$ with $\text{H}_3\text{BTTri} = 1,3,5\text{-tris}(1\text{H-}1,2,3\text{-triazol-5-yl})\text{benzene}$) upon coordination of CO studied by Reed et al. [130]. After the removal of methanol, the coordinatively unsaturated Fe^{2+} in this MOF binds carbon monoxide through a unique spin state change mechanism: the square pyramidal, high-spin Fe^{2+} centres switch to octahedral, low-spin Fe^{2+} centres upon CO coordination. The Fe^{2+} sites revert back to the high-spin ground state upon the desorption of carbon monoxide, enabling the facile reversibility of the material. The sample shows a high CO uptake at 298 K of 2.25 mmol/g at 0.15 mbar and 2.7 mmol/g at 0.27 bar due to the strong interactions between the low-spin state Fe^{2+} and CO. Highly selective binding towards CO over other gas molecules is shown by high IAST selectivities towards CO at 298 K and 1 bar in a 1:1 mixture with gases such as H_2 (1500), N_2 (250), CO_2 (28), CH_4 (110), and other hydrocarbons (C_2H_6 (16) and C_2H_4 (27)), while retaining

good reversibility. It is reported that the initial slope of the adsorption isotherm (below 0.22 bar) is steep due to strong metal-CO interactions ($\Delta H_{\text{CO}} = -65$ kJ/mol) and 75% of the preferential binding sites are occupied. Above this pressure, weak interactions were responsible for CO adsorption. The authors also claim that the sample is suitable for scavenging trace amounts of CO.

Another material that utilises such a spin-crossover to achieve a cooperative binding effect for CO is the metal-organic framework $\text{Fe}_2\text{Cl}_2(\text{bbta})$ as presented by Reed et al. [131] It consists of helical Fe^{2+} , Cl^- chains linked with each other via stiff, aromatic benzo(1,2-d:4,5-d')bistriazole $^{2-}$ (bbta) linkers that bond coordinatively to the Fe^{2+} ions, resulting in Fe^{2+} ions with one unsaturated octahedral site, meaning the coordination is square pyramidal. This results in a honeycomb pattern of hexagonal tubes with the unsaturated sites being available at the inside of the corner points of the hexagonal pore cross-section. The adsorption isotherm of CO on $\text{Fe}_2\text{Cl}_2(\text{bbta})$ has a sigmoidal-like shape which allows for an improved working capacity compared to regular Langmuir-like adsorption isotherms (Figure 2.11). This sigmoidal-like isotherm is caused by the change from a Fe^{2+} high spin state to a low spin state which is caused by the adsorption of CO. The spin change is shown to be dependent on two factors: temperature and the CO partial pressure. The adsorption of CO onto the metal site is the factor that changes the spin state, while the temperature affects the location of the adsorption step and the isotherm shape. Together these factors allow for a thermally switchable CO adsorbent which utilises the spin-crossover effect to obtain a more favourable isotherm shape. $\text{Fe}_2\text{Cl}_2(\text{bbta})$ is an attractive CO adsorbent as it has both a high capacity of CO chemisorption of 5.87 mmol/g, as well as a high selectivity of 85 and 232 towards CO compared to N_2 and H_2 , respectively, at a $\text{CO}:\text{H}_2/\text{N}_2$ ratio of 1:3 at 1 bar of total pressure.

Metal salts supported on metal-organic frameworks. Inspired by the performance of adsorbents like alumina, activated carbon and zeolites impregnated with Cu(I) salts, this route has also been explored with metal-organic frameworks as substrates. The size and geometry of pores and the surface area can be tuned much more easily for MOFs compared to the other aforementioned porous materials, making it a promising candidate as porous carrier.

Yin et al. [125] used the dry grinding method to impregnate HKUST-1 with CuCl. The impregnation of 10wt% CuCl resulted in an increased adsorption capacity of 0.54 mmol/g compared to the bare HKUST-1 capacity of 0.30 mmol/g, as well as an increased IAST selectivity in equimolar streams of 66.4 (CO/H_2) and 9.5 (CO/N_2) at 25 °C, 1 bar compared to the selectivity values of the bare HKUST-1 of 8.3 (CO/H_2) and 1.5 (CO/N_2).

Peng et al. [132] developed a wet impregnation method to uniformly insert the Cu(II) salts on the MIL-100(Fe) network using CuCl_2 and $\text{Cu}(\text{HCOO})_2$ as starting material, further the Cu(II) is reduced into Cu(I) under vacuum at 423K. The CO

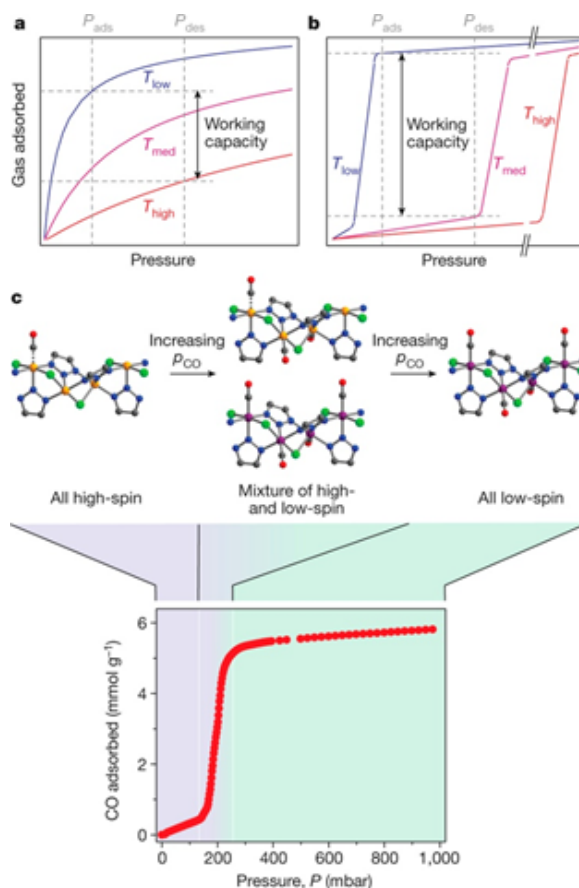


Figure 2.11 **a** and **b**, schematic of how working capacity is increased due to the sigmoidal adsorption curve caused by the spin crossover; **c**, schematic view of the mechanism of the spin crossover in $Fe_2Cl_2(bbta)$ due to the adsorption of CO. Colour code of the atoms in the structures shown: Fe (yellow), Cl (green), N (blue), C (grey), O (red). Reprinted by permission from Springer Nature: [131], copyright 2017.

adsorption capacity increases (from 0.38 to 2.78 mmol/g at 298 K and 1 bar) by increasing the CuCl loading (from 0 to 8 mmol CuCl/g adsorbents). Also the CO/N₂ adsorption selectivity of MIL-100(Fe) loaded with 8 mmol/g is with 169 also much higher than that of the original network (1.5). In accordance with the high selectivity, CuCl-incorporated MIL-100(Fe) has a high isosteric heat of adsorption of 50 kJ/mol for CO. The regeneration and stability of the absorbent are not mentioned.

Li et al. [133] used a double solvent method to impregnate and reduce Cu(I) in MIL-101(Cr) to prevent the aggregation of Cu(I) at the outside surface of the MOF. They placed the MIL-101(Cr) in hexane and added an aqueous CuCl₂ solution

with a volume roughly equal to the pore volume of MIL-101(Cr) dropwise to the MOF suspension under stirring. After leaving the suspension to stir for 3 hours, the particles were allowed to settle, the solvent was decanted and the particles were left to dry under vacuum at 373 K for 12 hours. For the reduction, the MIL-101(Cr) was again placed in hexane and an amount of aqueous Na_2SO_3 solution equimolar to the amount of Cu(II) was added dropwise under stirring. The sample was then filtrated, washed with water and dried under vacuum at 373 K for 12 hours. Plain MIL-101(Cr) showed a CO adsorption capacity of 1.33 mmol/g, while the highest adsorption capacity of 2.42 mmol/g was reached with a loading of 3.14 mmol/g Cu(I)@MIL-101(Cr), both at 298 K and 1 bar. Compared to the traditional wet-impregnation and liquid reduction, the samples prepared via the double solvent method showed higher surface area, higher pore volume and weaker CuCl XRD peaks, all indicating a better dispersion of CuCl compared to the conventional methods of wet impregnation and liquid reduction.

For practical application, the Cu(I) incorporated MOFs should not only exhibit high CO adsorption capability, but also good air stability, which may be compromised by Cu(I) being easily oxidised. Inspired by the commercialised COSORB process, Wang et al. [134] introduced CuAlCl_4 complex into the MIL-101(Cr) framework. The adsorbent exhibits the highest CO uptake capacity of (2.17 mmol/g) at 298 K and a CO/N_2 selectivity of 32 when loaded with 5 mmol $\text{CuAdlCl}_4/\text{g}$ MIL-101. The adsorbent can be regenerated under 4 mmHg at room temperature, after which the original adsorption capacity is recovered. It also exhibits good stability: most of its CO adsorption capacity can be retained after expose to air for a month. This is due to the molecular structure of CuAlCl_4 and to the interactions between Cl and Cu that prevent the reduction of Cu(I).

Another way to increase the stability of the adsorbents is using promoters such as vanadium or zinc species. A CuV-loaded MIL-101(Cr) is synthesised using both $\text{Cu}(\text{NO}_3)_2$ and VCl_3 as precursors. The vanadium ions are used to facilitate the reduction of the Cu(II). Because the synergetic effect between Cu and V, the Cu(II) can be reduced into Cu(I) at a relatively low temperature of 523 K. Note that MOFs tend to collapse at high temperature and lose their porosity. Moreover, the adsorbent shows good CO selectivity and stability, retaining up to 91.8% of the original capacity for 2 weeks upon exposure to atmospheric air due to the assistance of the vanadium species and its preferential oxidation over the the Cu(I) sites in the sample [135]. The Cu(I)Zn co-doped MIL-100(Fe) adsorbent has a CO working capacity of 1.45 mmol/g and a high CO/CO_2 selectivity of 104 [136].

Some MOFs that show relatively poor performance in their pure form, do gain improved CO adsorption capacities when impregnated with Cu(I). However, impregnation of Ni-MOF-74, which shows the highest CO adsorption capacity due to the unsaturated metal sites, with various Cu-salts did not result in dramatic differences with an overall increase of 0.5 mol/g in dynamic capacity and a 10% increase in $\text{mol}_{\text{CO}}/\text{mol}_{\text{metal}}$ compared to the pure Ni-MOF-74. This result is in

stark contrast to the results obtained with ACs and zeolites and some other MOFs (e.g., Fe-MIL-100)), where the increase in capacity can double or more. This effect is caused by the Cu-moieties competing with Ni-sites for space accessible for CO molecules, reducing the effectiveness of the added Cu-sites.

In conclusion, the use of Cu(I) salt could significantly increase the CO adsorption uptake of the metal-organic frameworks. However, the Cu^+ ion is sensitive to air and water, so in order to avoid the oxidation and hydrolysis, all operations, including preparation and storage, must be performed under dry and inert atmosphere. Though the use of complexes like CuAlCl_4 , $\text{CuNO}_3\text{-VCl}_3$ or CuClZnCl_2 has been shown to significantly slow down the Cu(I) oxidation.

Evaluative notes.

The aforementioned research show that it is difficult to directly use the conventional ACs, zeolites or mesoporous alumina as CO adsorbents, because of their low adsorption capacity and low selectivity for CO (< 0.5 mmol/g at 298 K, 1 bar). MOFs with unsaturated metal sites, on the other hand, e.g., MOF-74 display the best intrinsic CO adsorption performance with a maximum capacity of 6.06 mol/g and selectivities of 2000-5000 (CO/H_2) and 155-500 (CO/N_2) belonging to Ni-MOF-74.

Even though MOFs with unsaturated metal sites show excellent CO adsorption capacities and selectivities, there are also some drawbacks when they are used in real process conditions. Open metal sites can also strongly interact with water, causing the MOF (e.g., HKUST-1) to degrade structurally by hydrolysis. Water adsorption to these sites also results in a competitive adsorption mechanism, which would severely impact the adsorbent capacity. Therefore, competitive adsorption of CO and H_2O needs to be studied in these materials. Besides the impact of water, long-term exposure to oxygen also causes MOFs, where the transition metal is not in its highest oxidation state (like MOF-74 with $\text{M}=\text{Fe(II)}$, Co(II) or Mn(II)), to lose their high adsorption capacity due to oxidation of these metal centres.

Another widely followed strategies is to use ACs, zeolites, mesoporous alumina or MOFs as porous supports to achieve a high dispersion of metal salts, especially CuCl. The advantage is that the π -complexation between Cu(I) ions and CO, which is much stronger than the van der Waals forces or electrostatic interaction between the adsorbents and other gases, can help to achieve high adsorption capacity and high selectivity of CO. The Kobe Steel and PU-1 PSA processes utilise CuCl as the active material, which is sensitive to O_2 and moisture. For example, after exposing zeolite Y in which 5 mmol/g CuCl is dispersed for 24 hours to ambient air, the CO adsorption capacity decreased by almost 90 percent [105]. The original CO adsorption capacity could be regained exposing the material to a reducing CO atmosphere at 663 K. To circumvent the precarious handling of CuCl, recent studies are focused on employing Cu(II) salts, which are stable in air, as

precursors. However, it is still a challenge to control the reduction of Cu(II) into Cu(I) in a precise way. Meanwhile, it is of importance to choose suitable porous supports, which should have a good stability, a high surface area, and a suitable pore size to allow for high CuCl loading, as the more CuCl sites are dispersed, the higher the CO adsorption capacity will be. It is shown from the previous discussion on activated carbon [90, 91] and mesoporous alumina [113, 114] (Section 2.3.2 and 2.3.2) that a more hydrophilic surface will allow for a higher loading of CuCl with good dispersion. A similar concept based on hydrophilicity to increase the dispersion of Cu(I) was also utilised in MIL-101(Cr) via the impregnation and reduction of Cu(II) with a double solvent method [133]. Attempts have also been made to stabilise the Cu(I) by co-impregnating a sacrificial metal such as has been done in MOFs with CuAlCl_4 [134], $\text{CuNO}_3\text{-VCl}_3$ [135], or CuClZnCl_2 [136]. A recent review on CO adsorption by Feyzbar-Khalkhali-Nejad et al. [12] went into various other examples of non-standard methods of transition metal impregnation, stabilisation, and reduction in porous supports. To conclude, the stability of Cu(I), which is now mainly used as active metal site, remains a challenge for the reliable preparation of high surface area adsorbents, and means that the adsorbents can only be used for dry, probably oxygen free gas streams. The introduction of other π -complex active metal ions into porous supports can lead to other promising adsorbents, but the variety of active metal ions that has been investigated is very limited.

All in all, adsorbents have been identified with significantly higher CO-adsorption capacities (up to 6 mmol/g at 298 K, 1 bar) compared to only 1-2 mmol/g at the same conditions for the commercially used adsorbents (see Section 2.2.4). The reported CO/N_2 selectivities regularly are several 100's compared to 20-25 for the commercial adsorbents. Generally, many of the adsorbents that are promising in terms of CO/N_2 selectivity show strong physisorption up to chemisorption of CO (from -20 to -80 kJ/mol). As discussed above, N_2 and CO possess similar properties, rendering it difficult to achieve decent selectivity of CO and N_2 based on weak physisorption. Indeed, Table 2.3 shows that high CO/N_2 selectivity is associated with a higher adsorption enthalpy, which needs to be energetically overcome during the desorption stage.

While there are a series of adsorbents that perform well in terms of CO/N_2 selectivity and CO adsorption capacity, very little attention has been paid to their stability in humid and oxygen containing gas streams. In particular, no attention has been paid to the impact of competitive adsorption of water to the adsorption of CO. Regarding the performance test techniques, most research works use equilibrium adsorption setups that reports single-component adsorption isotherms for testing adsorption performance of the adsorbents. Sometimes, a single column dynamic adsorption setup is employed as a confirmatory technique to equilibrium adsorption. However, the transport and detailed kinetics of adsorption along with the adsorbate-adsorbent interaction at the molecular level are, thus, not tackled. The energy transport, that is to overcome the heat of adsorption, should be mentioned, which is certainly very impactful if one wants to employ

Table 2.3 A comparative overview of the adsorbents for CO separation process

Material	S _A BET [m ² /g]	Equilibrium CO capacity [mmol/g]	T/P	Dynamic CO capacity ^b [mmol/g]	Enthalpy of adsorption [−kJ/mol]	CON ₂ selectivity ^c	CO/H ₂ selectivity ^c	CO/CO ₂ selectivity ^c	Stability	Regeneration	Ref
Activated carbons											
AC	1170	0.2	298/1	-	-	-	-	-	-	-	[89]
CuCl (4 mmol/g)-AC	652	2.28	298/1	1.09	25	35 ^c	-	3.2 ^c	Sensitive to air	-	[89]
AC	1784	0.25	303/1	-	-	-	-	-	-	-	[87]
CuCl (7 mmol/g)-AC	478	2.95	303/1	-	-	44.6 ^c	-	6.2 ^c	Sensitive to air and moisture	No loss of capacity after 6 cycles	[87]
AC	1082	0.28	298/1	0.23	30-15	-	-	-	-	-	[92]
CuCl (4 mmol/g)-AC	505	1.85	298/1	0.94	50-47	34.3 ^d	-	2.6 ^d	-	-	[92]
AC	-	0.35	313/1	0.31	-	-	0.19 ^c	15 ^c	-	-	[90]
CuCl (0.5 mmol/g)-AC	-	0.54	313/1	0.38	-	-	0.31 ^c	20 ^c	-	-	[90]
CuCl (2 mmol/g)-AC	-	1.25	313/1	0.73	-	-	1.15 ^c	73.5 ^c	-	-	[90]
CuCl (3.5 mmol/g)-AC	-	1.69	313/1	1.05	-	-	2.25 ^c	121 ^c	-	-	[90]
CuCl (5 mmol/g)-AC	-	2.01	313/1	1.30	-	-	4.47 ^c	201 ^c	-	-	[90]
Ni(O)-PACS	1164	6.56	308/1	0.33	-	-	-	-	-	95% of max capacity after 10 cycles	[93]
Other porous carbon-based materials											
SNW-1	719	0.35	293/1	0.31	-	-	-	0.10 ^d	-	-	[95]
0.3Cu(O)@SNW-1	533	0.77	293/1	0.45	-	-	-	0.28 ^d	-	-	[95]
0.5Cu(O)@SNW-1	373	1.07	293/1	0.56	-	-	-	1.28 ^d	-	-	[95]
0.7Cu(O)@SNW-1	238	1.07	293/1	0.56	-	-	-	3.84 ^d	-	-	[95]
0.9Cu(O)@SNW-1	196	1.06	293/1	0.59	-	-	-	8.06 ^d	-	-	[95]
1.1Cu(O)@SNW-1	168	1.04	293/1	0.60	-	-	-	11.7 ^d	-	-	[95]
1.3Cu(O)@SNW-1	136	0.98	293/1	0.61	-	-	-	22.5 ^d	-	-	[95]
1.5Cu(O)@SNW-1	116	0.93	293/1	0.60	-	-	-	23.3 ^d	-	-	[95]
Zeolites											
5A	-	1.21	298/1	0.85	69-15	-	-	-	-	-	[101]
13X	-	0.47	298/1	0.37	70-36	-	-	-	-	-	[101]
ZSM-5 (SiO ₂ /Al ₂ O ₃ = 25)	371	0.93	303/1	0.66	33	1.8 ^c	-	-	-	-	[99]
ZSM-5 (SiO ₂ /Al ₂ O ₃ = 40)	379	0.66	303/1	0.49	30	1.7 ^c	-	-	-	-	[99]
ZSM-5 (SiO ₂ /Al ₂ O ₃ = 100)	348	0.45	303/1	0.35/UC	28	1.6 ^c	-	-	-	-	[99]
ZSM-5 (SiO ₂ /Al ₂ O ₃ = 400)	334	0.28	303/1	0.24	25	1.5 ^c	-	-	-	-	[99]
ZSM-5 (SiO ₂ /Al ₂ O ₃ = 900)	315	0.27	303/1	0.24	23	1.5 ^c	-	-	-	-	[99]
NaX	721	1.14	303/1	0.99	261	2.78 ^c	-	-	-	-	[103]
LIX	759	1.40	303/1	1.20	31.2	2.41 ^c	-	-	-	-	[103]
KX	537	0.60	303/1	0.53	21.3	2.23 ^c	-	-	-	-	[103]
DBX	550	0.43	303/1	0.38	20.1	1.95 ^c	-	-	-	-	[103]
C8X	423	0.37	303/1	0.32	19.2	2.08 ^c	-	-	-	-	[103]
NaX	692	1.14	303/1	0.97	26	2.78 ^c	-	-	-	-	[104]
Mg70NaX	711	0.78	303/1	0.28	17	2.00 ^c	-	-	-	-	[104]
Ca95NaX	704	1.88	303/1	0.59	33	1.80 ^c	-	-	-	-	[104]
Sr95NaX	622	1.87	303/1	1.07	31	2.37 ^c	-	-	-	-	[104]
Ba85NaX	565	1.23	303/1	0.94	30	2.39 ^c	-	-	-	-	[104]
13X	-	0.39	303/0.5	-	-	-	-	0.09 ^c	-	-	[107]
CuCl (0.523 g/g)-13X	-	3.41	303/0.5	-	-	-	-	1.86 ^c	-	-	[107]
H ⁺ Y (Si/Al = 2.4)	-	0.53	303/0.5	-	-	-	-	0.11 ^c	-	-	[107]

Table 2.3 continued from previous page

Material	S _A ^{BET} [m ² /g]	Equilibrium CO capacity [mmol/g]	T/P [K/bar]	Dynamic CO capacity [mmol/g]	Enthalpy of adsorption [-kJ/mol]	CO/N ₂ selectivity	CO/H ₂ selectivity	CO/CO ₂ selectivity	Stability	Regeneration	Ref
CuCl (0.554 g/θ-H ⁺ Y (S/Al = 2.4))	-	3.22	303/0.5	-	-	-	-	1.92 ^c	-	-	[107]
Na ⁺ Y (S/Al = 5)	694	0.21	303/1	-	-	-	-	-	-	-	[105]
CuCl (5.0 mmol/g)-Na ⁺ Y (S/Al = 5)	329	2.72	303/1	1.15	28	65 ^c	-	2.8 ^c	Sensitive to air	-	[105]
PU-1	-	2.36	293/0.75	-	-	26 ^c	52 ^c	1.93 ^c	-	-	[106]
4A	-	0.40	293/0.6	-	-	-	-	-	-	-	[106]
CuCl (0.25 g/θ-4A)	-	1.96	293/0.6	-	-	-	-	-	-	-	[106]
13X	-	0.58	293/0.6	-	-	-	-	-	-	-	[106]
CuCl (0.35 g/θ-13X)	-	2.94	293/0.6	-	-	-	-	-	-	-	[106]
Na ⁺ Y	-	0.48	293/0.6	-	-	-	-	-	-	-	[106]
CuCl (0.55 g/θ-Na ⁺ Y)	-	3.66	293/0.6	-	-	-	-	-	-	-	[106]
Cu ⁺ Y	-	1.45	293/0.6	-	-	-	-	-	-	-	[106]
SAPO-34	573	0.34	293/0.6	-	-	-	-	-	-	-	[106]
CuCl (0.1 g/g)-SAPO-34	481	0.30	298/1	0.30	-	1.63 ^c	-	-	-	-	[108]
CuCl (0.3 g/g)-SAPO-34	361	1.04	298/1	0.25	-	2.32 ^c	-	-	-	-	[108]
CuCl (0.4 g/g)-SAPO-34	323	1.30	298/1	0.27	-	11.3 ^c	-	-	-	-	[108]
CuCl (0.6 g/g)-SAPO-34	161	1.84	298/1	0.35	-	16.0 ^c	-	-	-	-	[108]
NaY	901	0.63	298/1	0.53	-	19.3 ^c	-	-	-	-	[110]
CuCl (27.7 wt%)-NaY	222	2.62	298/1	-	-	2.6 ^c	-	-	-	-	[110]
CeF	761	0.30	298/1	-	-	29.1 ^c	-	-	-	-	[110]
CuCl (28.0 wt%)-CeF	223	2.54	298/1	-	-	2.3 ^c	-	-	-	-	[110]
LaY	768	0.30	298/1	-	-	50.8 ^c	-	-	-	-	[110]
CuCl (29.5 wt%)-LaY	214	2.64	298/1	-	-	2.3 ^c	-	-	-	-	[110]
MA	334.2	0.04	298/1	-	-	52.8 ^c	-	-	-	-	[110]
Pd/MA	-	0.34	298/1	-	-	-	-	-	-	-	[115]
γ-Al ₂ O ₃	-	0.05	298/1	-	-	-	-	-	-	-	[115]
CuCl (0.20 g/θ-γ-Al ₂ O ₃)	-	1.09	293/0.6	-	-	-	-	-	-	-	[106]
CuCl/Beehmite	203	1.56	293/1	0.56	-	-	12.4 ^c	-	-	-	[113]
CuCl (30 wt%)/Bayerite	302	1.97	293/1	1.17	-	49.3 ^c	-	15 ^c	-	-	[114]
CuCl (36 wt%)/Bayerite	-	1.69	293/0.95	-	-	-	-	31.7 ^c	-	-	[114]
MOF-5	-	0.17	298/1	0.14	-	-	-	-	-	-	[101]
MOF-177	-	0.12	298/1	0.08	16	-	-	-	-	-	[101]
Cu(II)-HKUST-1	1070	0.30	298/1	0.25	22.18	-	1.3 ^d	-	-	-	[125]
CuCl (10 wt%)/Cu(II)-HKUST-1	855	0.54	298/1	0.29	62.50	8.3 ^d	9.5 ^d	-	-	-	[125]
Cu(II)-MOF-74	1455	0.91	300/1	0.4	-	6 ^d	-	-	Sensitive to air and moisture	-	[137]
Cu(II)-TDPAT	2633	1.23	300 /1	1.0	-	5 ^d	-	-	Sensitive to air and moisture	-	[137]
Cu(II)-MFU-4L	347	0.41	300 /1	0.28	-	96 ^d	-	-	Sensitive to air and moisture	-	[137]
Ni(II)-MOF-74	1574 ^a	5.78	298/1	0.84	52.7	216 ^d	1705 ^d	-	-	-	[123]
Cu(II)-MOF-74	1433 ^a	5.90	298/1	1.34	48.8	163 ^d	1040 ^d	-	-	-	[123]
Mg(II)-MOF-74	1957 ^a	4.28	298/1	3.13	35.4	10 ^d	179 ^d	-	-	-	[123]
Mn(II)-MOF-74	1797 ^a	2.96	298/1	2.43	29.7	10 ^d	86 ^d	-	-	-	[123]

Table 2.3 continued from previous page

Material	S _A ^{BET} [m ² /g]	Equilibrium CO capacity [mmol/g]	T/P [K/bar]	Dynamic CO capacity [mmol/g]	Enthalpy of adsorption [−kJ/mol]	CO/N ₂ selectivity	CO/H ₂ selectivity	CO/CO ₂ selectivity	Stability	Regeneration	Ref
Fe(D)-MOF-74	1535 ^a	5.95	298/1	2.61	43.6	68 ^d	507 ^d	-	-	-	[123]
Zn(D)-MOF-74	1105 ^a	1.72	298/1	1.47	27.2	7.5 ^d	47 ^d	-	-	-	[123]
Fe(DC) ₂ -BBTA	1055	5.83	298/1	5.40	65.4-38.0	47 ^d	128 ^d	-	-	-	[131]
Fe(DC) ₂ -BTDD	1897	3.38	298/1	3.26	61.3-34.5	-	-	-	-	No loss of capacity after 10 cycles	[131]
Fe(D)-BTTr	1630	-	298/1	-	75.0-65.0	250 ^d	1900 ^d	28 ^d	-	-	[130]
Cu(DIaIp)	-	7.15	120/1	1.79	19.0	2.2 ^c	-	-	Sensitive to moisture	-	[128]
Rh(II)-DUT-82	780	2.79	298/1	0.73	50.6	-	-	-	Thermally stable up to 250 °C	2nd and 3rd cycle show lower, constant capacity compared to the 1st cycle	[127]
IrOF-1	-	-	-	-	52.7-36.4	-	-	-	-	-	[138]
Fe(D)-MIL100	2042	0.38	298/1	0.33	39	1.5 ^d	4.44 ^d	0.16 ^d	-	-	[132]
CuCl (0.8 g/g)-Fe(D)-MIL100	762	2.78	298/1	1.26	49.5	17.5 ^d	55.8 ^d	3.9 ^d	-	-	[132]
Fe(D)-MIL-100	2458	1.2	303/1	-	-	-	-	-	-	-	[139]
CuCl (0.9 g/g)-@Fe(II)-MIL-100	898	3.52	303/1	1.61	-	677 ^d	-	29 ^d	-	CO adsorption capacity is maintained during 30 cycles of CO adsorption and desorption	[139]
CuCl (40 wt%)-Cr(III)-MIL-101	1030	2.82	298/1	-	-	315 ^d	-	34 ^d	Thermally stable up to 600 °C	Stable during 6 cycles	[140]
Cr(III)-MIL-101	3788	0.50	298/1	0.44	44.5-11.7	6.3 ^d	16.0 ^d	-	-	-	[135]
Cu(NO ₃) ₂ -VCl ₃ (6.5 mmol/g) Cr(III)-MIL-101	1697	1.19	298/1	0.62	52.0-20.0	70.1 ^d	641.7 ^d	-	91.8% efficient after 2 weeks of air exposure	Stable during 5 cycles	[135]
CuAlCl ₄ (5.0 mmol/g) Cr(III)-MIL-101	2391	2.18	298/1	1.13	-	31.5 ^d	-	-	87.5% capacity after 4 weeks of exposure	Stable during 5 cycles	[134]
Cr(III)-MIL-101	3615	1.33	298/1	0.74	-	4.8 ^c	-	-	Sensitive to air	-	[133]
Cr(III)-MIL-101	2045	1.55	298/1	0.90	-	6.7 ^c	-	-	Sensitive to air	-	[133]
CuCl (1.75 mmol/g) Cr(III)-MIL-101	1908	1.75	298/1	1.03	-	9.5 ^c	-	-	Sensitive to air	-	[133]
CuCl (3.14 mmol/g) Cr(III)-MIL-101	1843	2.42	298/1	1.19	-	18.6 ^c	-	-	Sensitive to air	-	[133]
CuCl (4.38 mmol/g) Cr(III)-MIL-101	1070	2.15	298/1	0.8	-	26.9 ^c	-	-	Sensitive to air	-	[133]
Cu (4 Cu(II)-Ni-MOF-74 Cu (2 Cu(II)-Co-MOF-74	1047 1204	- -	298/1 298/1	- -	- -	27 ^c -	- -	3 ^c -	- -	- -	[141] [141]
Cu ₂ ZnCl ₂ (10 wt%)-MIL-100(Fe)	342.9	3.16	298/1	1.45	58	-	-	104 ^d	Resistant to air	Stable during 5 cycles	[136]

^a S_A Langmuir, ^b defined as the difference in capacity between 1 and 0.1 bar at the given temperature, ^c idealised selectivity of an equimolar mixture given by comparison of the capacities of the two adsorbates at the given temperature and pressure, ^d IAST selectivity of an equimolar mixture at the given temperature and pressure

chemisorption at scale. Though many adsorbents mentioned in literature show good adsorption capacity and selectivity towards CO with an IAST calculation, it is of importance to use realistic process conditions (for example, in a mixture of gases) for fair comparisons between different materials. It is obvious that an adsorbent will have a higher adsorption capacity at cryogenic temperatures than at room temperature and a similar argument could be made for the adsorption and desorption pressure. Furthermore, the material should be tested for stability and reproducibility over multiple adsorption-desorption cycles to quantify the dynamic performance, while now mostly only equilibrium adsorption isotherms and isosteric heats of adsorption are reported. Materials with a high equilibrium CO capacity do not necessarily possess a high working capacity as part of the CO is bound irreversibly under desorption process conditions. An example of this behavior is Ni-MOF-74, showing a significant difference in its equilibrium and dynamic CO capacity, as summarised in Table 2.3. A high binding affinity towards CO is beneficial for the selectivity as well, but this comes at the cost of adsorption reversibility with the conventional temperature or pressure swing processes. Attaining a significant working capacity of a material with a high affinity for CO thus requires more extreme process conditions, which increases the energy usage of the process and could affect the performance over time. Conventional swing processes expend energy in pressurising or heating the entire adsorption system, in order to change the chemical potential of the entire system. An improvement could potentially be made via adsorbents placed on electrically heated SiC supports. Adsorption processes would also become more efficient if they could selectively target and switch the adsorbate-adsorbent bond. Overall, other than developing novel adsorbents which could be used in realistic conditions, there is also a need to choose the right technique which can help to fully understand and quantify the actual value of adsorbents for CO purification at the industrial scale. Moreover, new process variables other than temperature or pressure, that can trigger the adsorption/desorption processes in a more energy-efficient way are also worth exploring.

2.3.3. Progress in absorption and membranes for CO-separation

Recent efforts in search for new absorbents are focused on the development of ionic liquids (IL) as a solvent for metal-complexes that selectively coordinate with CO absorbent. Using these ILs the solubility, stability, or environmental issues of COSORB could be resolved [43, 142–145]. Other than ILs being used solely as a solvent for complexes, ILs that intrinsically, selectively absorb CO are also being developed [146, 147].

The cuprate-based ionic liquid of David et al. [142] reached a CO purity of 95% starting from a 1:1 mixture of CO and N₂. Although the first results were promising, the sluggish mass transport rate typically shown by viscous ionic liquids and still relatively low CO capacity (2 mmol/g) are hurdles that should still be overcome to develop a competitive process [143].

Tao et al. [147] developed an IL system based on carbanions which showed an exceptionally high CO solubility (0.11 mmol/g) for a metal-complex free IL. However, this also shows that without the use of a transition metal complex the CO capacity of ILs is too low.

Viable absorption processes based on ILs require more work, but the plethora of possibilities in the IL toolbox offer perspective. Cui et al. [148] sought to alleviate the mass transfer limitations by focusing on low viscosity deep eutectic solvents (DES). A DES consisting of 2-diethylaminoethanol chloride plus cuprous chloride (CuCl) plus ethylene glycol in a molar ratio of 1:1:4 showed the highest CO absorption capacity. However, this capacity is still only a modest 0.405 mmol CO/g at 1 bar and 293.3 K.

A novel absorption method was reported by Terry et al. [149] in which they used electrochemistry to modulate the complexation of CO with CuCl/CuCl₂. They note that Cu(II) shows low affinity towards CO and Cu(I) shows high affinity and that by changing the Cu-ion oxidation state the electrolyte's ability to absorb CO can be altered. They pass the electrolyte solution containing the Cu(II) through two porous carbon flow electrodes to produce Cu(I). This Cu(I) is then used to extract the CO from the feed gas stream in a hollow fiber membrane. The solution is then flowed through the two porous carbon flow electrodes oxidising the Cu(I) to Cu(II). The CO is then recovered by once again passing the stream through a hollow fiber membrane. The electrolyte solution can then be reused by reducing the Cu(II) again. By utilising this system they were able to change the CO and N₂ pressure in the feed cylinder from 0.61 and 0.44 atm to 0.07 and 0.40 atm, respectively, while the CO and N₂ pressure in the receiving flask changed from, respectively, 0.81 and 0.03 atm to 1.24 and 0.04 atm, at which point equilibrium was reached. The changes in pressure indicate that the electrochemically modulated absorption process selectively separated CO from N₂. They note, however, that there are limitations to this technique. Firstly, low current densities are observed, resulting in a need for high surface area electrodes. Secondly, the utilisation efficiency of the Cu(I) is highly limited, with only 1 out of every 5 complexes being used in CO absorption at the pressures reported, while all Cu-ions undergo reduction and oxidation through the electrodes. Lastly, while the technique looks promising for further research, no further follow-up papers were published on electrochemical separation of CO.

To avoid the energy-intensive nature of the absorption process, supported liquid membranes that act as facilitated transport membranes, have also been explored for CO/N₂ separation. Here the membrane liquid contains mobile carriers and is immobilized within the pores of a microporous support membrane that serves merely as a support layer [150, 151]. First Zarca et al. [152] studied ionic liquid supported membranes, namely 1-hexyl-3-methylimidazolium chloride with CuCl as CO-carrier. Depending on the conditions CO/N₂ selectivities of 2-4 were achieved,

which is rather low. Moreover, upon addition of CuCl the CO permeability (at 303 K, 150 kPa pressure difference) increased only from 11.8 Barrer to 16.4 to Barrer. The limited solid-state facilitated transport was attributed to the low equilibrium constant of the complex formation, as well as the lower diffusivity of the CO-Cu(I) complex in the room temperature ionic liquid medium.

Feng et al. [153] studied supported ionic liquid membranes using AgBF_4 as carrier. This is inspired by membranes for ethylene/ethane separation where AgBF_4 acts as carrier for ethylene via π -complexation [154]. Also complexation of CO with Ag^+ via π -complexation via the mechanism described in Section 2.2.2 is expected [155]. Feng et al. dispersed AgBF_4 in 1-ethyl-3-methylimidazolium tetrafluoroborate $[\text{emim}][\text{BF}_4]$ as ionic liquid on a porous polyethersulfone membrane. Here the CO/N_2 selectivity increased from ≈ 1 to ≈ 9 going from no AgBF_4 to 0.3:1 AgBF_4 : $[\text{emim}][\text{BF}_4]$ (measured at 293 K, 0.45 MPa). The permeability, however, decreased dramatically with increasing AgBF_4 content, from ≈ 300 Barrer to ≈ 20 Barrer.

Later, Kim et al. [156] achieved a slightly better result via combining AgBF_4 with $[\text{bmim}][\text{BF}_4]$ (1-butyl-3-methylimidazolium tetrafluoroborate) and a comb-like copolymer poly(2-hydroxypropyl-2-(methacryloyloxy) ethyl phthalate-co-acrylic acid), which were coated together on a polyethersulfone membrane. The highest achieved CO/N_2 selectivity was 16.2 and the CO permeance was 2.1 GPU (gas permeance units). A membrane containing the ionic liquid but not AgBF_4 for comparison was unfortunately not studied.

Solid state facilitated transport membranes have also been investigated. In 2019, Park et al. [157] reported on AgBF_4 and MgO nanosheets embedded in poly(ethylene glycol) behenyl ether methacrylate-poly(methacrylic acid). The latter polymer was chosen as the carboxylic acids groups would minimise CO_2 permeance, and the MgO nanosheets should stabilize AgBF_4 . A CO permeance of 79 GPU and separation performance of CO/N_2 of 14.7 and CO/CO_2 of 12 were achieved.

The most recent example of a solid state facilitated transport membrane is a system where AgBF_4 and Ag nanoparticles in metal-organic frameworks MIL-101 are proposed to work as dual carriers [158]. The materials are dispersed in a comb copolymer poly(glycidyl methacrylate)-co-poly(oxyethylene methacrylate) deposited onto a porous polysulfone support. Upon addition of 10 weight percent of Ag@MIL-101 (compared to the copolymer) the CO/N_2 selectivity increased from 3.3 of 11.8, and the CO permeance from 24.8 GPU to 30.7 GPU. Figure 2.12 provides an overview of the different reported CO/N_2 selectivities versus CO permeances for several membranes.

In conclusion, the intrinsic energy intensive nature of liquid phase absorption processes and complex stability issues render them incompatible with recent

sustainability ambitions. The use of ionic liquids and deep eutectic solvents makes them less harmful for the environment, but due to the relatively low CO absorption capacity and the high viscosity of the ILs, the high energy requirement for regeneration remains. Promising results have been achieved via membranes, an intrinsically less energy-intensive separation technology, based on facilitated transport via a carrier that selectively binds CO. However, these are based on Cu(I) and Ag(I) complexes and are studied in a water and O₂ free environment, probably because these complexes are likely unstable in presence of these molecules. It would be interesting to see future work on facilitated transport membranes particularly for wet flue gases.

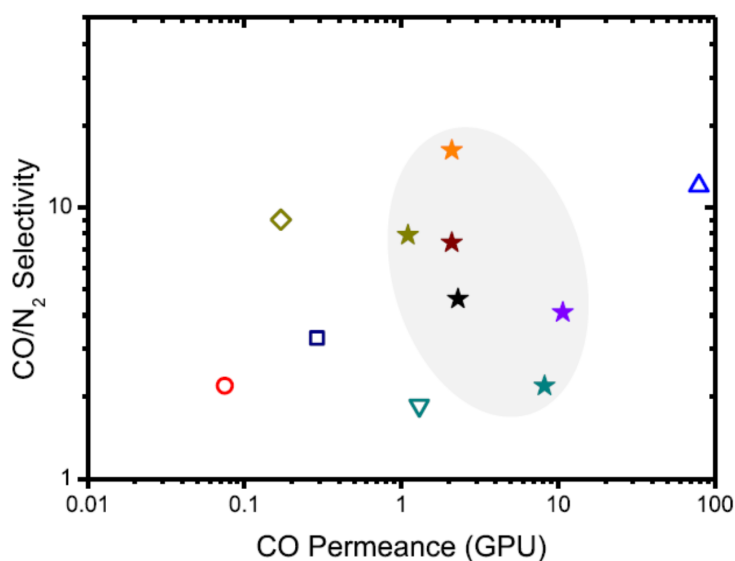


Figure 2.12 Plot of CO/N₂ selectivity versus CO permeance for various membranes. Star symbols (★) represent reference [156]. The blue triangle represents reference [157], the other symbols represent references [152, 153, 159, 160]. Reprinted from [156], Copyright (2021) with permission from Elsevier.

2.4. Traditional versus emerging CO sources

2.4.1. Traditional CO sources from industrial processes

Industrially, carbon monoxide can be produced by partial oxidation and steam reforming of carbonaceous feedstocks (e.g., natural gas, steam reforming: CO: 15.5%; N₂: 0.2%; CO₂: 8.2%; H₂: 75.5%; CH₄: 0.5%; dry basis), as well as via coal gasification (coal gasification: CO: 59.4%; N₂: 0.6%; CO₂: 10.0%; H₂: 29.4%; other species: 0.6%; dry basis) (Table 2.4 [161]). As a co-product mainly

along with hydrogen, carbon monoxide gases are then separated and purified by pressure swing adsorption and/or cryogenic distillation [162]. CO separated from these product streams can further be used as chemical building block in various chemical processes.

Meanwhile, large amounts of CO can also be found in the off gases of metallurgic processes, especially in the blast furnace gas (BFG: 20-28% of CO), basic oxygen furnace gas (BOFG: 55-80% of CO), and to a smaller extent in the coke oven gas (4-7%) of integrated steel mills (Table 2.4 [6]). However, most attention is paid to the separation of CO₂ from these off-gases and very little information is available in open literature regarding the industrial separation of CO from BFG or BOFG. Only the PSA process named “COPISA” is claimed to be used for the separation of CO from the BFG process by Kawasaki Steel Corporation and Osaka Oxygen Industries LTD (Section 2.2.4). In most cases, CO is currently not separated from these off-gases, the main bottleneck being the difficult separation of CO and N₂. Instead, it is being oxidised to CO₂ and emitted. Direct CO₂ emission from steel and iron manufacturing accounts for 5-7% of all man-made CO₂ emissions in the world [163]. Roughly one third of this CO₂ is created via oxidation of CO. Preventing avoidable CO₂ by capture of CO, hence, will have a significant impact in achieving carbon-neutrality.

Coal gasification and iron making off-gases are typically rich in carbon monoxide and show a low syngas ratio. Smelting reduction processes, such as COREX® and FINEX®, are a newer iron making technology [161]. With less impurity and lower nitrogen content (< 10%) than blast furnace gas, COREX® (with 40-50% of CO) and FINEX® (with 30-50% of CO) export gases seem to be attractive as alternative feedstock for the generation of CO. (Table 2.4 [1]) However, there are no reports concerning plants in operation for the utilisation of these two export gases as syngas in chemical industry nor are there reports regarding separating CO from these gases.

Table 2.4 Typical excess gas compositions from industrial processes [6, 161]

	Blast furnace gas	Coke oven gas	Basic oxygen furnace gas	COREX® Export gas	FINEX® Export gas
Gas production	~900 m ³ /ton steel	~50 m ³ /ton steel	~50 m ³ /ton steel	-	-
P _{abs} [MPa]	Up to 0.3	-	-	0.1	0.1
T[°C]	100-200	800	-	40	40
Gas component	Vol (%)				
CO	20-28	4-7	55-80	40-50	30-50
N ₂ + Ar	50-55	0-10	8-26	2	10
CO ₂	17-25	1-3	10-18	25-35	25-45
H ₂	1-5	39-65	2-10	15-25	12-25
CH ₄	-	20-42	-	2	1.5
C _x H _y	-	2-8.5	-	-	-
Other species	Water vapour, H ₂ S, sulfur, cyanide compounds	Water vapour, H ₂ S, benzene, toluene, xylene, ammonia, other hydrocarbons, sulfur compounds	Water vapour, H ₂ S, sulfur compounds	Water, H ₂ S	Water H ₂ S

2.4.2. Emerging non-traditional CO sources

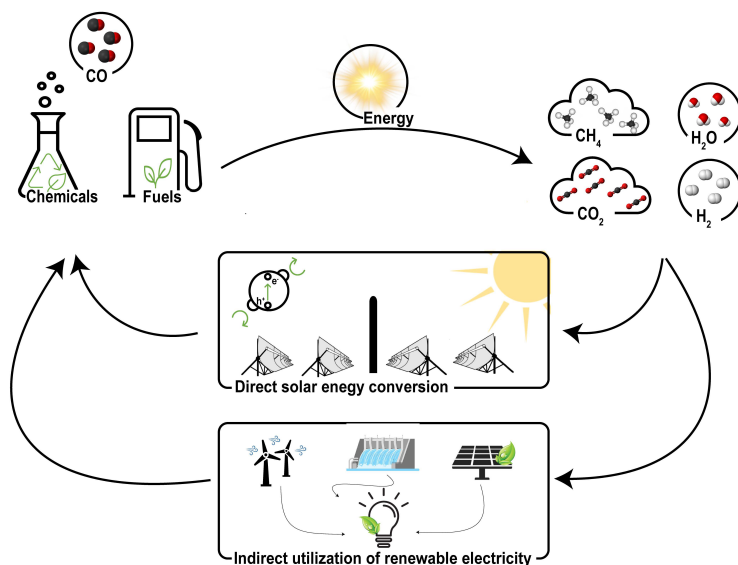


Figure 2.13 Schematic of emerging processes utilising renewable energy for the conversion of carbon dioxide enabling the development of carbon-neutral cycles.

With the transition towards a more sustainable chemical industry and the need for utilisation of carbon dioxide as an alternative carbon source, a variety of new carbon-chemical processes will emerge in the near future (Figure 2.13). Renewable electricity or direct solar light capture will be used to power the envisioned processes, ultimately leading to a carbon neutral cycle [164]. Similar to the addressed traditional fossil-based sources, CO will likely be present in a complex product stream and purification or recovery will be essential to enable carbon monoxide utilisation. Here we outline emerging processes that are foreseen as possible CO sources and discuss their status, i.e., technology readiness level (TRL). Moreover, the required energy input, the expected product compositions, the associated challenges for CO separation, and general limitations of the technologies will be briefly addressed.

Among the explored strategies, direct solar energy utilisation is of great interest. Here, additional energy input is not required and with an average solar flux of 175 W/m^2 sufficient energy is made available at the earth's surface within 2-3 hrs covering the annual worldwide energy consumption [164, 165]. Direct solar utilisation is classified into solar thermochemical and photon-driven processes. The latter direct photo-driven CO_2 reduction processes leverage the photon energy directly to drive a redox reaction, for example, using a semiconductor with appropriate valence and conduction band positions. Direct photo-driven CO_2 electrolysis eliminates the intermediate step of transferring electricity or

converting light into heat, offering a thermodynamic advantage. Still, the kinetic overpotentials of the CO_2 reduction reaction and concomitant oxygen evolution imply the use of semiconductor materials with band gaps larger than 2.5 eV and/or usage of multifunction photovoltaic cells [166, 167]. Photocatalytic processes are additionally hampered by internal and surface recombination as well as limited stability of photoelectrodes. Hence, a trend towards protecting or even separating photovoltaic layers from electrocatalytic layers has been ongoing, which has blurred the interface between direct photo-driven CO_2 electrolysis and CO_2 electrolyzers indirectly driven by solar energy via the power grid [168]. While for these indirect solar-to-CO conversion processes efficiencies >5% have been reported [169], the direct photocatalytic or photoelectrochemical CO_2 -to-CO conversion has arguably the lowest TRL level (TRL 3) among the technologies [167].

Solar thermal approaches are more advanced in their development. In fact, power generation using solar towers or dishes is currently applied on larger-scale and will potentially allow for a straightforward implementation of solar reactors [170, 171]. Generally solar thermochemical processes make use of concentrated solar heat to drive a thermochemical cycle. In a first step, generated solar heat enables reduction of metal oxides. Subsequent oxidisation of reduced metal oxides in a nonsolar exothermic reaction by CO_2 and/or water facilitates formation of CO and/or H_2 . The theoretical oxide-dependent (e.g., CeO_2) solar-to-fuel efficiency of solar thermal processes is typically 20% therefore being on par with the break-even point for cost competitive production of direct solar-driven CO_2 utilisation. Small prototypes for water splitting and/or CO_2 utilisation are already in operation (TRL 4–5) [172]. Thus, the final product stream of solar-thermal CO_2 conversion processes will at least be a mixture of CO and CO_2 , or $\text{CO}/\text{CO}_2/\text{H}_2$ and water in the case of concomitant water splitting. Hence, selective product separation technologies for practical CO_2 to CO conversion is needed.[171] Still, implementation of solar thermal processes is hampered by the insufficient durability of available metal oxides and new materials with fast oxygen exchange kinetics and high stability are required for commercial success [171].

In contrast to above mentioned technologies, electrochemical and plasma conversion rely on electricity. Their reliance on electricity might contradict the purpose of greenhouse gas mitigation. However, the global transition to solar and wind energy implies that both electrochemical and plasma conversion technologies can be considered carbon neutral [173–176]. Amongst other processes, plasma approaches allow for pure splitting of CO_2 to carbon monoxide and oxygen. Various versions of the specific implementation of the plasma technology exist (for a detailed understanding of the available plasma technologies the reader is referred to Snoeckx et al. [172]), however, all of them have in common that the CO_2 conversion efficiency is sacrificed by energy efficiency and vice versa. So far only gliding arc and microwave plasma are capable of reaching energy efficiencies of >60% with CO_2 conversions of up to 40%, whereas carbon dioxide conversions in the range of 40–90% are only achievable at energy efficiencies below 40%. The

TRL level of plasma technologies for CO₂ splitting is considered to be TRL 3-4. Plasma technologies also allow for CO₂ conversion with hydrogen (or water) and dry-reforming of methane. For both processes the product mixture is complex compared to pure CO₂ splitting and feed gas ratios largely influence conversion rates and energy cost/energy efficiency [175]. Still, conversion efficiencies for dry-reforming of methane in plasma reactor are often reported to exceed 70% at energy efficiencies of >50% [172].

At present, most scientific studies for CO₂ conversion are electrochemical, either at high temperature or low temperature operation, both at a slightly higher TRL compared to plasma technologies or solar driven conversion. These technologies have been demonstrated at tens of cm² scale [176–178] and are being developed by several companies (Siemens, Sunfire, Opus12, Shell, etc.) [179]. The designs for the electrochemical routes tap from the more developed electrochemical processes of, e.g., water electrolyzers, fuel cells and chlorine production. Hence, based on the available industrial experience it is expected that direct or indirect electrochemical CO generation is closest to industrial application and will be addressed in more detail in Section 2.4.3.

2.4.3. CO capture after electrochemical reduction of CO₂

As an alternative to obtaining syngas from steam reforming, syngas can be produced from renewable resources using electrochemistry. Two electrochemical routes for obtaining CO are available (Figure 2.14): 1. indirect CO₂ conversion via electrochemically produced hydrogen coupled with reverse water-gas shift reaction or 2. direct electroreduction of CO₂. Both routes provide a pathway to utilise CO₂ for hydrocarbon fuels and carbon-based chemicals thereby closing the carbon cycle. Regarding fuels, producing synthetic hydrocarbon fuel is typically less energy efficient than producing green hydrogen as an energy carrier, but hydrocarbon products are liquid or can be liquefied [180]. The EU predicts that up to 4% of their consumed energy is transported via e-liquids (and roughly 5% via e-gas) by 2050 [181]. In addition, currently 14% of our fossil oil is converted into petrochemicals [182] and needs to be replaced with a carbon-neutral alternative when completing the energy transition towards renewables. Because carbon monoxide is a versatile precursor for many hydrocarbon-based fuels and chemicals, electrochemical routes for synthetically produced CO have gained attention.

Synthetic carbon monoxide can be obtained using mature development technology via water electrolysis driven by renewable energy (producing green hydrogen) and applying the reverse water-gas shift reaction (RWGSR) to a mixture of hydrogen and CO₂ gas (Figure 2.14 right). This endothermic RWGSR, for example using Fe-, Cu- or Co-based catalysts, is favored at elevated temperatures to achieve high conversion to CO with fast kinetics [183, 184]. Typically, 40-70% of the CO₂ can be converted. Side products are possible, such as methane, but the

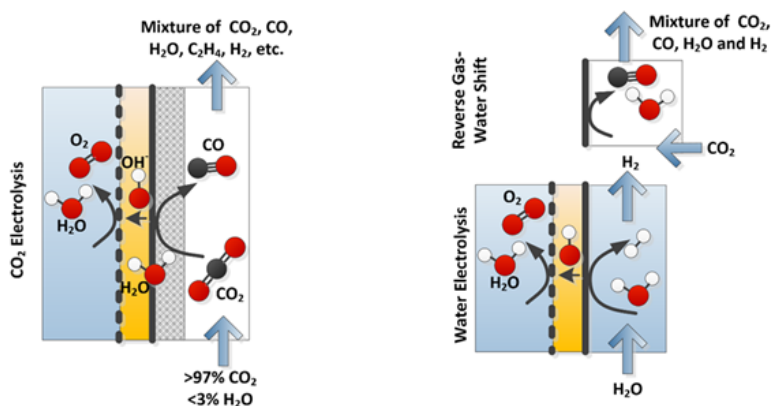


Figure 2.14 Direct CO₂ to CO conversion (left), in this case in a reactor with a liquid anode (zero-gap) and CO₂ reduction at the vapour-fed cathode, and indirect CO₂ conversion (right), via water electrolysis and Reverse Gas-Water Shift Reaction (RGWSR). For simplicity, reaction stoichiometry is ignored.

selectivity towards carbon monoxide is high (>90%) at elevated temperatures [185]. Hence, carbon monoxide separation technologies for this route should deal with a relatively high CO concentration in a matrix of H₂, CH₄ and CO₂.

A more challenging separation may be required for the carbon monoxide produced from direct CO₂ electroreduction (Fig. 2.14 left). A multitude of routes has been studied for direct electrochemical CO₂ conversion, including solid oxide electrolysis, molten carbonate electrolysis, low-temperature aqueous-dissolved CO₂ reduction and low temperature vapour-phase CO₂ reduction. From these technologies for direct CO₂ electroconversion, the latter has been developed in medium scaled cells by startup companies and industry. Scientific literature also shows extensive studies on the low temperature vapour-phase CO₂ reduction, which has achieved higher current densities (>1 A/cm²) owing to the high diffusivity of CO₂ in gas phase.

In the field of low-temperature (vapour-fed) electrochemical CO₂ reduction, most efforts have ignored the single pass conversion fraction of CO₂ to CO, and have fed excess of CO₂ to allow focusing on material development, high current density, energy efficiency and Faradaic efficiency. Therefore, the concentration of CO in the product stream is typically very low (<10%) in scientific studies, implying large efforts for the separation process. Some research has studied direct CO₂ electroreduction with a high fraction of CO₂ to CO conversion. However, still 40-80% of the CO₂ remains unreacted in a single pass conversion step, even when the CO₂ feed rate is optimised [186–188]. Moreover, a wide variety of products can be produced by CO₂ electroreduction (carbon monoxide, ethylene, hydrogen, ethanol, formic acid). In particular, to minimise the CO₂ concentration in the

outlet gas, the CO_2 supply must be limited, which increases the relative hydrogen production and the local pH at the electrode, favoring CO_2 conversion to formic acid (Figure 2.15). Two strategies can be pursued to increase CO concentrations. First, the CO_2 to CO single pass conversion fraction can be optimised, compromising the Faradaic efficiency and energy efficiency, but creating a product stream with concentrated (>50%) CO. Alternatively, a low CO concentration can be accepted if a highly selective separation technology is implemented to allow recycling of unreacted CO_2 . Hence, advancing separation technology of CO will largely impact the CO_2 electroreduction possibilities.

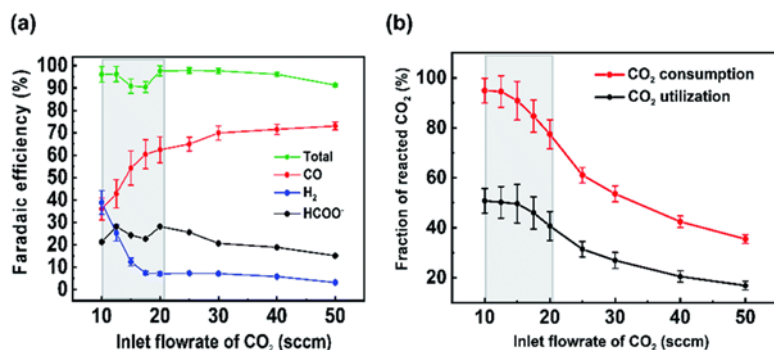


Figure 2.15 Faradaic efficiency of products for various inlet flow rates performed at a current density of 200 mA/cm^2 . (b) CO_2 utilisation and CO_2 consumption for different inlet flow rates at 200 mA/cm^2 . Greyed regions represent trade-offs between utilisation and selectivity. CO_2 consumption is always higher than CO_2 utilisation because CO_2 is crossing over to the analyte. Reproduced from [187] with permission from the Royal Society of Chemistry, copyright 2021.

2.5. Conclusions and outlook

Despite CO being a key chemical building block in the chemical industry (e.g., in Fischer Tropsch synthesis), advancements in its separation are still very much needed. On one hand, there are traditional technologies that produce process streams high in CO content, like metallurgic flue gases, where CO is barely recovered, but solely used for its caloric value via oxidising it to CO_2 . This constitutes 2.7 % of manmade CO_2 emissions [189]. On the other hand emerging processes produce complex product mixtures with variable CO concentrations. Even for the emerging process that are optimized for CO production, i.e., electrochemical carbon dioxide reduction to CO, product streams will likely contain impurities such as water, carbon dioxide, and (traces) of hydrogen, exemplifying the urgency of further research and industrial implementation of energy efficient CO separation processes. In fact, carbon neutrality and the electrification of the chemical industry poses a need for research and development of efficient CO

separation to be directly integrated into emerging and existing processes.

With regard to metallurgic off-gases, the main focus is on the separation of CO and N₂, which are hard to separate due to their very similar physical properties. Most commercial processes are thus based on chemisorption of CO via CuCl complexes. Among these, the absorption process (COSORB) shows the best performance in terms of CO purity and recovery, but is also very energy consuming due to its heating and cooling cycles. In contrast, adsorption processes are more energy-efficient, but high CO purity can only be achieved by compromising recovery. Particularly, for the separation process relying on strong physisorption (based on Na⁺ Mordenite), instead of chemisorption, the loss in recovery is particularly large (98% purity with 45% recovery). Moreover, all these processes require pretreatment to remove water to avoid competitive adsorption and/or decomposition of the CuCl complexes, which also comes at an energetic cost. The limited degree to which these processes are actually implemented to separate CO from metallurgic off-gases, indicates that a sufficiently satisfactory technology has not been developed so far.

The last decades has thus seen significant research effort in developing new CO separation processes. In the field of absorption, to mitigate the environmental risks associated with a solvent based absorption process, current research is focused on solvents with low volatility, like ionic liquids and deep eutectic solvents. However, the limited CO absorption capacities reached, combined with the ever-present high energy needs for the heating and cooling cycles, and mass transfer limitations of ionic liquids, poses the question of the expected impact of this direction of research. As such the research effort in finding new adsorbents was much larger. In the last decades, many different types of porous solids have been investigated, from activated carbon, zeolites, mesoporous silica and alumina to metal-organic frameworks. Most of these studies are based on the doping of these materials with transition metal complexes capable of π -complexation with carbon monoxide to achieve chemisorption. Most typically, like in the commercial ad/bsorption processes, CuCl is used, leading to CO/N₂ selectivities ranging from 35 to 66. Metal-organic frameworks themselves can also show high CO/N₂ selectivity if they contain coordinatively unsaturated transition metal sites capable of π -complexation with CO, especially for Cu(I), Co(II), Ni(II) and Fe(II) high CO/N₂ selectivities, ranging from 46 to 216, have been achieved. Particularly intriguing adsorbents (e.g., Fe₂Cl₂(bbta) [131]) based on a cooperative spin crossover mechanism accompanying CO adsorption have been found, which show a step CO adsorption isotherm, meaning that only a very small change in CO partial pressure would be needed to swing between adsorption and desorption. Such a mechanism has large potential to be energy-efficient.

The available studies generally provide an ideal CO/N₂ selectivity, the CO-adsorption capacity, as well as the adsorption enthalpy. Regularly adsorption capacities as high or higher than those of the commercial CO-adsorbents (>3

mmol/g) are measured, and in some cases also the dynamic capacity (defined as change in equilibrium adsorption between 0.1 and 1 bar at measured temperature) is above this value. Competitive adsorption of CO and N₂, however, is scarcely measured, but is needed to make a realistic assessment of the selectivity. Breakthrough profile measurements would, moreover, allow for assessment of whether significant changes in the amount of adsorbed CO can be obtained within a reasonable temperature or pressure range, thus improving the regeneration potential, as well as the stability of performance over many adsorption/desorption cycles. Performing this work in humid streams would additionally allow to assess both hydrolytic stability as well as competitive CO, H₂O adsorption. Currently, breakthrough studies nor studies on wet gases have rarely been conducted. It is very likely that the adsorbents based on doped CuCl have limited stability in wet gases. The metal-organic frameworks containing coordinatively unsaturated transition metal sites may be hydrolytically stable, depending on the framework [190]. Whether CO can be competitively absorbed in the presence of water would need to be investigated. In general, with regard to industrial applicability, it is also important that the adsorbents are tested with respect to 1. resistance to attrition (especially where circulating and moving bed process implementations are considered), 2. heat transport, as adsorption is an exothermic process, and 3. corrosion sensitivity for the feed stream by including impurities such as SO_x, NO_x and HCl.

Considering the importance of CO/CO₂ separation among emerging technologies perceived as being important to achieve defossilisation, e.g., electrocatalytic reduction of CO₂ to CO, it is vitally important to include CO capture of CO from streams rich in CO₂ and, again, ideally wet streams. Nevertheless, only a subset of the available studies include determination of the CO/CO₂ ideal selectivity revealing the need to steer research efforts in this direction. Due to the stronger physisorption of CO₂ compared to N₂, typically the CO/CO₂ is an order of magnitude lower than the CO/N₂ selectivity and is especially poor in materials with small micropores where the physisorption of CO₂ is strong. Considering the emerging importance of CO/CO₂ separation within the frame of defossilisation, this would deserve more attention in future research, ideally through breakthrough profile measurements of wet gas mixtures.

A limited amount of work has been performed regarding CO/N₂ separation via membrane separations. Regarding CO/N₂ membrane separation, some promising results based on facilitated transport membranes containing transition metal complexes (most notably AgBF₄) have been achieved. Considering that the scope of work is very limited and that membrane separations operate generally in an energy efficient manner, this might be an area where significant progress could be made. Again, ideally these membranes are also assessed for wet streams, and include CO/CO₂ separation. At the present, as they are based on Ag(I) and Cu(I) carriers they are unlikely to be stable in wet streams.

The emerging separation problem of separating CO from CO₂/H₂O/H₂ in the frame of electrochemically produced CO, might alternatively be tackled via removing CO₂ from the mixture for feedback to the reaction mixture via existing adsorbents and membranes for CO₂ removal. Thus in absence of transition metal cations, materials with a high CO₂/CO selectivity based on the often stronger physisorption and solubility of CO₂ compared to CO are useful. Still, any adsorbent or membrane for the removal of CO should be compared techno-economically against processes based on CO₂ selective materials.

These identified challenges provide a guidance for future research. For environmental concerns, meaning the need for energy-efficient separation processes, the likely focus will be on adsorption and membrane separations. With regard to adsorbents, strong CO₂ adsorption should be avoided. Through a large research effort in the last decades, an understanding of what structural features lead to strong CO₂ adsorption has emerged [118, 191]. This means that amine functional groups and ultramicropores should in general be avoided to achieve high CO/CO₂ selectivity. All well-performing adsorbents capable of CO/N₂ separation seem to be based on chemisorption via π -back bonding with transition metals. The stability of the redox state of the transition metal ion is the first concern for compatibility in the presence of H₂O and O₂. Cu(I) and Fe(II) have been the most studied, but they are unstable in these conditions. Potentially, via applying a sufficiently negative electrical bias to an adsorbent in an electrochemical cell, the lower oxidation state of Cu(I) and Fe(II) could be stabilised. Alternatively, the few adsorbents based on Co(II) and Ni(II) have an equally adequate adsorption enthalpy and CO/N₂ selectivity, while these elements are notably more stable in this oxidation state. Studying these materials for their water and oxygen stability is necessary, as well as developing new adsorbents based on these ions.

Many streams from which we want to separate CO are also humid streams. Ideally, the CO adsorbent can selectively adsorb CO, also at a relative humidity (RH) of relevance from a process technology point-of-view, e.g. 40 % RH. Competitive adsorption of CO over water via π -back bonding with transition metals is possible. For example, CO binds preferentially over water to the Fe(II) of haemoglobin. Although, that is if we consider a single adsorbed H₂O molecule versus a CO molecule. For haemoglobin this is a realistic situation, due to the hydrophobic pocket in which the Fe(II) site is embedded. However, when the Fe(II) porphyrin motif is surrounded by water, the extent to which hydrogen bonds need to be broken for the adsorption of a molecule of CO, probably makes competitive CO adsorption energetically unlikely. Hence, a search for microporous materials with motifs for CO chemisorption in an otherwise hydrophobic structure in which pore filling by water cluster formation does not take place at low to modest relative humidities (e.g., 40 %RH) is needed. Some structure-property relationships which lead to such water sorption behaviour are discussed in the literature for activated carbons [192] and metal-organic frameworks [193, 194], and can be applied in the search for new CO-adsorbents. Similar material design considerations as outlined

here for adsorbents, can also be used for the development of new and more stable facilitated transport membranes. The scant research on membranes for separation of CO via facilitated transport means that there is a large potential for progress in this field.

In short, while significant progress has been achieved in research literature regarding the separation of CO, we highlight the importance and the lack of investigating especially the separation of CO/N₂ and CO/CO₂ from humid streams in realistic dynamic conditions.

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Chapter 3

Activation of Prussian Blue Analogues: Temperature Effects on Structure, Porosity, and Open Metal Site Accessibility

Prussian blue analogues (PBAs) are low-cost porous materials with promising potential in gas separation, owing to their abundance of open metal sites. To access these open metal sites PBAs need to be activated through removal of water from the porous structure. However, the conditions required for effective activation and their structural consequences remain poorly understood, with existing effective methods being costly. Therefore, to gain insights in the activation process and its effects on structure, we systematically investigated the effect of activation temperature on three different ferricyanide-based PBAs (FePBA, CoPBA, and CuPBA) using a simple nitrogen flow activation procedure. We successfully synthesised these structures and optimised the activation procedure for micropore capacity and crystallinity. Infrared spectroscopy as well as CO₂ and CO adsorption measurements revealed that, even under optimized conditions, water remained within the PBAs, with only a limited number of open metal sites accessible. At higher activation temperatures, micropore capacity and crystallinity decrease. This hydrophilicity, however, also showed positives, for example in the application of PBAs as desiccants. CuPBA, specifically, boasts a water adsorption of 355 mg g⁻¹ at a relative humidity of $\leq 10\%$, competitive with zeolites and silica per weight unit, but higher per volume unit. Overall, however, while PBAs offer promise for gas adsorption owing to their high surface area and low cost, practical utilisation of their open metal sites remains challenging due to their strong affinity for water.

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3.1. Introduction

Due to the increasing population and wealth levels in the world, more and more resources are expended, resulting in more emissions of industrial waste gases. [1, 2] Polluting and useful chemicals should be separated out of these waste gas streams in order to achieve a cleaner environment and better resource utilisation. In view of climate goals, this separation should have a low energy consumption as well as a high selectivity for the target chemicals. One such a separation technique for gas separations, which has the potential to be used as a lower energy cost alternative to cryogenic distillation, is adsorption. [3] Adsorption has the additional advantage of having a large library of porous materials available such as porous carbons, [4] zeolites, [5] metal-organics frameworks, [6] etc. This range of materials allows for the targeting of specific properties and material features to obtain a more selective separation. Coordinatively unsaturated metal sites, also called open metal sites, are such a feature which can adsorb many of the typical gases in waste streams: CO₂, [7] CO, [8] NO_x, [9] etc., due to their strong interactions.

One class of materials that can contain open metal sites are Prussian blue analogues (PBAs). PBAs are coordination polymers consisting of transition metal cations and metal cyanide anions with structures similar to the eponymous pigment [10, 11] with the generalised chemical formula of $C_x M1[M2(CN)_6]_{1-y} \cdot \diamond_y \cdot wH_2O$. [12–14] In this formula C_x indicates alkali metal ions, $M1$ indicates transition metal cations, $[M2(CN)_6]^{n-}_{1-y}$ are the hexacyanometallate anions, $\diamond_y$ are the hexacyanometallate vacancies, and wH_2O are the water molecules in the PBA. We will generally refer to the PBA structures in this paper by the shortened $M1[M2(CN)_6]_{1-y} \cdot \diamond_y$ notation for easier legibility.

By choosing the correct ratios and oxidation states of the reactants, insoluble microporous PBAs can be produced [11] which have a network of linked voids created by $M(CN)_6$ -vacancies (Figure 3.1). [14] Other than porosity, having these vacancies is additionally advantageous due to the maximum of 6 open metal sites that are created per vacancy. This amounts to a theoretical open metal concentration of up to 1 per formula unit ($M1^{II}[M2^{III}(CN)_6]_{2/3} \cdot \diamond_{1/3}$) or 5 mmol g⁻¹ which is similar to the highest concentrations found in typical metal-organic frameworks [15] and higher than found in metal-exchanged zeolites. [16] Another advantage of PBAs compared to other tailorable porous solids is that they can be made from very abundant materials through a facile aqueous precipitation reaction. [10, 11, 17, 18] This makes PBAs promising for large-scale, industrial applications.

PBAs with their abundant open metal sites do have one major drawback, however, which is the potential inaccessibility of these sites due to the presence of coordinated water. Water is known to interact strongly with open metal sites [19, 20] and microporous materials are known to retain water due to capillary effects. [21, 22] Water, thus, competitively adsorbs on the same open metal sites as desired target molecules from waste gas streams. [8, 9, 23] This means that

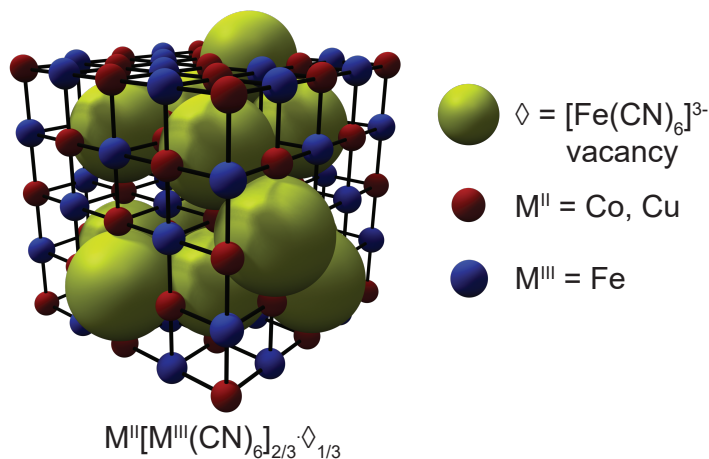


Figure 3.1 Schematic image of $M^{II}[Fe^{III}(CN)_6]_{2/3} \cdot \frac{1}{3}$ PBAs based on ref. [14]

the presence of humidity will negatively affect the adsorptive separation on PBAs. Moreover, water will already be present from the synthesis which means activation, i.e., the removal of water from the pores, is an important aspect in the feasibility of utilising the open metal sites in PBAs.

Previous research on gas adsorption in PBAs has shown that obtaining accessible open metal sites is possible by using high vacuum with long degassing times (≥ 24 h) while strenuously keeping the PBAs isolated from the atmosphere [17, 24]. In many other cases, however, little attention is paid to whether the activation procedure fully removes water and whether the structure is retained after activation. [18, 25–28] Another issue is that the aforementioned successful activation procedure is often unviable for large scale applications due to the required high vacuum and long degassing times. Therefore, we investigated whether microporous PBAs could be activated while optimising their micropore structure using a simple sub-24 hour N_2 -based activation procedure. This research aims to provide insight into the feasibility of accessing open metal sites in PBAs, while taking into account effects on the structure due to the removal of water.

We chose to perform this research using $[Fe(CN)_6]^{3-}$ ions, as this is the cheapest and most readily available $[M_2^{III}(CN)_6]^{3-}$ ion, to create $M_1^{II}[M_2^{III}(CN)_6]_{2/3} \cdot \frac{1}{3}$ PBAs with inherent microporosity. As the other metal (M_1^{II}) in these PBAs, we chose Fe^{2+} , Co^{2+} , and Cu^{2+} as these are transition metals which lead to interesting structural characteristics in PBAs. Co should lead to the prototypical $M_1^{II}[M_2^{III}(CN)_6]_{2/3} \cdot \frac{1}{3}$ PBA with a space group of $Fm\bar{3}m$, which will serve as a baseline to the other PBAs. Cu is interesting due to Cu-based PBAs having the highest reported storage capacity for H_2 compared to other PBAs. [25] Unlike the other two structures, Fe will not show an inherent pore network such as shown

in Figure 3.1. This is caused by the difference in the most stable oxidation state between the dissolved ions (Fe^{2+} and $\text{Fe}(\text{CN})_6^{3-}$) and the solid PBA (Fe^{3+} and $\text{Fe}(\text{CN})_6^{4-}$). In the end, this change in oxidation states of the individual ions, which create the PBA, leads to a $\text{Fe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]_{3/4} \cdot \diamond_{1/4}$ PBA [14, 29], in which only structural defects, rather than the inherent charge-balancing $[\text{Fe}(\text{CN})_6]^{3-}$ -vacancies that can be found in $\text{M}^{\text{II}}[\text{M}^{\text{III}}(\text{CN})_6]_{2/3} \cdot \diamond_{1/3}$ structures, lead to an extended micropore network. [14] The Fe-based PBA is interesting as a general comparison to the Co- and Cu-based PBAs, but it also shows if our methodology is more generally applicable.

3.2. Experimental section

3.2.1. Materials

$\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ ($\geq 99\%$), $\text{CoSO}_4 \cdot 7 \text{H}_2\text{O}$ ($\geq 99\%$), $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ ($\geq 98.0\%$), and $\text{K}_3[\text{Fe}(\text{CN})_6]$ ($\geq 99\%$) were purchased from Sigma-Aldrich and used without further purification.

3.2.2. Synthesis of PBAs

MPBAs ($\text{M}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]_{2/3} \cdot \diamond_{1/3}$, $\text{M}=\text{Co}$, Cu and $\text{Fe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]_{3/4} \cdot \diamond_{1/4}$, $\diamond=[\text{Fe}^{\text{III}}(\text{CN})_6]^{n-}$ vacancy with $n=4$ for Fe and 3 for Co and Cu-based PBAs) were synthesised by dropwise addition of $\text{K}_3[\text{Fe}(\text{CN})_6]$ (8.231 g, 25 mmol, 1 equiv.) dissolved in 250 ml of demiwat, into $\text{MSO}_4 \cdot x\text{H}_2\text{O}$ (75 mmol, 3 equiv.) in 250 ml of demiwat at 50 °C under stirring. After complete addition of the $\text{K}_3[\text{Fe}(\text{CN})_6]$ -solution, the mixture was left to stir at 50 °C for another 2 hours. The resulting solids were separated by centrifugation (4000 RCF, 5 min) and washed with fresh demiwat 3 times by redispersing and centrifuging. The solids were then dried in a vacuum oven at 60 °C until dry.

3.2.3. Methods

Powder X-ray Diffraction (PXRD) was performed on a Bruker Advance D8 with a Cu K α source ($\lambda = 1.5418 \text{ \AA}$) and a Ni monochromator over a 2θ range of 5-50°.

Elemental composition was determined by Mikroanalytisches Laboratorium Kolbe, Germany. C, H, and N were determined using an Elementar Model Vario Mikro CHNS analyser. Fe, Cu, Co, and K were determined by a Spectro Model Spectro Acros ICP after microwave digestion in a CEM MARS 6. No repeat measurements were performed.

Degassing for N_2 , CO_2 , and CO adsorption was performed on a Micromeritics SmartPrep with a heating rate of 5 °C min⁻¹ under a flow of 20 mL min⁻¹ N_2 . Degassing was done for 15 hours at various temperatures for the N_2 adsorption

of the PBA samples to investigate temperature effects on the degassing: FePBA (60, 90, 100, 110, 120, 140 °C), CoPBA (60, 90, 100, 110, 120, 140 °C), and CuPBA (60, 100, 110, 120, 130, 140 °C). In case the degassing temperature was 90 °C or higher, a pre-drying step was performed at 90 °C for 1 hour before the final degassing temperature to prevent samples from being damaged by rapid evaporation of water in the pores. Degassing for CO₂, CO, and H₂O adsorption were done at the optimal temperatures as determined by N₂ adsorption (FePBA, 100 °C; CoPBA, 100 °C; CuPBA, 120 °C). Due to the high vacuum under which water adsorption is performed, these samples were additionally degassed under vacuum in a Micromeritics VacPrep for 1 hour at their optimal temperature and overnight thereafter at 25 °C.

N₂ and CO₂ adsorption isotherms were measured on a Micromeritics TriStar II at 77 K and 298 K, respectively. H₂O adsorption isotherms were obtained on a Micromeritics 3Flex at 293 K. CO adsorption was performed on a Micromeritics ASAP 2020C at 303 K. Sample size for N₂, CO₂, and H₂O adsorption was around 150 mg before degassing, while a larger sample of ≥ 350 mg was used for CO adsorption. BET values were calculated from the N₂ adsorption data for the optimally degassed samples according to the Rouquerol criteria [30] in the BETSI programme. [31]

DRIFTS was measured on a Thermo Nicolet Nexus FT-IR equipped with a Harrick Praying Mantis and a high temperature reaction chamber with ZnSe windows. All DRIFTS measurements were performed at 25 °C with a flow of 30 mL min⁻¹ N₂ against a KBr background measured under the same conditions. The in-situ drying followed the same procedure as was used for the degassing for the N₂ adsorption. Under the aforementioned N₂ flow, the samples were heated to 90 °C for 1 hour with a heating rate of 5 °C min⁻¹, after which they were heated with a heating rate of 5 °C min⁻¹ to their optimum temperature (FePBA, 100 °C; CoPBA, 100 °C; CuPBA, 120 °C) which was kept for 15 hours and then left to naturally cool to 25 °C.

SEM measurements were performed using a JEOL JSM-IT700HR using an accelerating voltage of 5 kV and working distance of 10 mm. Samples were prepared by placing the powder onto carbon tape stuck onto an aluminium sample stub. No coating was applied. Collected images were analysed using ImageJ.

TEM measurements were performed in a JEOL TEM-1400Plus electron microscope using Cu-supported continuous carbon grids with an accelerating voltage of 120 kV. TEM samples were prepared by making a slurry using a very small amount of powder sample and grinding it together with a small amount of isopropyl alcohol using a mortar and pestle. 10 µL of this slurry was then deposited on the grid and left to dry before measuring. Collected images were analysed using ImageJ.

Thermogravimetric analysis (TGA) was performed on a Mettler Toledo TGA/SDTA851e under 100 mL min⁻¹ of N₂ with an isothermal step at 30 °C for 10

minutes followed by a heating step with a rate of $1\text{ }^{\circ}\text{C min}^{-1}$ from 30 to $250\text{ }^{\circ}\text{C}$.

3.3. Results and discussion

Figure 3.2 shows the results of the synthesis of the FePBA, CoPBA, and CuPBA. It is clear that all PBAs show the same overall structure as Prussian blue, as the major peaks at 17.5 , 25 , 36 , 40 and 44° match that of the simulated pattern. Both CoPBA and CuPBA show a high degree of crystallinity with well-defined peaks without much broadening. FePBA, on the other hand, does show significant amounts of broadening which is indicative of a smaller crystallite size compared to the CoPBA and CuPBA and might be caused by a more defective $\text{Fe}^{\text{III}}_4[\text{Fe}^{\text{II}}(\text{CN})_6]_3$ structure rather than a $\text{M}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]_{2/3} \cdot \diamond_{1/3}$ structure due to the suboptimal reactant stoichiometry and oxidation states for this structure. [29]

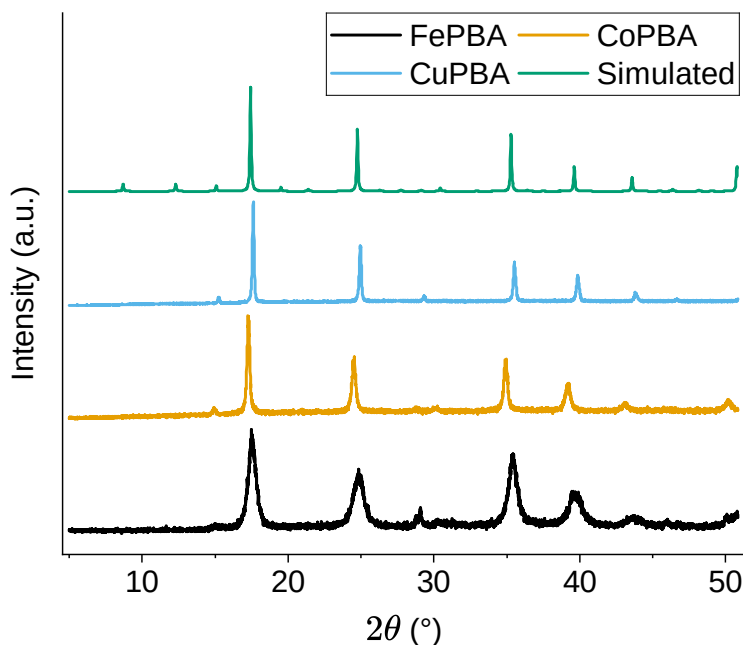


Figure 3.2 Normalised PXRDs of the as-synthesised PBAs compared to a simulated pattern. The simulated pattern is reproduced using single crystal data of Prussian Blue from ref. [32]

The SEM analysis of the as-synthesised particles (Figure 3.3a, c, and e) shows that the synthesised PBAs all show relatively anhedral particles which clump together in larger aggregates. The TEM measurements (Figure 3.3b, d, and f) confirm that in FePBA and CoPBA the particles are all amorphous, while CuPBA has a mixture of anhedral and cubic particles which was not visible in the SEM results. The

TEM images also show that the particle size of FePBA is much smaller than the similarly sized CoPBA and CuPBA particles, which is in agreement with the results of the PXRD.

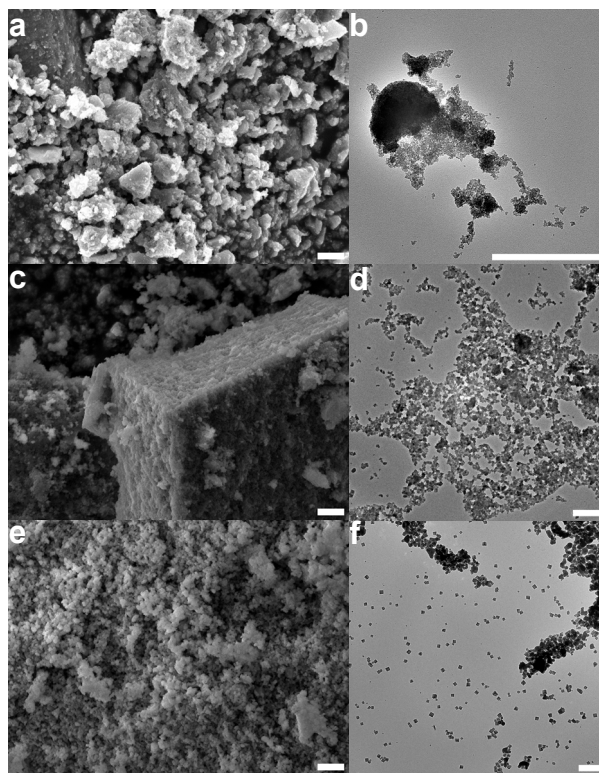


Figure 3.3 SEM and TEM images of as-synthesised FePBA (a,b), CoPBA (c,d), and CuPBA (e,f). The scale bar is 1 μm and 500 nm for the SEM and TEM images, respectively.

The elemental composition is similar to the expected values (Table 3.A.1). In terms of atomic ratios this can be translated to: FePBA (C:H:N:Fe:K, measured 1:2.30:0.96:0.35:0.03, expected 1:0:1:0.39:0 from $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$), CoPBA (C:H:N:Fe:Co:K, measured 1:2.33:1.04:0.16:0.24:0.01, expected 1:0:1:0.17:0.24:0 from $\text{Co}_3[\text{Fe}(\text{CN})_6]_2$), CuPBA (C:H:N:Fe:Cu:K, measured 1:2.33:1.04:0.17:0.20:0, expected 1:0:1:0.17:0.25:0 from $\text{Cu}_3[\text{Fe}(\text{CN})_6]_2$). While the ratios of the expected elements are largely close to the expected values, there is also H and K present. The H content can simply be attributed to the presence of water, while K comes from K^+ -ions which are known to potentially intercalate in the PBA structure. However, the K^+ concentrations are small and we do not expect major effects on the adsorption capacity and the activation procedure.

The thermogravimetric analysis (Figure 3.4) shows a typical decrease in relative

weight with some plateaus at which weight loss is minimal. These plateaus appear at around 150, 110, and 90 °C for FePBA, CoPBA, and CuPBA, respectively, with weight losses between 15 to 25%. However, the plateaus are relatively sloped and choosing a degassing temperature purely based on the TGA still leaves uncertainty on the removal of water and the structural stability of the PBAs. Hence, we chose to systematically vary the degassing temperature to obtain the highest microporosity. After the degassing, N_2 adsorption and PXRD were performed to observe degassing related changes in the structures (Figure 3.5 and Table 3.A.2).

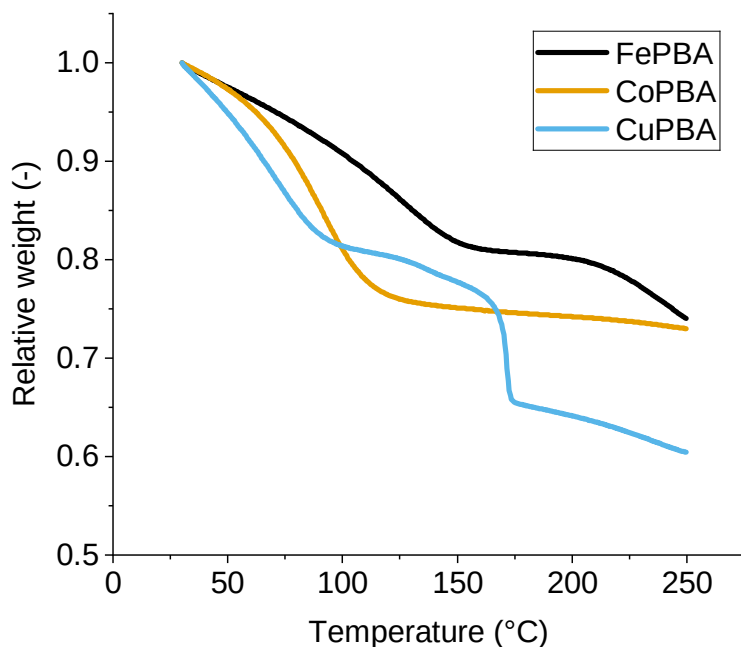


Figure 3.4 Thermogravimetric analysis of PBA samples, $1\text{ }^{\circ}\text{C min}^{-1}$ under $100\text{ mL min}^{-1}\text{ }N_2$.

The N_2 sorption isotherms of FePBA (Figure 3.5a) show a sharp increase in adsorbed N_2 at a relative pressure below 0.1 and a clear continuous increase with relative N_2 pressure beyond that point up to a relative pressure of 0.8. A clear hysteresis is also visible in the desorption part of the measurement between a relative pressure of 0.9 to 0.4. These observations in the isotherms are indicative of clear mesoporosity with some microporosity. The mesopore capacity stays constant for activation temperatures up to 100 °C as can be seen in the constant slope of the isotherm between 0.1 and 0.8 relative pressure. Above 100 °C, on the other hand, the mesopore capacity starts to increase as seen by the increasing slope in the adsorption isotherm between 0.1-0.8 relative pressure. The micropore capacity, on the other hand, increases from $51\text{ cm}^3\text{ g}^{-1}$ STP using a degassing of 60 °C to $64\text{ cm}^3\text{ g}^{-1}$ STP at 100 °C (see Table 3.A.2 for values and methodology),

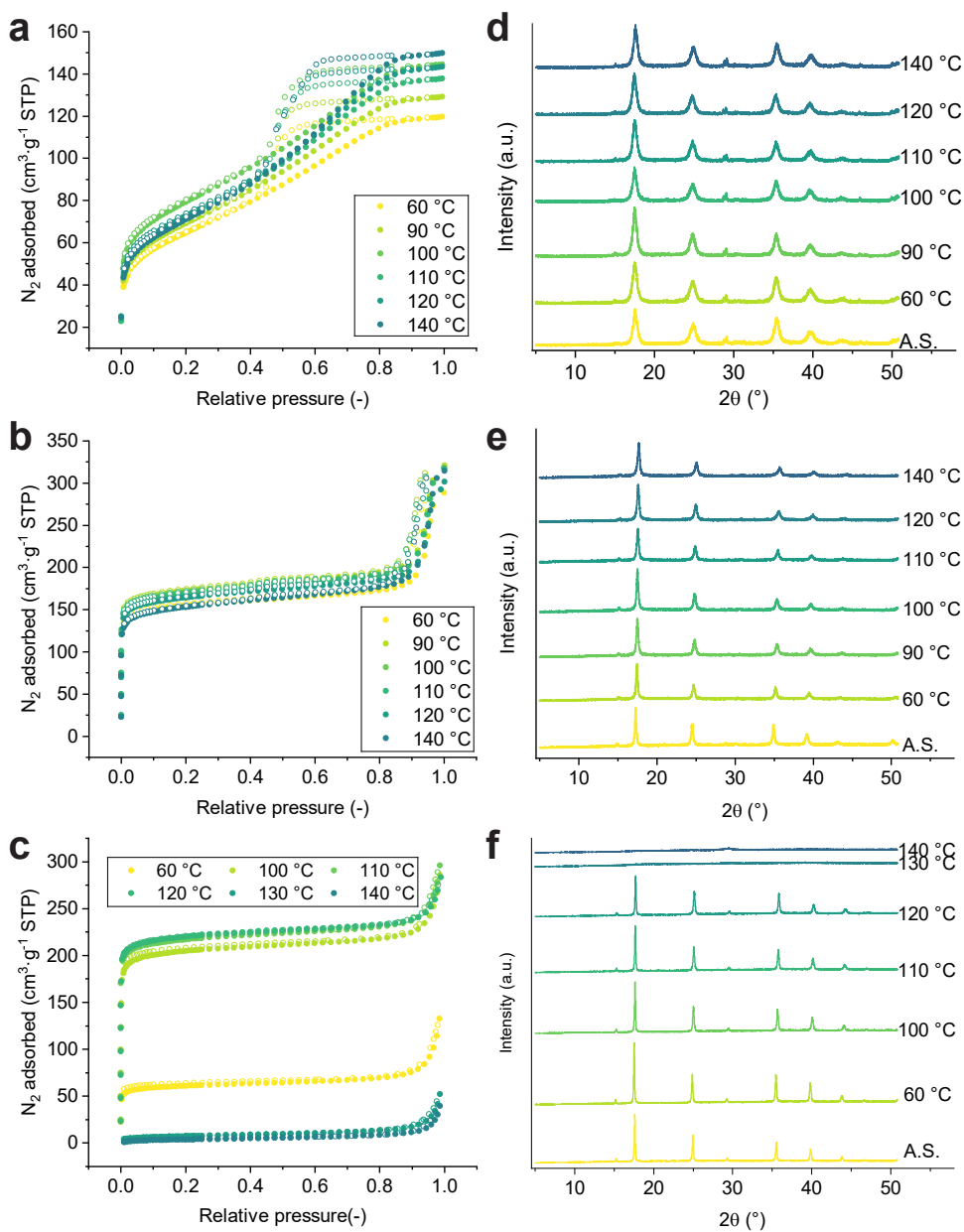


Figure 3.5 N_2 adsorption at 77 K and PXRD results of FePBA (a,d), CoPBA (b,e), and CuPBA (c,f). Temperature in the figures indicates the degassing temperature. Closed and open symbols indicate the adsorption and desorption branches of the isotherm, respectively.

after which it again decreases. This leads to an overall capacity that increases between 60 °C and 100 °C from 120 to 145 cm³ g⁻¹ STP. Degassing temperatures above 100 °C cause an overall loss of capacity due to a higher decrease in micropore capacity than the gain in mesopore capacity until these effects equal at about 120 °C. Above 120 °C, the overall capacity then increases again due to the dominant effects from the increasing mesopore capacity, resulting in a maximum adsorption capacity of 150 cm³ g⁻¹ STP. If we compare the results from the N₂ adsorption with the PXRD (Figure 3.5d), we can see that the overall structure of the FePBA is retained. While there are some small changes in the peak intensities and FWHM values (Table 3.A.3), no clear structural degradation is visible.

CoPBA (Figure 3.5b, e), on the other hand, has a largely microporous structure with limited mesoporosity which can be seen by the sharp increase in adsorbed N₂ at P/P₀ < 0.1 and the slight slope in the isotherm between a relative pressure of 0.1 and 0.8, respectively. The micropore volume lies around 150 cm³ g⁻¹ STP which is stable within about 15 cm³ g⁻¹ STP over the temperature range of degassing. The sharp increase in adsorption at P/P₀ ≥ 0.8 can be attributed to N₂ condensing in the narrow voids between nanoparticles (Figure 3.3c and d). The maximum micropore capacity, while maintaining framework crystallinity, is achieved at a degassing temperature of 100 °C. Unlike FePBA, no mesopores are generated at higher degassing temperatures; instead, micropore capacity decreases above 100 °C. Crystallinity is preserved up to 100 °C, as evidenced by the intensity and sharpness of the PXRD peaks. Beyond this temperature, a slight reduction in peak intensity and an increase in FWHM (Table 3.A.3) are observed, indicating a progressive loss of crystallinity. These results suggest that degassing temperatures exceeding 100 °C begin to degrade the framework structure, in contrast to what can be deduced from looking at the TGA results (Figure 3.4).

Similarly to CoPBA, CuPBA (Figure 3.5c, f) shows mostly microporosity as can be seen by the sharp increase in adsorbed N₂ at P/P₀ < 0.1 with a similar, albeit smaller, increase in adsorption due to condensation of adsorbate between small particles (Figure 3.3e and f) at P/P₀ ≥ 0.8. Unlike in CoPBA, however, there is a strong effect of the degassing temperature on the porosity of CuPBA. The micropore volume increases from 57 cm³ g⁻¹ STP using a degassing temperature of 60 °C to a maximum of 211 cm³ g⁻¹ STP at a degassing temperature of 120 °C. Above that temperature, however, the structure completely collapses which is indicated by both the almost complete loss of N₂ adsorption and the loss of crystallinity in the PXRD at degassing temperatures of 130 °C and above. At a degassing temperature of 120 °C and below, the overall crystallinity is well-maintained with some small variations in peak intensity and FWHM values (Table 3.A.3). These crystallographic changes are, however, not accompanied by significant morphological changes as can be observed in the TEM analysis after degassing (Figure 3.A.8 and 3.A.9).

We conclude that the optimal degassing procedures to obtain the highest micropore capacity for FePBA, CoPBA, and CuPBA are at 100 °C, 100 °C, and 120

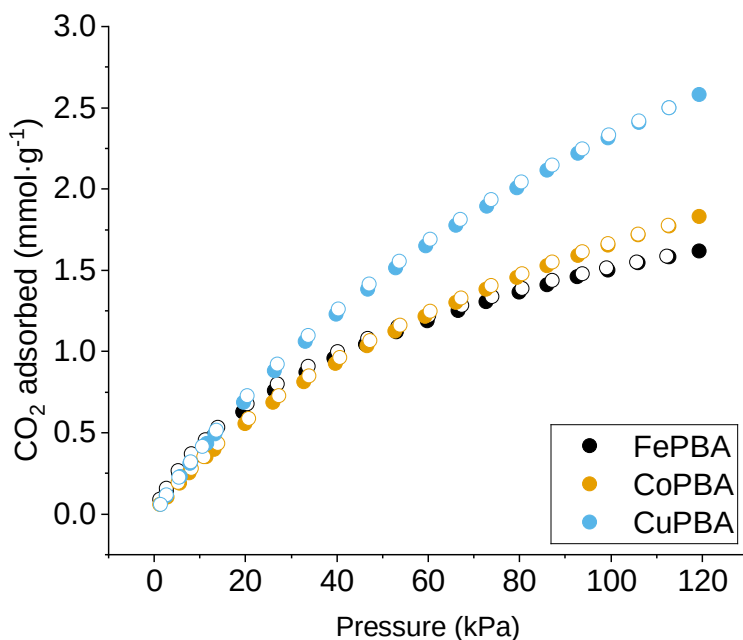


Figure 3.6 CO_2 adsorption at 298 K on the PBAs after the optimal degassing procedure (FePBA: 100 °C, CoPBA: 100 °C, CuPBA: 120 °C). Closed and open symbols indicate the adsorption and desorption branches of the isotherm, respectively.

°C, respectively, with BET values of 271, 635, and 890 $\text{m}^2 \text{g}^{-1}$ (Figure 3.A.1-3.A.4 and Table 3.A.4). If this corresponds to successful water removal from the open metal sites, a strong interaction with CO_2 should ensue. [33, 34]

Figure 3.6 shows the CO_2 adsorption isotherms for the three PBA's activated at the optimal temperatures. The uptake at 120 kPa lies at 1.6, 1.8, and 2.6 mmol g^{-1} for FePBA, CoPBA, and CuPBA, respectively, which is substantial. However, the Henry coefficient around 0.03 $\text{mmol g}^{-1} \text{kPa}^{-1}$ for the initial uptake is rather modest, indicating the lack of strong interaction between CO_2 and the PBA, indicative of a lack of available open metal sites. The significant CO_2 adsorption at high partial pressure is likely physisorption of CO_2 via Van der Waals interactions with the small micropores. Indeed the trend in total uptake at 120 kPa (CuPBA>CoPBA>FePBA) also corresponds to the trend in micropore volume (see Figure 3a-c). This serves as a first indication that we have not fully removed water from the open metal sites.

In addition, water removal was assessed in-situ via DRIFTS measurements during the activation procedure at the optimised temperatures (see Methods). Figure 3.7 shows the large spectral features associated with water, such as the peak at 3700 cm^{-1} (non-hydrogen bonded O-H stretch vibration), the broad

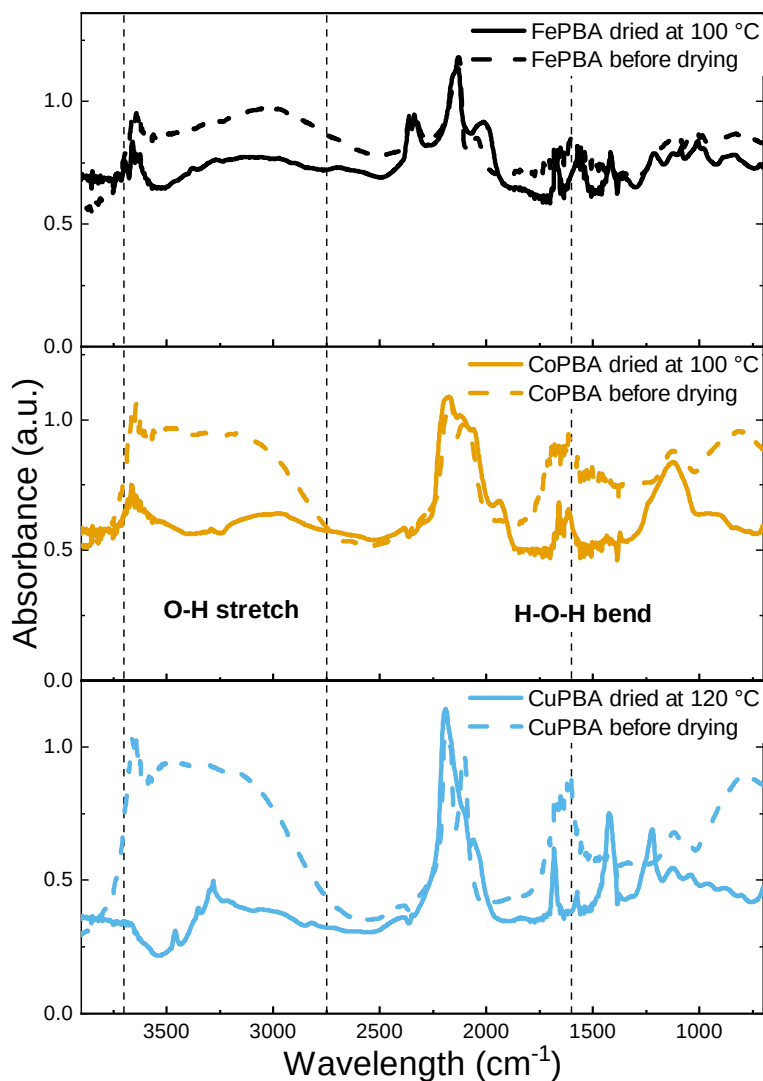


Figure 3.7 DRIFTS measurements of the PBAs before and after the in-situ drying procedure.

peaks at $3500\text{--}2750\text{ cm}^{-1}$ (hydrogen bonded O-H stretch vibration), and the peaks around 1600 cm^{-1} (H-O-H bending vibrations), in all PBAs before the drying procedure. After the in-situ drying procedure, the intensity of these signals decreases strongly, indicating the removal of water. However, in all cases water signals in the region of 3700 cm^{-1} to 2275 cm^{-1} are still clearly present in the spectra, indicating that while a substantial amount of the bulk water was removed, complete removal was not achieved using the drying procedure. Even

when using degassing temperatures above the point where each respective PBA starts structurally deteriorating, water-related IR signals can still be seen in the DRIFTS graph, indicating that the N_2 -based degassing method will not fully remove water even at higher temperatures (Figures 3.A.5- 3.A.7: XRD, N_2 -sorption and FTIR spectra for FePBA and CoPBA activated at 220 °C and CuPBA at 130 °C).

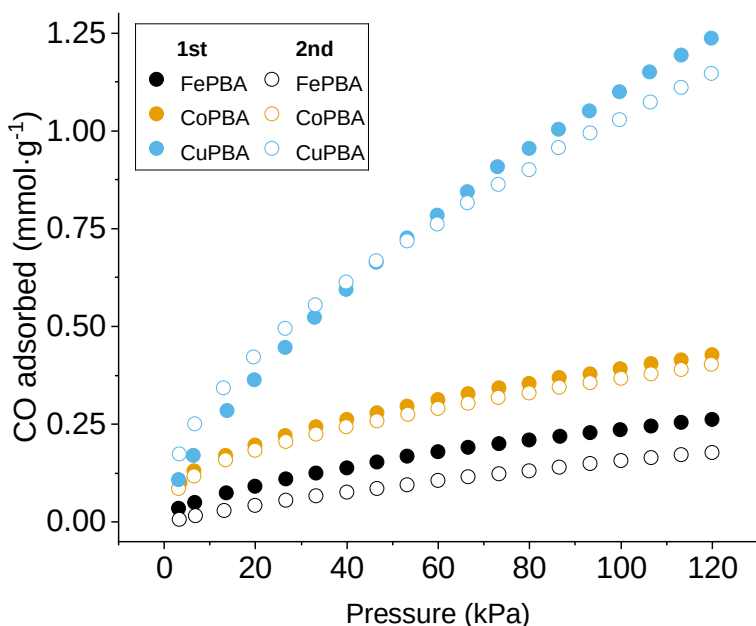


Figure 3.8 CO adsorption at 303 K in chemisorption mode after the optimal degassing procedure.

As a final measurement to conclude whether some of the open metal sites can still be accessed, physisorption and chemisorption of CO was measured, since CO is known to interact with many open metal sites, potentially competitively, in the presence of water. Moreover, if the PBAs are capable of selectively adsorbing CO it will be of interest in the usage for the CO/N_2 separation for which there is no industrially relevant method yet. [8] The CO adsorption measurement consists of two consecutive adsorption isotherm measurements per sample. The first one is performed after degassing at the optimised temperature. After this measurement, vacuum is applied for 1 hour at the measurement temperature to desorb physisorbed CO, but not chemisorbed CO. After this vacuum treatment a second adsorption measurement is started. This results in two isotherm lines, the difference between which is presumed to be the chemisorption part of the total adsorption, while the second adsorption isotherm is presumed to be the physisorption part.

Figure 3.8 shows the results of the CO adsorption measurements. The overall adsorption from the first measurement at 120 kPa by CuPBA is on the same order of magnitude as the best performing CO adsorbents known [8] at 1.24 mmol g^{-1} , while CoPBA and FePBA adsorb a more modest 0.43 and 0.26 mmol g^{-1} , respectively. Similarly to the CO_2 adsorption, the overall CO adsorption follows the trend of micropore capacity ($\text{CuPBA} > \text{CoPBA} > \text{FePBA}$) with no strong adsorption visible in terms of Henry coefficient of 0.005 , 0.01 , and $0.02 \text{ mmol g}^{-1} \text{ kPa}^{-1}$ for FePBA, CoPBA, and CuPBA, respectively. When looking at the differences between the first and second CO adsorption measurement, interesting observations can be made. In the case of FePBA and CoPBA, a significant, constant difference between the first and repeat measurements can be seen, indicating 0.08 and 0.02 mmol g^{-1} of chemisorption as well as 0.40 and 0.18 mmol g^{-1} of physisorption at 120 kPa, for FePBA and CoPBA, respectively. For CuPBA, we observe differences between the two measurements which are not consistent across the pressure range. We can see a higher initial increase in CO uptake at low pressures ($<45 \text{ kPa}$) in the second measurement compared to the first. After this point we see a lower uptake in the second measurement compared to the first one. We presume this phenomenon occurred due to the vacuum step between the two measurements, in which additional adsorbed gases are removed. We hypothesise that this 1 hour high-vacuum step removed some of the bound water leading to the increase at low pressures, while more strongly bound CO that remains after the vacuum step leads to the overall lower adsorption at higher pressures. If we assume that the difference at 120 kPa is the overall chemisorption, that would mean a value of 0.09 mmol g^{-1} of chemisorption and 1.15 mmol g^{-1} of physisorption at 120 kPa.

If we compare the chemisorptive adsorption values with the expected amount of open metal sites, we can see that there is a large difference. Experimentally, we observe chemisorption values of 0.02 , 0.08 , and 0.09 mmol g^{-1} for CoPBA, FePBA, and CuPBA, respectively. Theoretically, however, we expect to see 6 open metal sites per $[\text{Fe}(\text{CN})_6]^{3-}$ removed from the structure for a perfect $(\text{M}^{\text{II}}[\text{M}^{\text{III}}(\text{CN})_6]_{2/3} \cdot \diamond_{1/3})$ crystal. This translates to 1 open metal site per formula unit, which is equal to about 5 mmol open metal site per gram of PBA. Not all open metal sites, however, would necessarily chemisorb CO. Previous work has shown a strong interaction between Co^{2+} -sites and CO through IR and CO adsorption studies. [35] Fe^{3+} and Cu^{2+} ions, on the other hand, generally do not have such strong interactions with CO even though significant physisorption can still occur. [8] However, due to the electron donating presence of the N-side of the CN^- ligands we expect a reduced effective charge on these metal ions, which may help strengthen the metal-CO interaction, [25, 36] potentially leading to a strong enough binding to be observed through our CO adsorption measurement. Nevertheless, the large difference between the measured and theoretical maximum CO adsorption indicates that only a small percentage of the total open metal sites was successfully activated and water-free. This result shows that water cannot be fully removed through a simple N_2 -based activation procedure, and that the degree to which CO can competitively

adsorb in the presence of water is very limited.

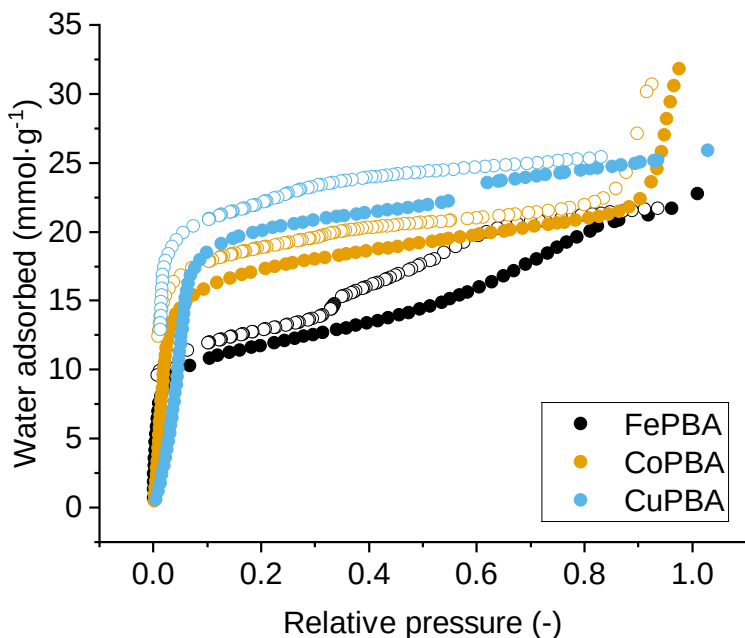


Figure 3.9 Water adsorption at 293 K of the optimally degassed PBAs. Closed and open symbols indicate the adsorption and desorption branches, respectively.

The water adsorption isotherms of the different PBAs are shown in Figure 3.9. The overall uptake at a relative pressure of 1 is about 22, 35, and 25 mmol g^{-1} for FePBA, CoPBA, and CuPBA, respectively. In all cases, we can see a sharp, large uptake of water at very low relative pressures (<0.05), indicating that in addition to water adsorbed on open metal sites, water condensation into the micropores already occurs at very low humidity levels. We can also see some additional uptake between a relative pressure of 0.05 and 0.9 with some hysteresis in the desorption curve, which is most prominent in FePBA. This is in line with the higher mesopore capacity of FePBA: for increasingly larger mesopores condensation is expected at increasingly high relative humidity. [37] All tested PBAs exhibit pronounced hydrophilicity, as evidenced by the sharp uptake of water at low relative pressure. Comparison of the N_2 and water isotherms highlights this behaviour. The N_2 isotherms yield micropore volumes of 0.099, 0.248, and 0.327 mL g^{-1} for FePBA, CoPBA, and CuPBA, respectively (Table 3.A.2). In contrast, the water isotherms at a relative pressure of 0.1 show adsorption values of 10.8, 15.8, and 18.5 mmol g^{-1} , corresponding to 0.195, 0.286, and 0.334 g g^{-1} for FePBA, CoPBA, and CuPBA, respectively. These results demonstrate that at a relative pressure of 0.1 (10% relative humidity), the micropores are already saturated with

water. Consequently, even under optimal activation, PBAs are unsuitable for gas adsorption in humid environments, as water condensation rapidly renders the micropore space inaccessible to other molecules. Notably, the water uptake of PBAs is comparable to that of high-performing zeolites used for drying applications, which typically adsorb around 0.4 g g^{-1} [38]. CuPBA exhibits a water adsorption capacity of 0.335 g g^{-1} at a relative pressure of 0.1. Given the lower volume per mass of PBA's compared to zeolites, PBAs warrant further evaluation as candidate materials for drying applications where compact volumes are advantageous.

3.4. Discussion

Through a set of experiments such as CO_2 and CO adsorption, we have shown that we are only able to obtain a small amount of open metal sites in the PBAs via a N_2 flow based degassing procedure. Through DRIFTS with in-situ degassing we were also able to conclude that there is still a significant amount of water present in the samples after degassing.

Comparing our results with literature on adsorption in PBAs, we can see that activation in these materials is indeed not a trivial matter. Only the research done by the Long group on $\text{Cu}[\text{Co}(\text{CN})_6]_{2/3} \cdot \diamond_{1/3}$ is conclusive on the removal of water and the retention of the structure, as well as the location of the adsorption sites for H_2 gas. [17, 24] To obtain these results, however, a degassing procedure of 48 hours under high vacuum with vacuum transfer steps was required.

These requirements are contrary to other adsorptive materials with open metal sites such as MOFs or zeolites. While the open metal sites in those materials are still highly hydrophilic and contact with water should be avoided, the actual degassing can be done using a N_2 flow method similar to the one we employed due to their better thermal stability which allows higher degassing temperatures. [5, 39]

Investigations on gas adsorption in PBAs showcase a general lack of attention paid to the effects of degassing on the structures of PBAs. For example, degassing temperatures are chosen without showing verification of the complete removal of water. [18, 25–27] Sometimes, multiple temperatures are used for seemingly similar materials for unexplained reasons. [18, 25, 27] In a similar vein, material properties after activation using techniques such as IR or XRD are often not reported, [17, 18] and generally the complete removal of water is assumed through the outgas rate [17, 18, 25] which is the rate at which gases are coming off the sample under vacuum. However, this is not a truly conclusive metric since it only accounts for weakly bound water and not necessarily for strongly bound water. Similarly, the outgas rate does not indicate whether structural degradation takes place.

These assumptions about activation can then lead to unexpected behaviour and underestimated adsorption compared to full activation. One example is the physisorption of CO_2 [26] in PBAs rather than the expected chemisorption when open metal sites are water-free [33, 34]. This is similar to what we observed in our CO_2 adsorption experiments when water was still present on the metal sites (Figure 3.6). In some other adsorption applications such as the adsorption of NH_3 , the presence of water is not as noticeable since NH_3 can react with water into NH_4OH which masks incomplete activation. [27, 28] Lastly, the effect of degassing on the structure, if reported in the first place, is typically only done through XRD comparison with the as-synthesised material [27, 28] or is done to show chemical stability rather than thermal stability [26, 27]. However, these tests do not capture the full effect of the degassing temperature on the porosity which we can show through our investigation combining XRD and N_2 adsorption (Figure 3.5).

Our results, therefore, indeed indicate that, depending on the evacuation conditions, reduction in crystallinity and micropore capacity as well as incomplete water removal might be a regular occurrence in PBA-related research. This observation points to a general need to better describe **i)** degassing procedures, **ii)** their effects on the structure via post-activation measurement of N_2 adsorption and X-ray diffraction, and **iii)** the presence of water. The latter can be done via infrared spectroscopy and the use of probe molecules that strongly adsorb on open metal sites, as done in this work. TGA, by itself, on the other hand, is not sufficiently clear and accurate in determining the degassing temperature for these materials. Our TGA results do not show no clear, flat plateaus that match the results of the optimal degassing temperature determined by N_2 adsorption and PXRD, meaning that a poor choice of degassing temperature, resulting in a suboptimal adsorption capacity, is easily made.

That being said, to retain the structure while completely removing water from the open metal sites, cumbersome vacuum procedures are likely needed. Similarly, any streams in contact with the PBAs should be meticulously dry as well due to the highly hydrophilic nature of the materials (Figure 3.9). These requirements will potentially limit the use of the open metal sites in PBAs for industrial commercial adsorptive separations. If we focus on the hydrophilic properties, however, then using the PBAs as drying agents, similar to zeolites could be of interest, especially if smaller desiccant volumes and therefore higher densities are required.

3.5. Conclusion

We performed the first systematic study on the effect of the degassing temperature on the structure, performance, and, in particular, the accessibility of open metal sites using a N_2 -based degassing procedure in three distinct PBAs based on the $[\text{Fe}(\text{CN})_6]^{3-}$ ion: FePBA, CoPBA, and CuPBA. The activation procedure for each PBA was optimised using a systematic sub-24-hour degassing under N_2 , allowing us to

investigate how degassing temperature influences pore structure, crystal integrity, and, most critically, the activation of open metal sites. Our results indicate that increasing the degassing temperature initially enhances micropore capacity up to an optimal point, beyond which further temperature increases lead to a decrease in microporosity. For CoPBA and CuPBA, this reduction coincides with deterioration of the crystalline structure, whereas the crystallinity of FePBA appears to remain intact, initially. The temperatures corresponding to maximum micropore capacity were found to be 100 °C for FePBA, 100 °C for CoPBA, and 120 °C for CuPBA.

Using these optimised conditions, CO₂ adsorption measurements revealed no strong interactions and DRIFTS analyses after in-situ degassing confirmed that residual water remained in the PBAs. However, CO adsorption demonstrated that a small fraction of open metal sites was accessible, indicating partial activation and likely water-free sites. Consequently, while sub-24-hour N₂ flow-based degassing can achieve partial activation, complete activation of the tested PBAs is not attainable under these conditions.

These findings highlight that PBA activation is a non-trivial process. Careful control of degassing conditions is essential to both expose open metal sites and preserve structural integrity, which is critical for gas adsorption applications. In practice, this may necessitate prolonged vacuum degassing to effectively remove moisture and ensure the adsorbent remains dry, as well as reliable methods for assessing adsorbent dryness. In gas separation applications, such extensive vacuum treatment may pose practical limitations for the use of PBAs. Additionally, to fully exploit open metal sites, the humidity of the adsorption gas must be minimized to prevent competitive adsorption and water retention. Notably, water condenses in the micropores even at low relative humidity, reaching gravimetric adsorption capacities comparable to those of zeolites and volumetric capacities exceeding them. This suggests that microporous PBAs hold significant potential for drying applications, particularly where compact adsorbent volumes are desirable.

3.A. Appendix - Chapter 3

Table 3.A.1 Results of the elemental analysis with O and S added from H₂O and SO₄²⁻, based on chemical interpretation of the missing wt%.

Wt%												
Sample name	C	H	N	Fe	K	Cu	Co	O (H2O)	Sum	S	O(SO4)	Sum SO4 incl.
FePBA	17.23	3.33	19.27	28.37	1.97	-	-	26.43	96.60	1.14	2.27	100.00
CuPBA	17.21	3.37	20.81	13.74	0.21	17.94	-	26.75	100.03	0.00	0.00	100.03
CoPBA	16.63	3.25	20.12	12.58	0.44	-	19.59	25.79	98.40	0.53	1.06	100.00

Wt% w/o water										
Sample name	C	H	N	Fe	K	Cu	Co	O	S	Sum
FePBA	24.53	0.00	27.43	40.39	2.80	-	-	3.23	1.62	100.00
CuPBA	24.62	0.00	29.77	19.65	0.30	25.66	-	-	-	100.00
CoPBA	23.44	0.00	28.36	17.73	0.62	-	27.61	1.50	0.75	100.00

Expected wt% w/o water										
Sample name	C	H	N	Fe	K	Cu	Co	O	S	Sum
FePBA	25.16	0.00	29.34	45.5	0.00	-	-	0.00	0.00	100.00
CuPBA	23.45	0.00	27.35	18.17	0.00	31.02	-	0.00	0.00	99.99
CoPBA	23.99	0.00	27.98	18.59	0.00	-	29.43	0.00	0.00	99.99

In the case of FePBA and CoPBA, the addition of the weight of O from water does not add up to 100% of the weight, indicating the presence of another element which was not probed. Most likely, this is caused by the presence of SO₄²⁻-ions which were not completely removed during the washing steps. However, similar to K, the quantities are low and we do not expect a large effect on the overall adsorption.

Table 3.A.2 Micropore and overall volume of all PBA samples measured by N₂ adsorption. Micropore and overall volume are determined by taking the adsorption value at a relative pressure of 0.05 and 1.0, respectively. ml g⁻¹ values (at -196 °C) are calculated from cm³ g⁻¹ STP using the densities of N₂ at STP and that of boiling liquid nitrogen.

	Degassing temperature	Micropore volume		Overall volume	
	(°C)	(cm ³ g ⁻¹ STP)	(ml g ⁻¹)	(cm ³ g ⁻¹ STP)	(ml g ⁻¹)
FePBA	60	51	0.079	120	0.186
	90	55	0.085	129	0.200
	100	64	0.099	145	0.224
	110	58	0.090	134	0.207
	120	58	0.090	143	0.221
	140	58	0.090	150	0.232
CoPBA	60	146	0.226	288	0.446
	90	162	0.251	321	0.497
	100	160	0.248	317	0.491
	110	158	0.245	318	0.492
	120	154	0.238	301	0.466
	140	142	0.220	314	0.486
CuPBA	60	57	0.088	132	0.204
	100	195	0.302	286	0.443
	110	208	0.322	296	0.458
	120	211	0.327	284	0.440
	130	5	0.008	52	0.080
	140	2	0.003	39	0.060

Table 3.A.3 FWHM values of PXRD measurements using the peak at 17.5° fitted using a Gaussian function.

	Sample	FWHM	Fitting Error
FePBA	A.S.	0.63516	0.0162
	60 °C	0.67507	0.01381
	90 °C	0.64806	0.01019
	100 °C	0.65809	0.01404
	110 °C	0.65770	0.01033
	120 °C	0.66559	0.01068
	140 °C	0.64735	0.01272
CoPBA	A.S.	0.24067	0.00541
	60 °C	0.2892	0.00427
	90 °C	0.32044	0.00472
	100 °C	0.30749	0.00426
	110 °C	0.33387	0.0048
	120 °C	0.35222	0.0049
	140 °C	0.37208	0.00517
CuPBA	A.S.	0.14417	0.00263
	60 °C	0.14267	0.00281
	100 °C	0.14993	0.00303
	110 °C	0.1537	0.00333
	120 °C	0.14968	0.00384
	130 °C	26.63048	0.27713
	140 °C	24.71699	0.27728

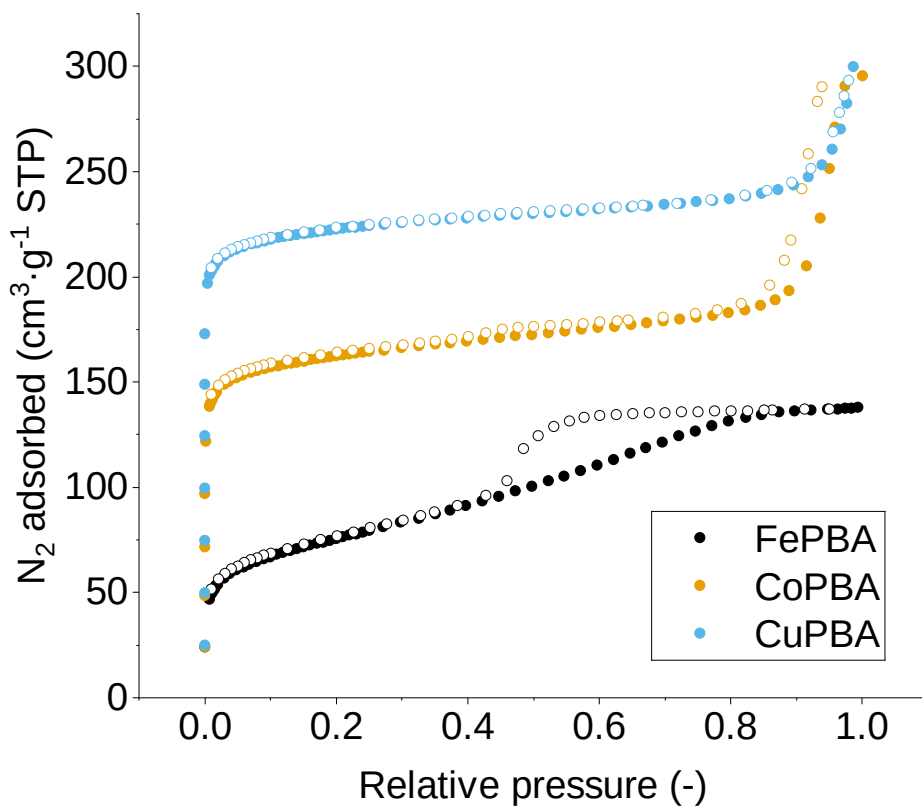
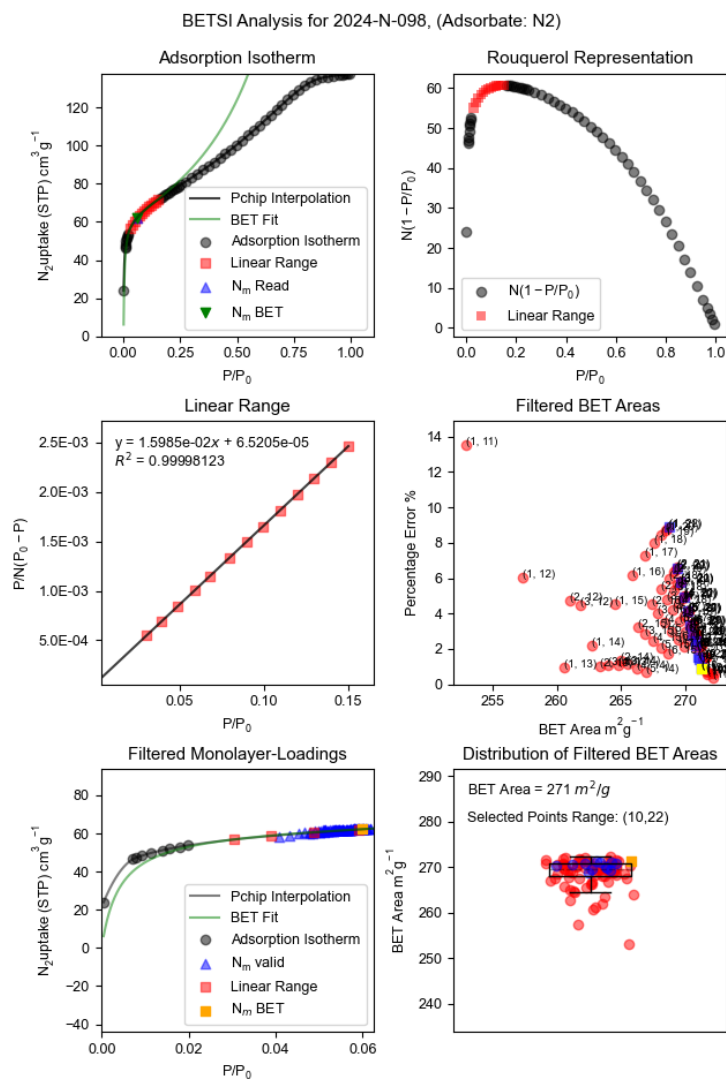


Figure 3.A.1 N_2 adsorption isotherms of PBAs at their optimal activation temperature.

Table 3.A.4 Summary of optimally degassed samples and their BET areas.

Adsorbent	Optimal degassing temperature [°C]	BET area [$\text{m}^2 \text{g}^{-1}$]
FePBA	100	271
CoPBA	100	635
CuPBA	120	890



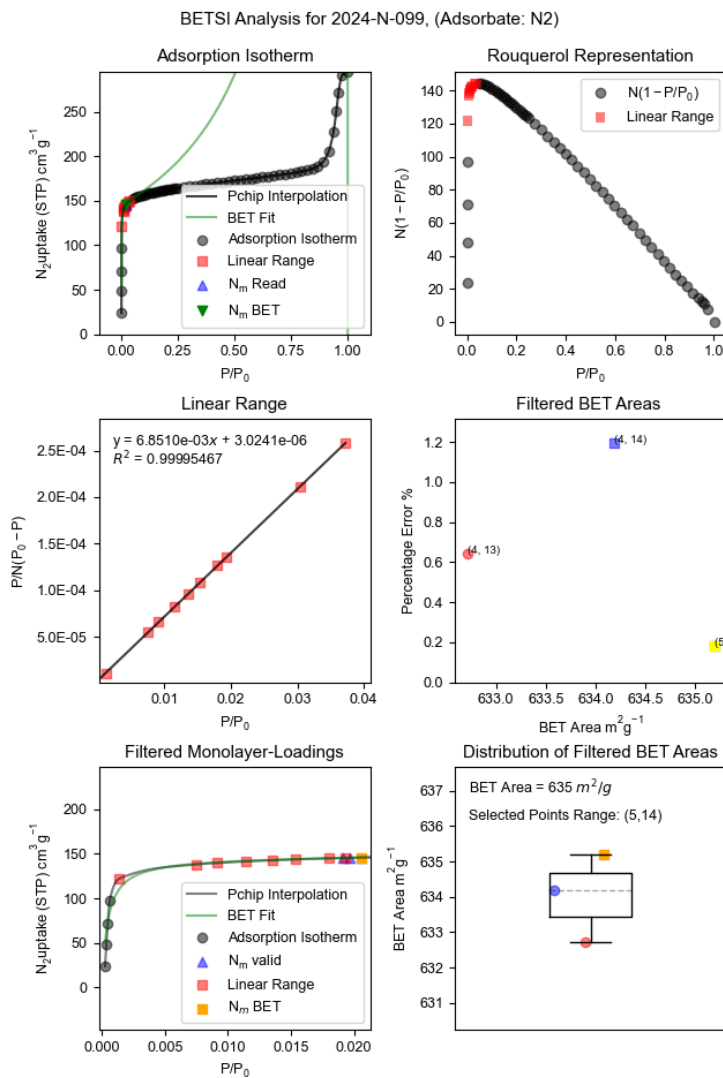


Figure 3.A.3 BETSI analysis report for CoPBA degassed at 100 °C.

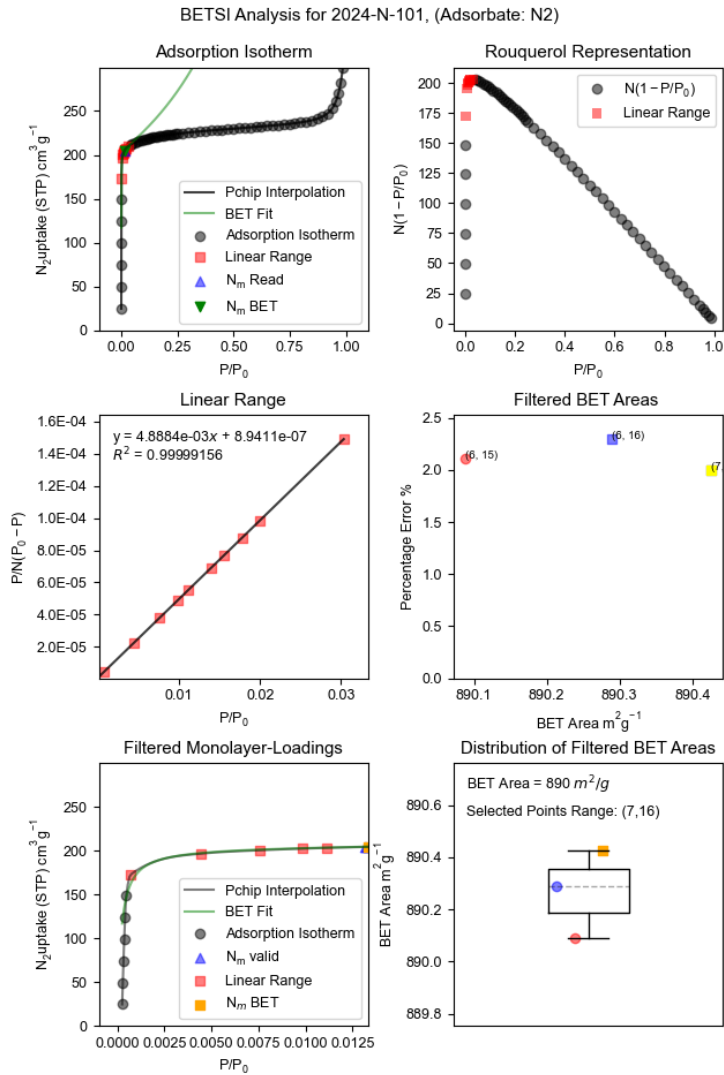


Figure 3.A.4 BETSI analysis report for CuPBA degassed at 120 °C.

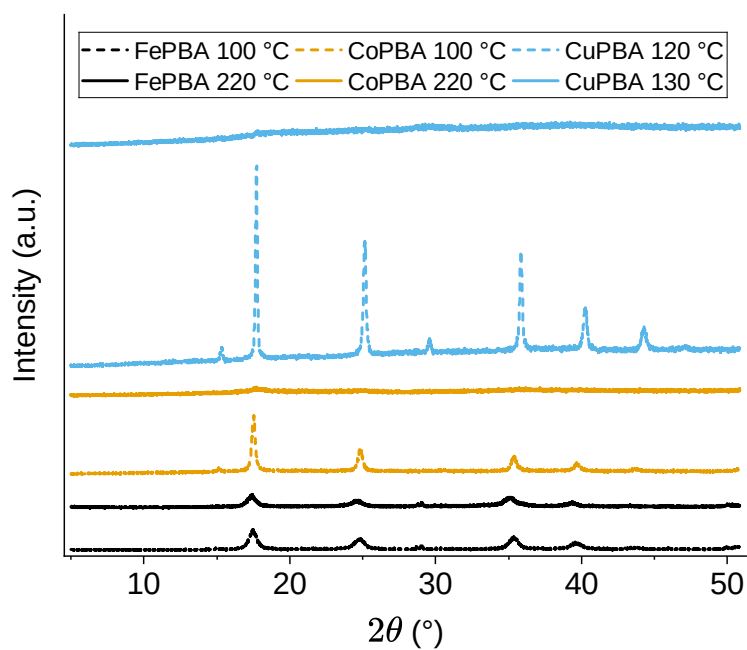


Figure 3.A.5 PXRD of samples degassed at temperatures at which structural degradation is visible. Optimally degassed samples are included for reference.

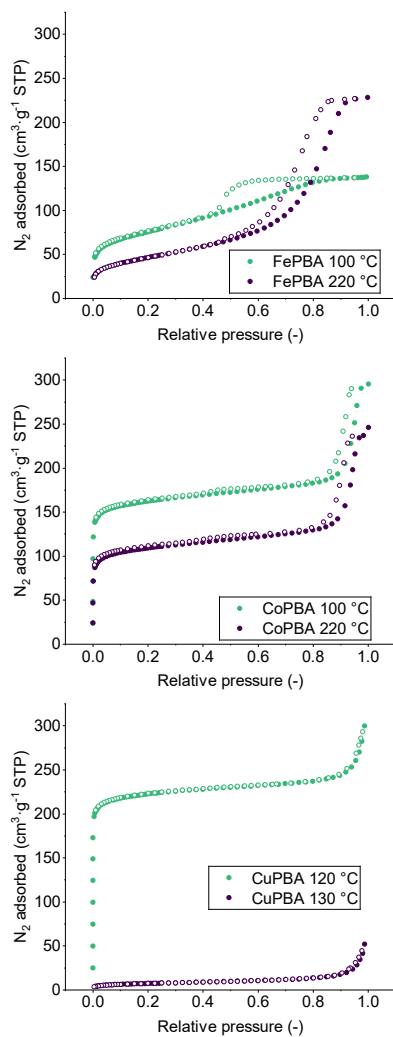


Figure 3.A.6 N_2 adsorption of samples degassed at temperatures at which structural degradation is visible. Optimally degassed samples are included for reference.

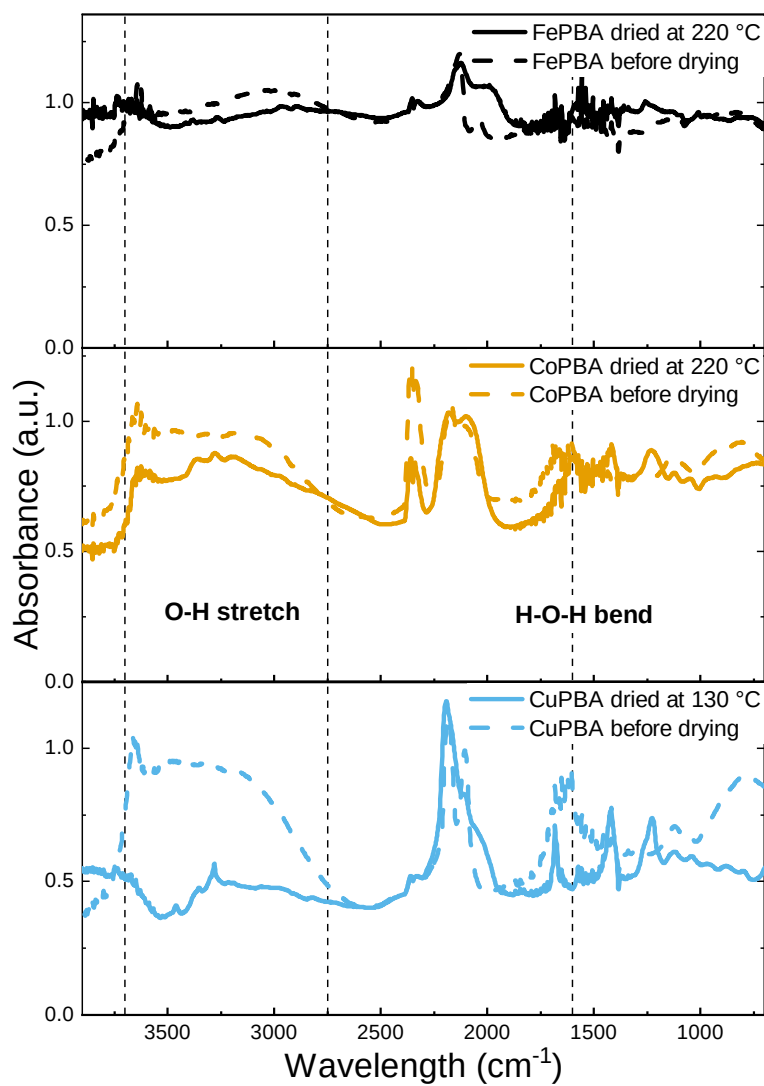


Figure 3.A.7 DRIFTS of samples before and after an in-situ degassing procedure at temperatures at which structural degradation is visible.

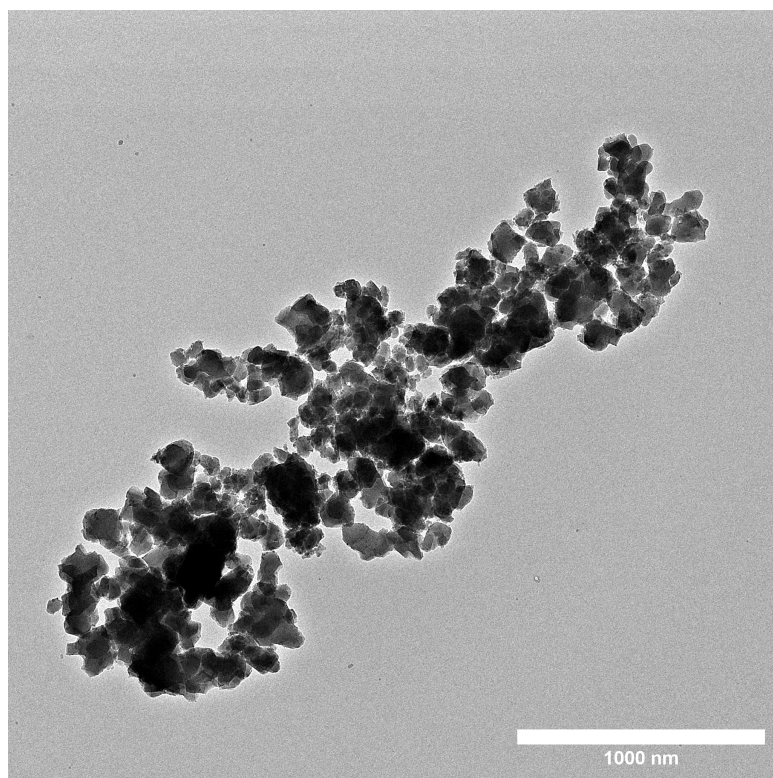


Figure 3.A.8 TEM analysis of CuPBA particles after degassing at 120 °C.

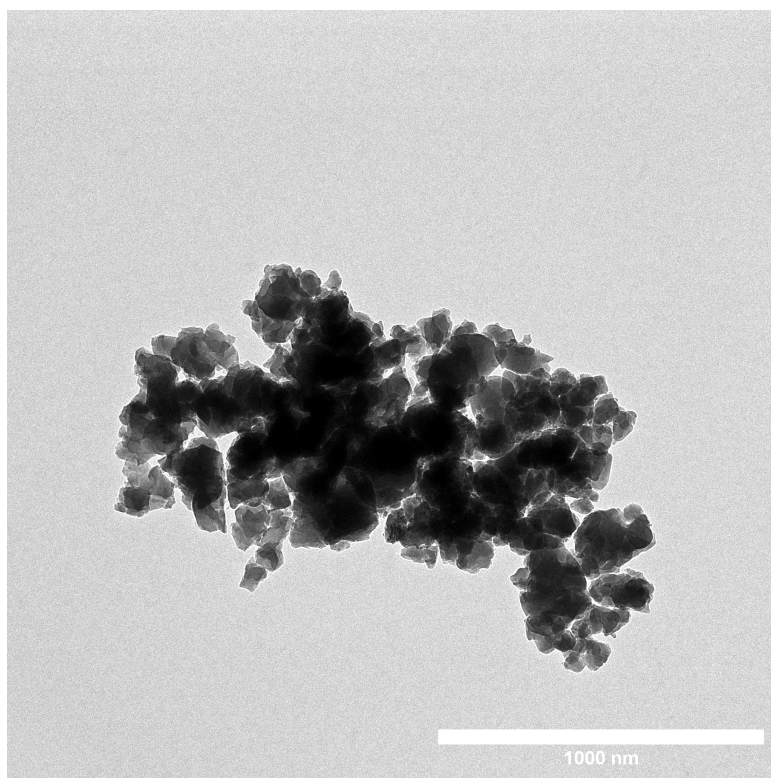


Figure 3.A.9 TEM analysis of CuPBA particles after degassing at 130 °C.

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Chapter 4

Redox-Switchable CO Affinity in Macrocyclic Complexes

Carbon monoxide (CO) emissions from industrial processes contribute significantly to global CO₂ emissions, for example from burning CO in mixed CO/N₂ streams in the steel industry. If, instead, the CO could be recycled industrially this would save more than 2% of the total CO₂ emissions. However, separating CO and N₂ is a technological challenge. Electroswing sorption, an electrochemical technique, allows for the selective capture and release of CO offering a method for CO/N₂ separation. Here, we investigate four macrocyclic complexes based on 5,10,15,20-tetraphenylporphyrin (TPP) and phthalocyanine (Pc) - FeTPP, FePc, CoTPP, and CoPc - using density functional theory (DFT) and cyclic voltammetry (CV). DFT calculations show oxidation state-dependent affinity for CO in all complexes, identifying several redox couples as candidates for electroswing sorption. Experimental CVs confirm CO-induced potential shifts for FeTPP and FePc, consistent with theoretical trends, while CoTPP and CoPc show no shifts due to competitive binding of the solvent and solubility limitations. Quantitatively, the FeTPP⁻/FeTPP couple shows a potential shift of -0.24 V at 50 vol% CO, corresponding with a change in ΔG of 23.16 kJ mol⁻¹, while the FePc⁻/FePc couple shows a shift of -0.14 V at 50 vol% CO, corresponding with a change in ΔG of 13.51 kJ mol⁻¹. These findings demonstrate the feasibility of using DFT as a screening tool for potential complexes for CO electroswing sorption, but also highlight the need for experimental validation to account for limitations in the theory.

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Data repository: doi.org/10.4121/7367d15a-9382-4623-8734-71b3bcde871d

4.1. Introduction

In order to mitigate climate change, significant effort is being placed in reducing, reusing and recycling chemicals in waste streams in an effort to lower the emissions of greenhouse gasses such as CO₂. [1] Carbon monoxide (CO) is one of the key targets for these efforts. CO is a toxic chemical that is a regular waste product of the chemical, steel, and energy industries. It is also one of the components of syngas and a major feedstock chemical for C1-based industrial chemistry. Unfortunately, it is currently often used for its caloric value, leading to a large output of CO₂: 2.7% of the global anthropogenic CO₂ emissions comes from the burning of CO from the steel industry alone. [2]

4

One of the major reasons why CO is not yet recycled is its difficulty to separate from N₂-gas with which it is commonly mixed in waste gas streams. [3, 4] Currently, there are no economically feasible means of separating the two gasses that are applicable in industrial settings, [2] making it a very attractive research goal. Most efforts in separating CO from N₂ have focused on thermal or pressure swing-based adsorptive separations. [2, 5, 6] The adsorbents used for this separation are capable of targeting the electronic structure of CO through its metal-carbonyl interactions. A common problem, however, is that the M-CO bond is too strong, requiring either elevated temperatures and/or strong vacuum to induce desorption. [7]

Inspired by the work of the separation of electro-swing adsorption of CO₂ [8–12] and early work on the electrochemical absorptive separation of CO and N₂, [13] as well as C₂H₄ and C₂H₆, [14] we investigated the potential of using electro-swing absorption for CO separation. Electro-swing absorption functions on the basis of having a differing affinity for the target molecule, CO, in different oxidation states. So, rather than swinging in pressure or temperature, a swing in oxidation state using electrochemistry is used (Figure 4.1). Recently, we showed the proof of concept of the electro-swing absorption for CO based on Ni(cyclam)Cl₂ in an H₂O/MeCN-mixture [15] as well as an optimisation of the process using aqueous CuCl. [16] Both these examples showed electrochemically switchable interaction with CO in earlier literature [13, 17, 18] and follow the general trend that a lower oxidation state of the metal ion (Cu⁺ and Ni⁺) leads to a stronger π -backbonding interaction and therefore binding with CO compared to the higher oxidation state (Cu²⁺ and Ni²⁺). However, both these complexes suffer from drawbacks either from the potential release of toxic Ni(CO)₄ gas from overreduction, in the case of Ni(cyclam)Cl₂, [15] or poor kinetics and carrier utilisation, in the case of CuCl, [13, 16] highlighting the need for further exploration in the material space.

Another set of complexes that was studied for its interaction with CO in various oxidation states, 5,10,15,20-tetraphenylporphyrin (TPP) chelating a metal ion in its central moiety, was shown to be more unpredictable, however. When TPP chelated Fe (FeTPP), the binding with CO was found to be stronger in the reduced Fe(II) state compared to both the Fe(III) and Fe(I) states. [19] Yet, when chelating Co (CoTPP),

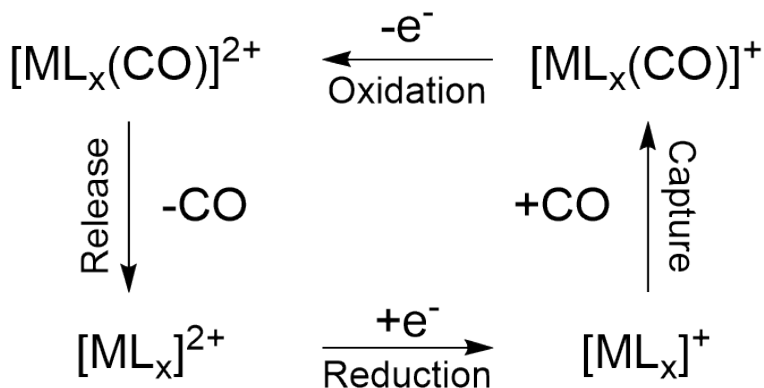


Figure 4.1 Schematic overview of the electroswinging process for CO with a generic complex (ML_x), assuming the reduced complex has a higher affinity.

the binding of CO is shown to be more favourable in the oxidised Co(III) state compared to the Co(II) state. [20] In both cases, two CO molecules are bound to the central metal ion with only the metal cation being different, which makes for an interesting study as to why these complexes behave differently. Furthermore, these porphyrins have no dangerous side reactions and offer tunability in the CO binding affinity through the addition of functional groups. [19]

In addition to porphyrins, phthalocyanine (Pc) was also shown to have strong interaction with CO when chelating Fe (FePc) [21–23], while phthalocyanine chelating some other metals (Co, Ni, Cu, Zn) have been shown to also have a strong interaction from computational results [24]. Out of these complexes, only FePc and CoPc have redox active metal sites [25] which are of interest to us for their electrochemically switchable affinity towards CO. Curiously, the interaction with CO is strong in the M^{2+} oxidation state for both FePc and CoPc, unlike what was observed in the TPP complexes. The only other oxidation state for which a CO affinity was reported, chemically reduced FePc^- , was shown to have a slightly lower affinity towards CO compared to the neutral FePc with a ΔG , based on the K_{eq} , of $-8.27 \text{ kJ mol}^{-1}$ compared to the $-9.63 \text{ kJ mol}^{-1}$ of the neutral FePc. [21] This matches the general trend of higher oxidation states leading to lower π -backbonding interaction and, thus, lower affinity. Unlike the porphyrin complexes, however, no electrochemical studies with phthalocyanines have been conducted in the presence of CO.

Therefore, in order to get a better understanding of how changing the oxidation state of the metal affects the CO-complex interaction and with the aim of finding new materials and potential molecular design principles for CO electroswinging absorption, we investigated FeTPP, CoTPP, FePc, and CoPc (Figure 4.2) and their

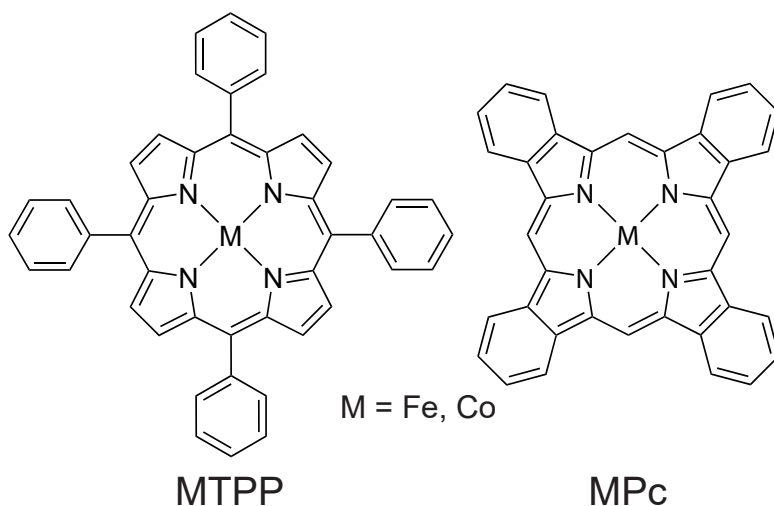


Figure 4.2 The porphyrin and phthalocyanine complexes shown to have potential for CO electroswinging sorption

interaction with CO using a combined theoretical-experimental approach.

4.2. Methods

4.2.1. Computational details

All DFT calculations were performed using ORCA 6 [26] with the PBE0 hybrid-GGA functional [27, 28] and Karlsruhe def2 basis sets. [29] Grimme's D3 dispersion with Becke-Johnson damping [30, 31] was used to take dispersion into account. Implicit solvation with N,N-dimethylformamide (DMF) was modelled with the Solvation Model based on Density (SMD). [32] Calculations were accelerated using the RIJ-COSX [33] approximation using the def2/J auxiliary basis set. [34]

Geometry optimisations were performed using the def2-SVP basis set, while the single point calculations were performed with the def2-TZVPP basis set to approach the basis set limit. Frequency calculations were performed to obtain the thermochemistry data and to check for imaginary modes to confirm energetic minima were achieved during structure optimisation. The obtained geometries had their symmetries determined using libmsym [35] in order to be able to symmetry-correct the rotational entropy. The resulting thermochemistry data was then used to determine individual binding energies for the 1st and 2nd CO, as well as the overall binding energies for 2 CO molecules.

Normal-coordinate Structural Decomposition (NSD) [36, 37] was performed on

the lowest energy TPP complexes to determine and quantify the distortions in the porphyrin ring caused by the changes in oxidation state, spin state, and the addition of CO ligands.

4.2.2. Experimental details

Materials

Fe(III)-5,10,15,20-(tetraphenyl)porphyrin chloride (FeTPP, 98%) and Co(II)-5,10,15,20-(tetraphenyl)porphyrin (CoTPP, 98%) were purchased from Porphychem. Fe(II) phthalocyanine (FePc, 96%) was purchased from Alfa Aesar. Co(II) phthalocyanine (CoPc, 97%) and N,N-dimethylformamide (DMF, 99.8%) were purchased from Sigma Aldrich. Tetra-n-butylammonium hexafluorophosphate (TBAPF₆, 98%) was purchased from Brunschwig. All chemicals were used as received without further purification.

Methods

Cyclic voltammetry (CV) measurements were performed to study the binding of CO to the transition metal complexes. The electrolyte solution consisted of 50 mL DMF with 0.1 M TBAPF₆ and 0.5 mM of the porphyrin or 0.2 mM of the phthalocyanine material. The working electrode was a glassy carbon rod (diameter 2 mm, type 1, Thermo Scientific), the counter electrode was a platinum wire (diameter 0.3 mm, 99.9%, Thermo Scientific), and the reference electrode was an Ag/AgCl micro-reference electrode (LF-1-45, Alvatek). Ferrocene was used as an internal standard. The measurement was performed in an airtight cell with a gas inlet and outlet. A gas flow of 2 ml min⁻¹ with a CO concentration ranging between 0 and 50 vol% in N₂ was fed to the electrolyte solution by mass flow controllers (MFC, Bronkhorst). Between each CV measurement at a different CO concentration, the solution was sparged with the gas for 2.5 hours. An Iviumstat2.h potentiostat was used to perform the cyclic voltammetry measurement and different scan rates (50, 100, 200, and 400 mV s⁻¹).

4.3. Results & Discussion

To assess if our chosen computational system can reproduce the overall results of the experiments from literature for porphyrin complexes and to predict properties for the non-studied phthalocyanine complexes, we performed DFT calculations on FeTPP and CoTPP as well as FePc and CoPc to observe changes in affinity towards CO. The resulting physical properties of the lowest energy states are summarised in Table 4.1, while the geometries are shown in Figures 4.3-4.6 and HOMO/LUMO orbitals as well NSD analyses are available on the 4TU Data repository [†].

[†]doi.org/10.4121/7367d15a-9382-4623-8734-71b3bcde871d

Table 4.1 Overview of physical properties of lowest energy complexes at a specific charge. Charge (C); multiplicity (2S+1); point group of the central macrocycle excluding phenyl rings and CO (PG); distance between C and O (d(C-O)); distance between metal ion and C (d(M-C)); angle between metal ion, C, and O ($\angle(\text{M-C-O})$); and wavenumber of the (asymmetric) CO vibration are indicated in the columns for each complex ($\nu(\text{CO})$). CO is added as a reference for the free C-O distance and wavenumber of the free CO vibration.

Complex	C	2S+1	PG	d(C-O) (Å)		d(M-C) (Å)		∠(M-C-O) (°)		ν(CO) (cm ⁻¹)
CO	0	1		1.128						2201
FeTPP	-1	2	D _{2h}							
	0	3	C ₁							
	1	4	C ₁							
FeTPP(CO)	-1	2	C ₁	1.148		1.703		179.99		2034
	0	1	C _{2v}	1.144		1.714		179.93		2061
	1	4	C ₂	1.126		2.088		179.77		2196
FeTPP(CO) ₂	-1	2	C ₁	1.137	1.137	1.832	1.832	179.82	179.91	2074
	0	1	C ₁	1.134	1.134	1.842	1.842	179.89	179.79	2099
	1	2	C ₁	1.132	1.132	1.848	1.847	179.94	179.74	2124
CoTPP	-1	3	C ₁							
	0	2	C ₁							
	1	5	D _{4h}							
CoTPP(CO)	-1	3	C ₁	1.136		1.959		160.92		2108
	0	2	C ₁	1.132		1.988		165.33		2142
	1	3	C ₁	1.129		2.022		178.34		2177
CoTPP(CO) ₂	-1	3	C ₂	1.133	1.133	1.867	1.867	179.48	179.45	2124
	0	2	C ₁	1.131	1.131	2.130	2.172	153.91	149.53	2143
	1	1	D _{4h}	1.123	1.123	1.861	1.860	178.94	179.06	2232
FePc	-1	2	D _{4h}							
	0	3	D _{4h}							
	1	2	D _{4h}							
FePc(CO)	-1	2	C _{2v}	1.145		1.712		179.95		2056
	0	1	C _{4v}	1.141		1.724		180.00		2084
	1	2	C _{4v}	1.139		1.735		179.99		2103
FePc(CO) ₂	-1	2	D _{2h}	1.135	1.135	1.843	1.843	179.99	180.00	2095
	0	1	D _{4h}	1.132	1.132	1.854	1.854	179.98	179.98	2121
	1	2	D _{4h}	1.131	1.131	1.864	1.864	179.98	180.00	2138
CoPc	-1	1	D _{4h}							
	0	4	D _{2h}							
	1	3	D _{4h}							
CoPc(CO)	-1	3	C _{2v}	1.132		1.980		179.73		2145
	0	2	C _{4v}	1.129		2.016		179.86		2172
	1	3	C _{4v}	1.128		2.036		179.85		2188
CoPc(CO) ₂	-1	3	D _{2h}	1.131	1.131	2.169	2.169	152.41	152.44	2142
	0	2	D _{4h}	1.127	1.127	2.224	2.224	179.83	179.98	2193
	1	3	D _{4h}	1.126	1.126	2.240	2.241	179.83	179.70	2204

Although the TPP and Pc macrocycles look similar, they differ in geometry

and flexibility. TPP complexes show flexibility in their inner ring which causes shifts from the perfectly planar D_{4h} symmetry. To visualise and quantify these distortions, NSD was performed on all TPP complexes shown in Table 4.1. These analyses show that most of the investigated TPP complexes have ruffled out-of-plane distortions which correspond to the B_{1u} irreducible vibrational mode of D_{4h} . Notable exceptions are the FeTPP^- , CoTPP^+ , and $\text{CoTPP}(\text{CO})_2^+$ complexes which are near planar, the $\text{FeTPP}(\text{CO})^+$ complex which has a saddle distortion (B_{2u}), and the CoTPP^- complex which has a combination of a ruffled and a saddle distortion. For the in-plane distortions, most of the complexes show isotropic expansion or contraction (A_{1g}) with minor contributions from other vibrational modes. The main exception is $\text{CoTPP}(\text{CO})_2^-$ in which the symmetry is broken due to contraction of two opposing pyrrole units while the others expand (B_{1g}).

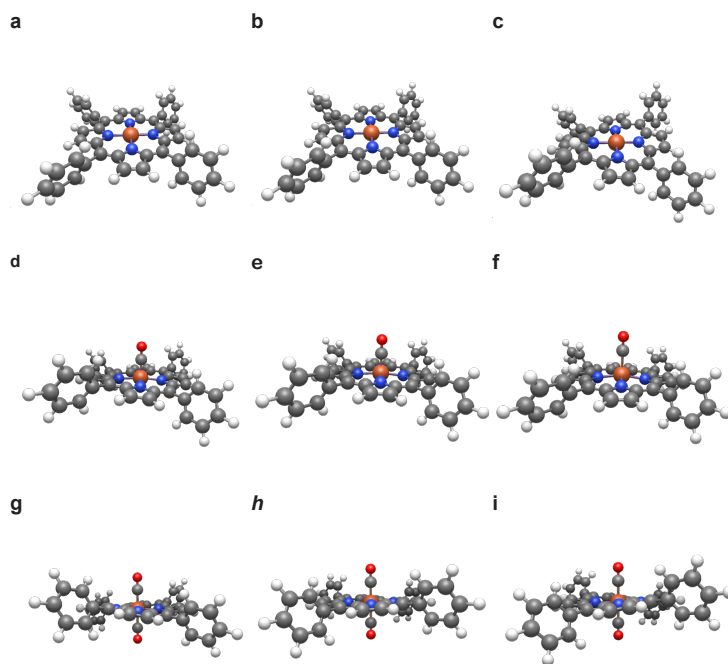


Figure 4.3 Geometries of FeTPP complexes. **a:** FeTPP^- , **b:** FeTPP , **c:** FeTPP^+ , **d:** $\text{FeTPP}(\text{CO})^-$, **e:** $\text{FeTPP}(\text{CO})$, **f:** $\text{FeTPP}(\text{CO})^+$, **g:** $\text{FeTPP}(\text{CO})_2^-$, **h:** $\text{FeTPP}(\text{CO})_2$, **i:** $\text{FeTPP}(\text{CO})_2^+$. Atom colours: C (gray), H (white), O (red), N (blue), Fe (orange).

For the Pc ligand, on the other hand, the analysis is more straightforward due to the rigidity of the ligand retaining the planar structure, as well as only having minor overall changes in the geometry. The original D_{4h} symmetry often persists, while C_{4v} occurs when a single CO binds, as the metal ion shifts out

plane. The D_{2h} and C_{2v} point groups in $\text{FePc}(\text{CO})^-$, $\text{FePc}(\text{CO})_2^-$, CoPc , $\text{CoPc}(\text{CO})^-$, and $\text{CoPc}(\text{CO})_2^-$ are caused by a distortion in structure similar to the distortion in $\text{CoTPP}(\text{CO})_2^-$ described earlier with two opposing benzotriazole units contracting while the other two expand.

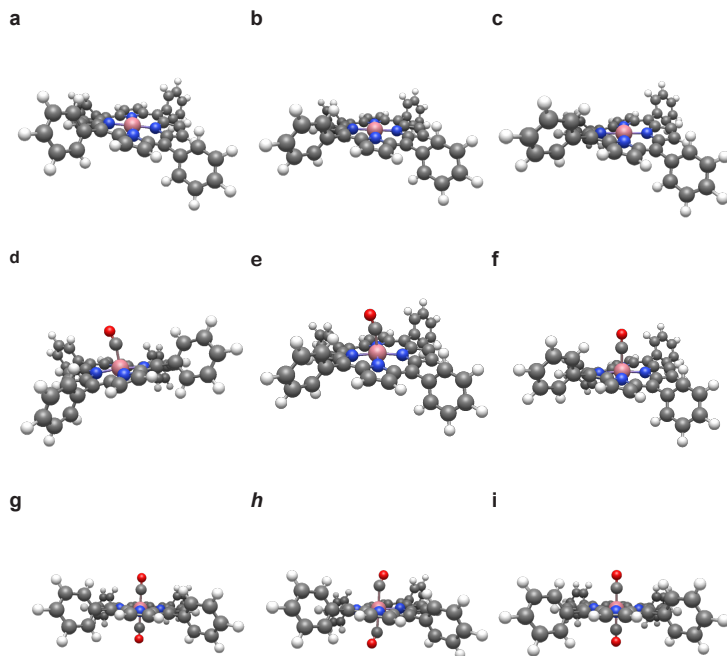


Figure 4.4 Geometries of CoTPP complexes. **a:** CoTPP^- , **b:** CoTPP , **c:** CoTPP^+ , **d:** $\text{CoTPP}(\text{CO})^-$, **e:** $\text{CoTPP}(\text{CO})$, **f:** $\text{CoTPP}(\text{CO})^+$, **g:** $\text{CoTPP}(\text{CO})_2^-$, **h:** $\text{CoTPP}(\text{CO})_2$, **i:** $\text{CoTPP}(\text{CO})_2^+$. Atom colours: C (gray), H (white), O (red), N (blue), Co (pink).

When CO is bound to these complexes, $\nu(\text{CO})$ increases with a rise in oxidation state (Table 4.1). This correlates with an increased C-O bond length, consistent with expected changes in π -backbonding interaction. Similarly, the addition of a second CO ligand causes the wavenumber to decrease, with the notable exception of $\text{FeTPP}(\text{CO})_2^+$. For the Fe-based macrocycles, we can also see that the M-C-O angle remains very close to 180° , regardless of the amount of CO ligands or the oxidation state. Notably, some CoTPP and CoPc show M-C-O angles of $150\text{--}165^\circ$ as an exception to this general trend.

However, the trends for the resulting binding energies are much less predictable than those of the physical properties (Table 4.2). For FeTPP, the binding of the first CO molecule is only spontaneous ($\Delta G < 0$) for the neutral FeTPP with a

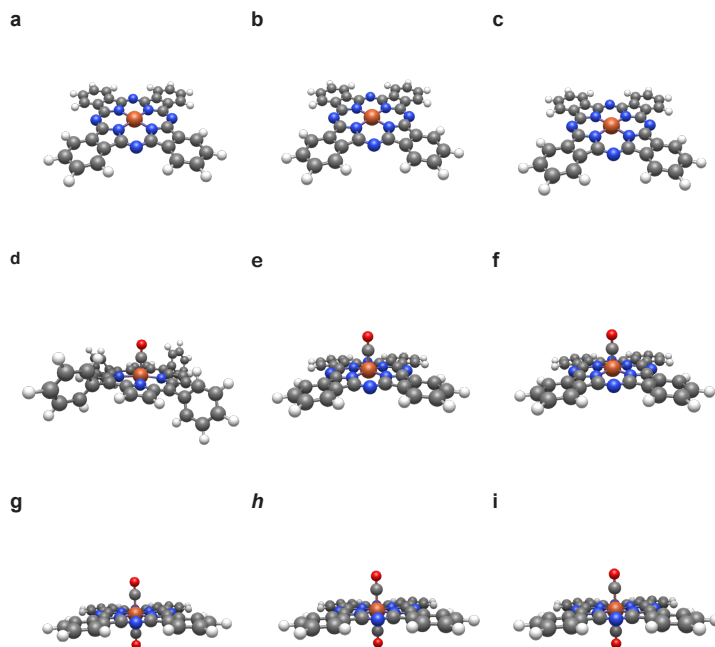


Figure 4.5 Geometries of FePc complexes. **a:** FePc^- , **b:** FePc , **c:** FePc^+ , **d:** $\text{FePc}(\text{CO})^-$, **e:** $\text{FePc}(\text{CO})$, **f:** $\text{FePc}(\text{CO})^+$, **g:** $\text{FePc}(\text{CO})_2^-$, **h:** $\text{FePc}(\text{CO})_2$, **i:** $\text{FePc}(\text{CO})_2^+$. Atom colours: C (gray), H (white), O (red), N (blue), Fe (orange).

significantly more negative heat of adsorption compared to the other oxidation states. These binding energies for the 1st CO imply that the most likely binding oxidation state is the neutral FeTPP, while the other oxidation states can serve as non-binding states. The binding of the second CO, however, is spontaneous for all oxidation states and the overall reaction of the binding of 2 CO molecules is as well, with the neutral oxidation state still having the most negative ΔG . Similarly, the heat of adsorption of the second CO is significantly more negative compared to the binding of the 1st CO for all oxidation states. We can conclude from this that the presence of the first CO molecule stabilises the binding of the second. Thus, once the second CO binds, removal after oxidation or reduction is no longer spontaneous, as shown by the overall ΔG being negative in all cases. Therefore, it can be presumed that FeTPP is the binding state while both FeTPP^- and FeTPP^+ are potential partial releasing states. When 1 CO is bound, this is obvious from the ΔG values being positive for both FeTPP^- and FeTPP^+ . When two CO are bound, however, additional electrical energy is required to remove CO molecules due to the stabilising effect of the binding of the first CO.

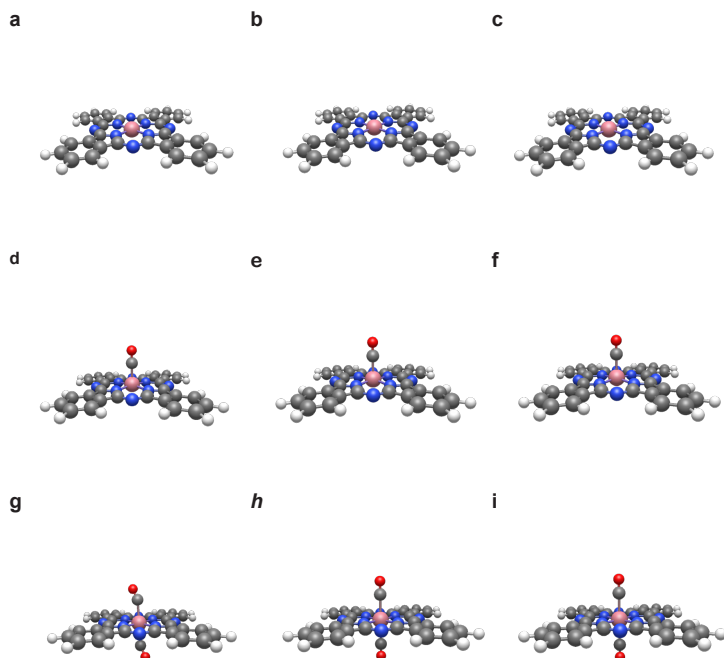


Figure 4.6 Geometries of CoPc complexes. **a:** CoPc^- , **b:** CoPc , **c:** CoPc^+ , **d:** $\text{CoPc}(\text{CO})^-$, **e:** $\text{CoPc}(\text{CO})$, **f:** $\text{CoPc}(\text{CO})^+$, **g:** $\text{CoPc}(\text{CO})_2^-$, **h:** $\text{CoPc}(\text{CO})_2$, **i:** $\text{CoPc}(\text{CO})_2^+$. Atom colours: C (gray), H (white), O (red), N (blue), Co (pink).

Table 4.2 Binding enthalpies and Gibbs free energies associated with the binding of CO to the complexes at different oxidation states. Energies are split into the binding of the 1st CO, binding of the 2nd CO after the binding of the 1st CO has already occurred, and the overall energy of binding two CO ligands to the complex.

Complex	Charge	1st CO ΔH (kJ mol^{-1})	1st CO ΔG (kJ mol^{-1})	2nd CO ΔH (kJ mol^{-1})	2nd CO ΔG (kJ mol^{-1})	Overall 2 CO ΔH (kJ mol^{-1})	Overall 2 CO ΔG (kJ mol^{-1})
FeTPP	-1	-44.44	3.50	-74.76	-28.01	-119.20	-24.51
	0	-55.62	-4.42	-76.37	-29.71	-131.99	-34.13
	1	-21.84	18.47	-93.41	-35.25	-115.25	-16.78
CoTPP	-1	-47.17	-2.13	1.79	45.78	-45.37	43.65
	0	-45.79	-1.72	-18.49	23.37	-64.28	21.64
	1	-64.02	-15.20	-60.35	-8.70	-124.37	-23.90
FePc	-1	-37.25	6.90	-73.60	-25.10	-110.86	-18.19
	0	-53.61	-3.76	-74.92	-26.25	-128.54	-30.02
	1	-53.81	-6.36	-77.00	-28.14	-130.82	-34.50
CoPc	-1	-62.67	-26.67	-11.28	31.82	-73.95	5.15
	0	-142.34	-94.29	-11.79	28.58	-154.13	-65.70
	1	-42.10	-0.10	-14.49	26.31	-56.59	26.21

CoTPP, on the other hand, shows a negative ΔG value for all oxidation states when binding the first CO with affinity of $\text{CoTPP}^+ > \text{CoTPP} \approx \text{CoTPP}^-$ with the identical trend being true for the ΔH . The second CO, however, only binds spontaneously to the CoTPP^+ , with a clear difference in both ΔH and ΔG values compared to the other oxidation states, showing the higher affinity for CO. These results show that CoTPP^+ is the binding state while CoTPP and CoTPP^- are releasing states which would make the $\text{CoTPP}/\text{CoTPP}^+$ couple the likely target redox reaction for the electroswing absorption.

FePc shows a ΔG value with a trend of $\text{FePc}^- > 0 > \text{FePc} > \text{FePc}^+$, indicating that the first CO only binds spontaneously to the neutral and singly oxidised form of the complex. The second CO, however, binds spontaneously in all cases with a ΔG of $0 > \text{FePc}^- > \text{FePc} > \text{FePc}^+$ which also leads to the overall binding of 2 CO ligands to be spontaneous. Similar to the results for the FeTPP, the binding of the first CO ligand stabilises the overall complex. Most logically, these results indicate that the binding states are FePc and FePc^+ , while FePc^- is the releasing state. This suggests the $\text{FePc}^-/\text{FePc}$ couple is a promising candidate for electroswing absorption.

CoPc shows ΔG values of $0 > \text{CoPc}^+ > \text{CoPc}^- > \text{CoPc}$ with a very strong interaction with the neutral CoPc with a binding enthalpy of $-142.34 \text{ kJ mol}^{-1}$. The second CO ligand, on the other hand, shows only positive ΔG values, resulting in only the neutral CoPc having an overall negative ΔG value for 2 CO ligands. This indicates CoPc being the binding state and both CoPc^- and CoPc^+ being releasing states, meaning both $\text{CoPc}^-/\text{CoPc}$ and $\text{CoPc}/\text{CoPc}^+$ redox couples are potential CO electroswing separation candidates.

Overall, the trends of the calculated interactions match very well with literature. CO shows stronger interaction with the neutral FeTPP complex compared to both the oxidised and reduced FeTPP^+ and FeTPP^- , respectively, as was shown in earlier experimental work. [19] For CoTPP the stronger interaction between CO and the CoTPP^+ versus the neutral CoTPP also matches experimental results, while the reduction towards CoTPP^- was located outside the tested electrochemical window. [20] The FePc-CO interaction was also predicted to be stronger in the neutral FePc state compared to the reduced FePc^- state, while no predictions were made on the oxidated complex. [21] Lastly, while no predictions were made regarding the oxidation state dependent interaction strength between CO and CoPc, a strong interaction was predicted for the neutral CoPc, as is seen in our computational results. [24]

The DFT results were further analysed to obtain correlations between binding energies and molecular properties to make predictions for other complexes. Notably, no clear predictors emerged indicating a strong binding with CO (Figure 4.A.1). On the contrary, typical predictors for CO bond strength such as the CO wavenumber and the C-O bond length show no correlation with the binding energies in these complexes. Similarly, overall molecular charge and even atomic

charges, both Mulliken and Löwdin, are of limited use as a predictor for binding affinity from this dataset.

To summarise the computational results, we expect all complexes to potentially have binding and releasing oxidation states for CO. Specifically, from the results of our DFT calculations, we expect the $\text{FeTPP}/\text{FeTPP}^+$, $\text{FeTPP}^-/\text{FeTPP}$, $\text{CoTPP}/\text{CoTPP}^+$, $\text{FePc}^-/\text{FePc}$, $\text{CoPc}^-/\text{CoPc}$, and $\text{CoPc}/\text{CoPc}^+$ redox couples to have the highest chance of showing the CO-induced shifts in peak positions.

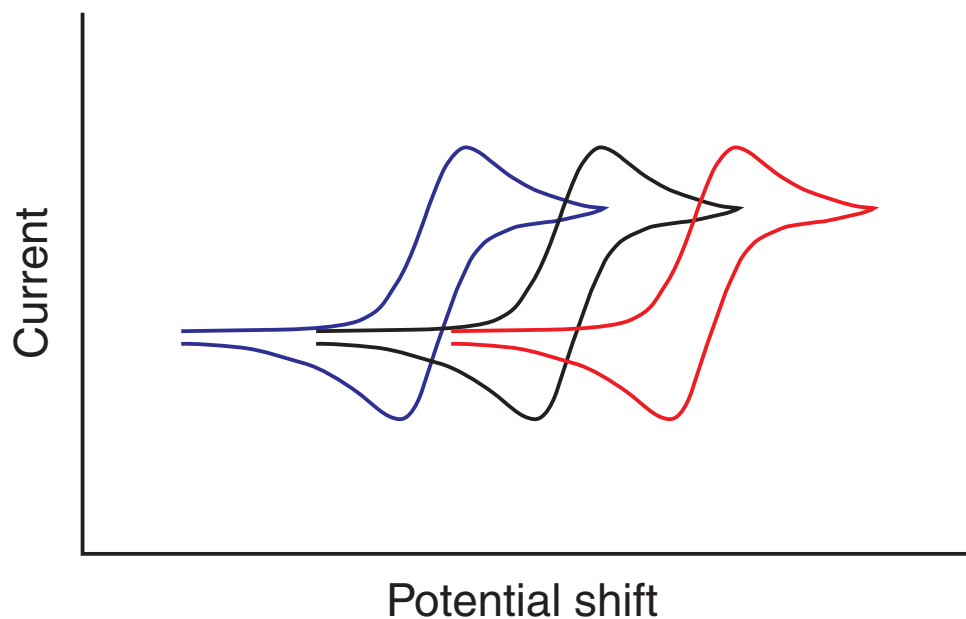


Figure 4.7 Schematic overview of the effect of the CO atmosphere on the shift of redox couples compared to the same redox couples under a N_2 atmosphere. Black line: redox couple has no interaction with CO. Red line: lower oxidation state binds more strongly to CO. Blue line: higher oxidation state binds more strongly to CO

To validate this experimentally, we performed cyclic voltammetry on the 4 complexes of interest in DMF under 0, 10, 50, and finally 0 vol% of CO to observe whether potential shifts of redox couples occur which indicate interaction with CO (Figure 4.7) and to assess their chemical and electrochemical reversibility.

In FeTPP (Figure 4.8) we can see three redox couples present in the potential range of -2.5 to 0.0 V versus Fc/Fc^+ under N_2 at half wave potentials of -2.17, -1.54, -0.65 V. Introducing CO into the atmosphere induces two major changes in two of these redox couples. We can see the oxidation peak at -1.50 V vs Fc/Fc^+ at 0 vol% CO, associated with the $\text{FeTPP}^-/\text{FeTPP}$ couple [38], shift to more negative

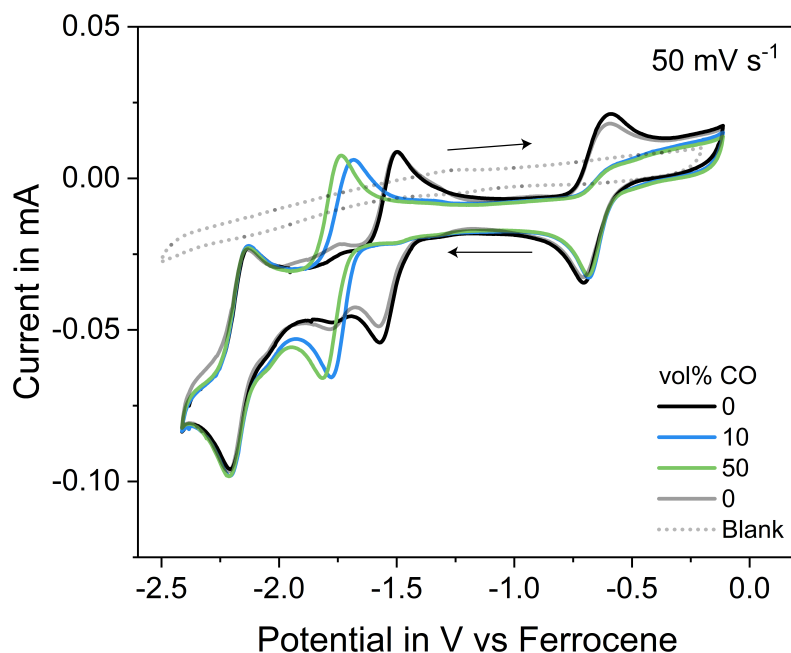


Figure 4.8 Cyclic voltammetry measurements of 0.5 mM FeTPP in 0.1 M TBAPF₆ in DMF under various vol% of CO.

potentials at -1.68 and -1.74 V vs Fc/Fc⁺ at 10 and 50 vol% CO, respectively, with a similar shift happening to the reduction peak. The peak associated with the FeTPP/FeTPP⁺ couple [38] at a half-wave potential of -0.65 V vs Fc/Fc⁺ can be seen to split into two separate processes in which the oxidation peak shifts to a more positive potential around 0.2 V vs Fc/Fc⁺ (Figure 4.A.2) while the reduction peak remains at the same potential. The redox couple at a half wave potential of -2.17 V, associated with the oxidation and reduction of the porphyrin ring [38] is unaffected by the introduction of CO, which is in line with expectations. From these CVs we can see that the most promising couple to perform the electroswing separation with is, indeed, the FeTPP⁻/FeTPP couple as the redox couple remains electrochemically reversible conform our prediction.

The potential shift at 50 vol% CO of -0.24 V leads to change in ΔG values of 23.16 kJ mol⁻¹ ($\Delta(\Delta G) = -nF\Delta E$), which is even higher than our DFT derived change in ΔG of 7.92 and 9.62 kJ mol⁻¹ when changing the oxidation state of FeTPP to FeTPP⁻ in the presence of one or two CO ligands, respectively. The experimentally measured shift can also be translated to a ratio of equilibrium

constants ($K_2/K_1 = \exp(-\frac{\Delta(\Delta G)}{RT})$) analogous to the distribution coefficient between two phases in extraction which can be used as a separation metric. The resulting K_2/K_1 ratio of $1.15 \cdot 10^4$ shows significant affinity towards FeTPP over FeTPP⁻, which is promising for electroswing absorption using these two oxidation states in FeTPP.

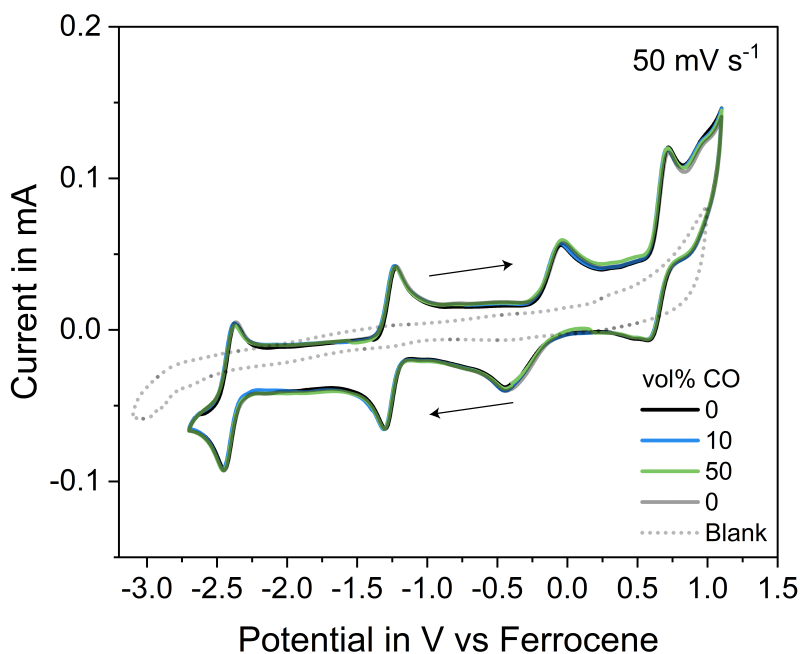


Figure 4.9 Cyclic voltammetry measurements of 0.5 mM CoTPP in 0.1 M TBAPF₆ in DMF under various vol% of CO.

In the case of the CVs of CoTPP (Figure 4.9), 4 clear redox couples at half-wave potentials of -2.41, -1.27, -0.25, and 0.65 V vs Fc/Fc⁺ in the range of -2.7 to 1.1 V under N₂. Unlike in the CV of FeTPP, we cannot see any significant changes in the potential or current of the redox couples in the CV of CoTPP when CO is present. We expected the CoTPP/CoTPP⁺ pair at 0.65 V vs Fc/Fc⁺ [20] to shift to lower potentials indicating a stronger binding to the CoTPP⁺ state. This peak likely remains in place due to the competitive binding of DMF to the Co centre of the CoTPP. Performing additional DFT calculations with explicit DMF on CoTPP shows that the DMF binds slightly more favourably to the CoTPP⁺ compared to CO (Table 4.A.1) while also being present in a far higher concentration due to it being the solvent. Obviously, this causes competitive adsorption which explains the lack of potential shift

even though stronger interaction was expected from the CoTPP^+ state from both our calculations and previous research. [20] This electrostatic interaction-induced adsorption of solvent molecules causing competitive adsorption in cationic complexes is not foreseen when using implicit solvation, showing the need for more careful analysis of solvent interactions when cationic complexes are involved.

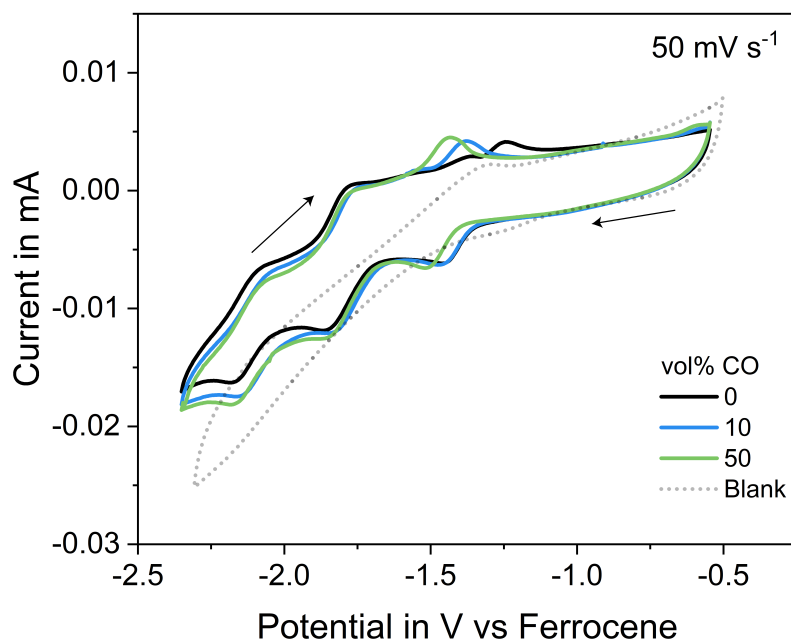


Figure 4.10 Cyclic voltammetry measurements of 0.2 mM FePc in 0.1 M TBAPF_6 in DMF under various vol% of CO.

In the FePc CV (Figure 4.10), 3 redox couples are visible at half-wave potentials of -2.11, -1.78, and -1.34 V vs Fc/Fc^+ under N_2 . When CO is introduced we see some minor changes in the current with no shift in potential for the couples at a half-wave potentials of -2.11 and -1.78 V vs Fc/Fc^+ . The peaks with half-wave potential of -1.34 V vs Fc/Fc^+ associated with the $\text{FePc}^-/\text{FePc}$ redox couple, [39] however, do show a shift to lower potentials, indicating most favourable binding to FePc. Most clearly, the oxidation peak shifts from -1.24 V under N_2 to -1.38 and -1.44 V under 10 and 50 vol% CO, respectively. The reduction peak shifts by a lesser amount to -1.48 and -1.52 V vs Fc/Fc^+ under 10 and 50 vol% CO, respectively. Taking the average shift in half-wave potential of -0.14 V, we can calculate a $\Delta(\Delta G)$ of $13.51 \text{ kJ mol}^{-1}$ for the system under 50 vol% CO compared to the system under

N_2 , while our DFT calculations show a $\Delta(\Delta G)$ of $11.83 \text{ kJ mol}^{-1}$. The experimental shift in potential translates into a K_2/K_1 ratio of $2.33 \cdot 10^2$ in favour of FePc over FePc^- .

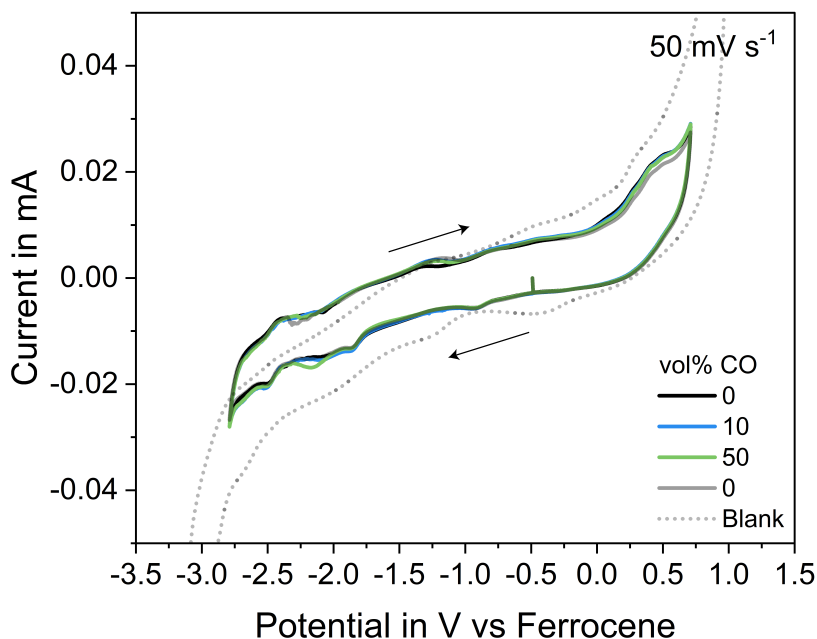


Figure 4.11 Cyclic voltammetry measurements of 0.2 CoPc in 0.1 M TBAPF_6 in DMF under various vol% of CO.

Unfortunately, for the CoPc CVs (Figure 4.11), we cannot draw any conclusions as the solubility of the complex is too low, resulting in too low a signal compared to the blank measurement.

Comparing the accuracy of our predicted potential shifts with DFT-derived E^0 values from literature, we generally obtain similar accuracies for the systems with no experimental problems. For the FeTTP, we underestimated the change in ΔG by $13.54 \text{ kJ mol}^{-1}$, while underestimating the change in ΔG by 1.68 kJ mol^{-1} for FePc. These differences between DFT and experimental results are largely in accord with the accuracy of DFT methods for deriving E^0 values from literature. These are typically accurate within 20 kJ mol^{-1} , although larger deviations are possible and the chosen basis-set and functional affect the results strongly. [40–42]

These results show that DFT can be utilised as a screening tool to test novel complexes for the CO electroswing absorption process. Experimental results, however, are still crucial to confirm performance and highlight limitations such as model incompleteness (e.g., implicit versus explicit solvent) or experimental limitations (e.g., solubility).

4.4. Conclusion

We performed geometry optimisations and frequency calculations by DFT on FeTPP, CoTPP, FePc, and CoPc complexes and analysed their interaction with CO at various oxidation states. Generally, the results match expected trends in the geometry and CO-related physical parameters. The results show oxidation state dependent CO affinity for all studied complexes. The FeTPP⁻/FeTPP, FeTPP/FeTPP⁺, CoTPP/CoTPP⁺, FePc⁻/FePc, CoPc⁻/CoPc, and CoPc/CoPc⁺ were identified as potential redox couples for the electroswing separation of CO. Correlation analysis of binding energies and molecular properties showed no reliable predictors for CO affinity.

We then performed CV measurements of the complexes dissolved in DMF under 0, 10, 50, and again 0 vol% CO to observe changes in the potential of the redox peaks. The experiments show that only the FeTPP⁻/FeTPP, FeTPP/FeTPP⁺, and FePc⁻/FePc show shifts in their potential. The peaks of CoTPP did not shift which was explained by the competitive adsorption of the DMF to the metal centre through additional DFT calculations. CoPc showed no peaks compared to the blank measurement which was caused by the poor solubility.

The theoretical and experimental $\Delta(\Delta G)$ values of the FeTPP⁻/FeTPP and FePc⁻/FePc redox couples were shown to match. The experimental $\Delta(\Delta G)$ couples (FeTPP: 23.16 kJ mol⁻¹ and FePc 13.51 kJ mol⁻¹) show agreement in terms of trends with the theoretical values (9.62 and 11.83 kJ mol⁻¹, respectively). The resulting K_2/K_1 ratios from the experimental $\Delta(\Delta G)$ values of $1.15 \cdot 10^4$ and $2.33 \cdot 10^2$ for FeTPP and FePc, respectively, are indicative of a high potential selectivity and utilisation of the binding complexes. [16]

As a practical final note, the results shown in this work serve only as an indication of separation potential. Electroswing sorption with monitoring of gas concentrations should be performed to confirm the efficacy of the proposed redox couples in the CO/N₂ separation.

4.A. Appendix - Chapter 4

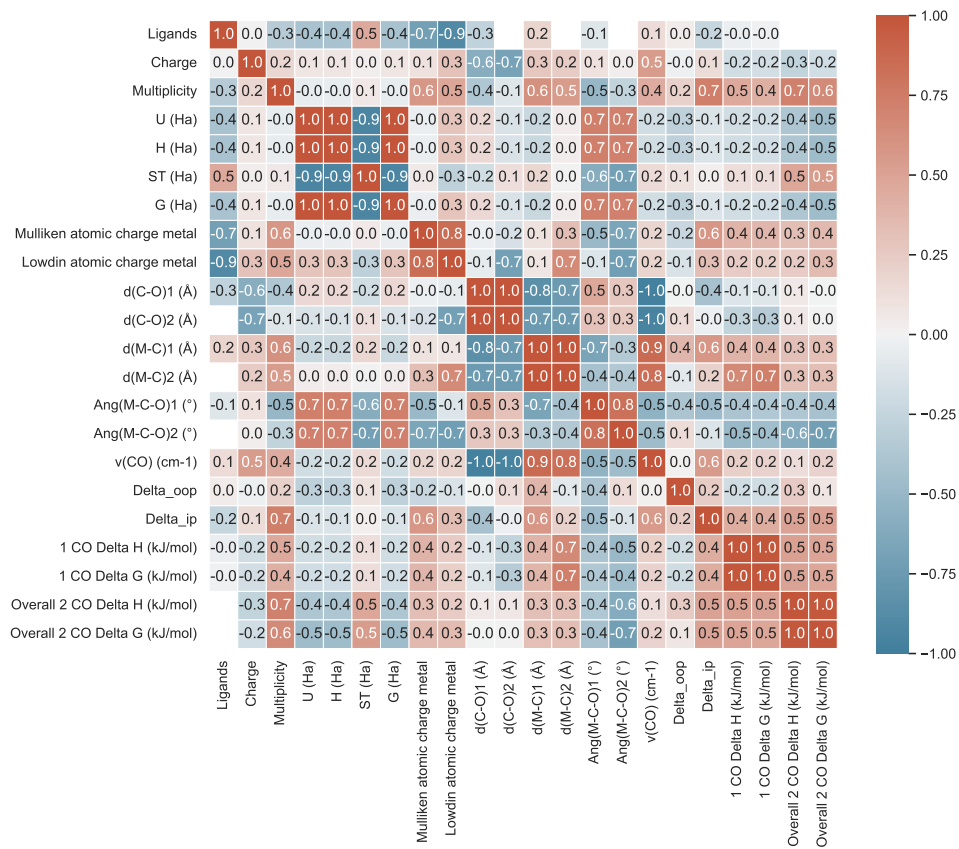


Figure 4.A.1 Matrix of Spearman's correlation of results from the DFT calculations and the NSD analysis.

Table 4.A.1 Binding enthalpies and Gibbs free energies associated with the binding of DMF to CoTPP at different oxidation states. Energies are split into the binding of the 1st DMF, binding of the 2nd DMF after the binding of the 1st DMF has already occurred, and the overall energy of binding two DMF ligands to the complex.

Complex	Charge	1st DMF ΔH (kJ mol ⁻¹)	1st DMF ΔG (kJ mol ⁻¹)	2nd DMF ΔH (kJ mol ⁻¹)	2nd DMF ΔG (kJ mol ⁻¹)	Overall 2 DMF ΔH (kJ mol ⁻¹)	Overall 2 DMF ΔG (kJ mol ⁻¹)
CoTPP	-1	-32.12	23.73	-24.23	30.26	-56.35	53.99
	0	-41.20	11.13	-30.59	25.91	-71.78	37.04
	1	-75.46	-18.39	-94.19	-23.94	-169.65	-42.34

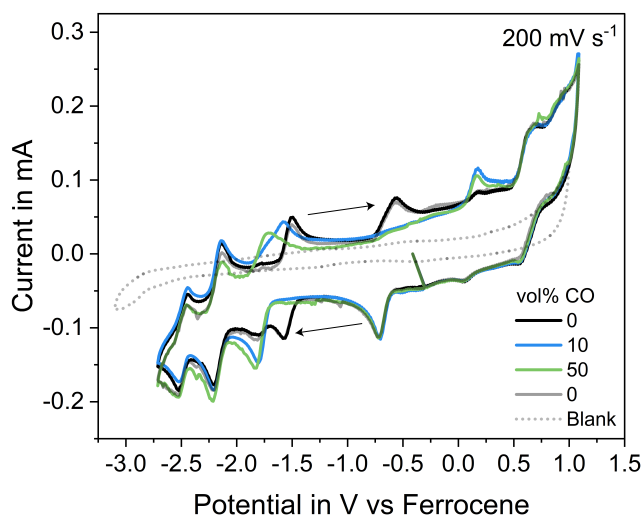


Figure 4.A.2 CV of FeTPP measured in an extended range with a scanning rate of 200 mV s⁻¹

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Chapter 5

Liquid Phase Exfoliation of CoHHTP and CuHHTP

Two-dimensional materials have been of great interest ever since the discovery of graphene. Typically, these are produced by top-down methods on stacked bulk materials. Liquid phase exfoliation is the most widely used top-down method to create 2D materials in research, making it suitable as a starting point for new materials. One of these new classes of materials of interest is metal-organic frameworks (MOFs), in particular conductive 2D MOFs. MOFs based on the 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) linker are the prototypical example of conductive 2D MOFs. Currently, however, no good methods exist to exfoliate this class of MOFs. Therefore, using some best practices from literature, we attempted to exfoliate CoHHTP and CuHHTP in acetonitrile or ethanol as the dispersing liquid using an ultrasonic bath. We were able to create stable suspensions with the acetonitrile, while the suspensions in ethanol quickly settled. However, we were unable to create thin sheets or monolayers of the original MOFs, indicating underlying problems. We hypothesise that a combination of the flexibility in the MOF structure, the unconventional metal-organic linkage in CoHHTP and CuHHTP, and relatively strong π - π -interactions between the MOF layers cause these MOFs to not be able to be exfoliated using an ultrasonic bath.

5.1. Introduction

Currently, two dimensional materials are of great interest to electronics, [1, 2] batteries, [3] sensing, [4] and catalysis [5] owing to their high surface areas and excellent transport phenomena. However, these materials typically do not exist as loose, distinct monolayers, but rather as a stacked bulk material. The prototypical case is that of graphene and graphite, where the two dimensional graphene stacks and forms a three dimensional bulk material, graphite, with weak interlayer bonds. [6, 7]

Herein also lies the main challenge of using 2D materials: obtaining the individual monolayers rather than the bulk material. [6, 8, 9] The first successful attempt in obtaining monolayers was made with graphene in 2004 using tape to repeatedly peel off layers from graphite. [10] This is, however, an obviously inefficient method to create 2D sheets at scale. Therefore, finding better methods of separating multilayer structures into monolayers, i.e. exfoliating, is of great research interest. [8, 9]

5

In the field of inorganic materials, liquid phase exfoliation has shown great promise for its use for a wide range of materials such as graphene [8, 11] and related materials like reduced graphene oxide, [12] and hexagonal boron nitride; [9] transitional metal dichalcogenides and oxides; [9, 13] and MXenes. [14, 15] Especially exfoliation using a bath sonicator offers a low-cost, readily available method for research labs to perform exfoliation experiments. [16]

These factors also make bath sonication suitable for exfoliation testing on more types of materials, one of which is Metal-Organic Frameworks (MOFs). While MOFs exist in many shapes, sizes, and dimensionalities, the ones of high interest for their unusual properties are the MOFs based on chelating functional groups, such as ortho-diols, -diamines, or -dithiols, resulting in square planar coordination around the metal ions (Figure 5.1). These MOFs are two dimensional and, unlike most MOFs, semiconducting. [17, 18] This semiconducting behaviour, in combination with their inherent high density of unsaturated metal sites, makes these materials highly interesting to the fields of electrocatalysis, [19] sensing, [20] and batteries. [17] In order to benefit from the high density of unsaturated metal sites, however, monolayers or at least thin multilayers are required as the metal sites in a 2D layer are blocked by adjacent MOF layers due to stacking.

A major challenge, however, lies precisely in obtaining monolayers or even thin multilayers of these materials using top-down methods. While bottom-up methods using Langmuir-Blodgett [21] or Langmuir-Schäfer [22] deposition allow for large, thin films to be produced relatively easily, top-down methods using exfoliation are far less successful for this class of materials. The smaller nanosheets created through top-down methods, however, are much more suitable for spray-coating which allows for the usage of more active material due to buckling of the sheets during the drying procedure [23] which would assist in increasing the surface area and preventing re-stacking.

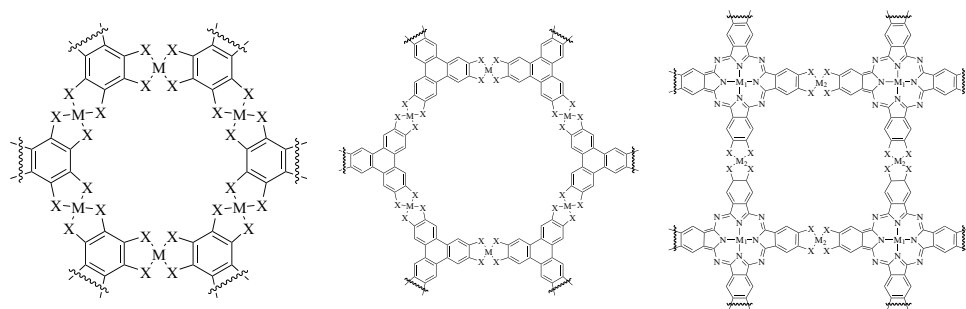


Figure 5.1 Diagram showing the layer structure of **a**: HXTP (triphenylene), **b**: HXB (benzene), and **c**: MPcX (metallophthalocyanine)-based linkers. X = O, NH, or S.

Therefore, we investigated the exfoliation of two prototypical catecholate 2D MOFs, based on the 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) linker: CuHHTP and CoHHTP. Currently, the state-of-the-art in exfoliating CuHHTP, without inclusion of bottom-up methodologies in the synthesis, results in 50-500 nm thick flakes, a far cry from the monolayer thickness of ≈ 0.5 nm. [24] Therefore, by using some of the best practices presented in the established field of inorganic material exfoliation, [16] as well as some recent success stories in paddlewheel-based MOF exfoliation, [25–27] we want to investigate whether liquid-phase exfoliation of the bulk material into monolayers using a bath sonicator is possible for this class of MOF.

5.2. Theory

5.2.1. Liquid phase exfoliation

Liquid phase exfoliation (LPE) is the process in which a multilayered bulk material is separated into smaller layers, down to monolayers in the most extreme case, while suspended in liquid that helps stabilise the layers. There are 3 requirements to be able to perform LPE: weaker bonds in one crystal direction, a force to pull apart the layers, and the liquid itself which needs to be able to stabilise the smaller particles and keep them from re-aggregating. [8, 16]

In order to break apart the layers of bulk multilayered structures, the interlayer bond strength needs to be weak enough so that the layers can be separated without damaging the bonds within the layer. Simultaneously, that also implies that the intralayer bonds should be stable and strong enough to retain structural integrity. In practice, this causes materials that can be exfoliated to have interlayer

bonds based on (a combination of) van der Waals interactions, hydrogen bonds, and π - π interactions, while having intralayer bonds consisting of stable covalent or ionic bonds.

The required force to break apart the layers in LPE is typically applied through sonication, as sonicators, either bath or tip sonicators, are commonplace in research labs. [8, 9, 28] Other sources such as industrial mixers, which can apply high shear forces, are of interest as well especially in the LPE of graphene, [11] but these are generally less available. Sonication or ultrasonication uses high frequency sound waves, applied through either an ultrasonic probe or an ultrasonic bath, in a liquid to cause acoustic cavitation. This cavitation is the rapid expansion and collapse of small bubbles within the liquid with two possible regimes depending on the lifetime of the bubbles. If the bubbles have a long lifetime it is referred to as stable cavitation, while shorter lived bubbles are typical for inertial cavitation. The forces that are released through these two regimes are significantly different as stable cavitation causes shear forces through microstreaming, while the inertial cavitation causes localised high energy shockwaves. Both these phenomena can typically be present simultaneously in bath sonicators. [29]

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Lastly, we need a liquid which can suspend and stabilise the produced sheets in order to prevent them from re-aggregating. From the exfoliation of inorganic materials, several indicators for good stabilising solvents have been proposed from refractive index [30] to Hildebrand parameters. [31] However, the most commonly used parameter is matching the surface energy of the sheets with the surface tension of the liquid. [8, 16] While this offers an easy first route towards narrowing the range of liquids, it is highly simplified and still requires some trial-and-error, especially for MOFs which have inhomogeneous surfaces and do not have surface energy information readily available.

In terms of the actual liquids, there are three major options for solvents systems: pure solvents, mixed solvents, and solvents with surfactants. Pure solvents offer the easiest usage, but can run into problems of matching the surface energy while retaining a low enough boiling point desired for spray coating. This problem is clear in the exfoliation of graphene in which the usage of N,N-dimethylformamide (T_b : 153 °C) or N-methyl-2-pyrrolidone (T_b : 202 °C) are common. [16] This can be resolved through either mixing multiple solvents together or by adding surfactants, typically in aqueous solutions, which allows for a wider range of surface tensions. The mixture of solvents retains some of the inherent problems of the parent solvents, while the surfactant molecules are difficult to remove after exfoliation and can block important surface sites on the sheets. [32] In the end, this is a choice that needs to be made based on the final requirements for the application. [16]

5.2.2. Mechanism of LPE

The mechanism of LPE can be described in three stages based on the process in producing graphene from graphite. [33]

The first stage consists of the most macroscopic effects with graphite particles rupturing into smaller fragments. This is caused by the formation of kink bands that occur to release the tension caused by the shock wave originating from the collapsing cavitation bubbles. These kink bands appear as ridges on the surface of the graphite, with voids underneath them caused by defects. These kink bands then form the starting point from which the subsequent processes can occur.

The second stage consists of the peeling of graphite strips. Due to the high curvature at the ridges of the kink bands at the surface, oxidation of the graphite occurs there. These oxidised ridges then form the weak spots from which flakes are released from the bulk graphite. Depending on the penetration depth of the kink bands, the flakes can have various thicknesses. If the flakes are thick enough, the first stage can re-occur on the flakes, reducing lateral dimensions.

Lastly, the third stage consists of the exfoliation of the released flakes into thin layers. This process cannot follow the same process as in the first stage when the flakes are sufficiently thin (≈ 30 layers) due to bending becoming energetically favourable compared to kinking. This last stage is highly inefficient and generally makes monolayer yield low, as the physical-chemical process responsible for most of the exfoliation can no longer occur other processes start to potentially dominate such as intercalation of ions or bubbles. [34]

5.2.3. Parameter optimisation

Since sonicators rely on sound waves to produce the forces necessary for LPE, both the frequency and the power of the sound waves are important factors in determining the efficacy of exfoliation. Generally, it is found that a higher frequency leads to larger sheets which is hypothesised to be caused by bubbles intercalated between the 2D layers, which helps in obtaining thin sheets in the last phase of LPE [33, 34]. Higher frequencies lead to smaller bubbles that are more capable of intercalating between the layers and forcing them apart, while lower frequencies create larger bubbles which are not able to penetrate between the layers. Power, on the other hand, needs to be balanced more carefully. While higher power, typically found in tip sonicators, yields higher concentrations of graphene, [35] it can also cause undesirable damage to the sheets leading to smaller lateral sizes and defects. [34] Similarly, longer exfoliation times also lead to higher yields, but, especially in combination with high power, can cause damage to the sheets.

5.2.4. Size separation

After LPE, there is typically a large distribution in size and thickness of the resulting sheets. In order to obtain more consistent properties from the sheets, the size distribution needs to be narrowed down, which is usually done through centrifugation. [16] Typically, there are two options depending on if only the unexfoliated particles need to be removed or if a truly narrow fraction needs to be obtained: single step centrifugation (SSC) or liquid cascade centrifugation (LCC), respectively. [28] In either case, this is best done through centrifuging using a low relative centrifugal force (RCF) and letting the particles sediment during this procedure. This has the benefit of a much higher concentration of particles, with the drawback that every centrifugation step typically takes an hour or more. [16, 28] If using a single step separation, one can take the supernatant and use it while discarding the sediment. Using LCC, however, one can use the supernatant of the a centrifugation step as the input for a further centrifugation step at a higher RCF and so on. By retaining the sediments of each step (except the first) and redispersing them, this method allows for the splitting of the original suspension into relatively discrete particle sizes. [28]

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5.2.5. CoHHTP and CuHHTP

MOFs based on the HHTP linker were first synthesised and characterised by Hmadeh et al. [36] in 2012. These MOFs are based on two linkers surrounding a single metal site in a square planar fashion with, potentially, two additional water molecules as ligands to attain octahedral coordination, which can form a hexagonal 2D network using tritopic linkers (Figure 5.3d). Typically, the transition metal in these types of coordination is in a 2+ oxidation state, while the linkers are anionic radicals with a single negative charge per two oxygen molecules (Figure 5.2). This type of stable anionic radical facilitates the in-plane, extended conjugation transport of electrons, while the overall 2D stacked structure of the MOFs allows for in-space transport normal to the 2D layers. These added transport modes for electrons cause MOFs based on these types of linkages to be semiconducting, making HHTP-based MOFs the prototypical electrically conductive MOF. [18, 24]

Between CoHHTP and CuHHTP, specifically, there are two major differences in the crystal structure. One is the layer structure of the MOFs: CuHHTP consist of only the 2D layers stacked on top of eachother, while CoHHTP has 0D $\text{Co}_3\text{HHTP}(\text{H}_2\text{O})_{24}$ complexes that lie between the HHTP linkers of the 2D layers (Figure 5.3). Similarly, only CoHHTP has aquo ligands on the metal ion, ensuring an octahedral coordination environment on all Co cations both in the 2D and 0D complexes. CuHHTP, however, only forms the square planar dicatocatechol complex around the Cu metal ion, meaning no aquo ligands are bound to the Cu and, therefore, no water is present in-between the layers.

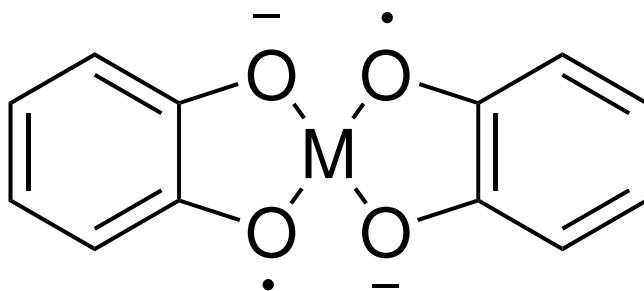


Figure 5.2 Coordination environment around divalent metal cation in HHTP MOFs. $M = \text{Cu}^{2+}$, Co^{2+} .

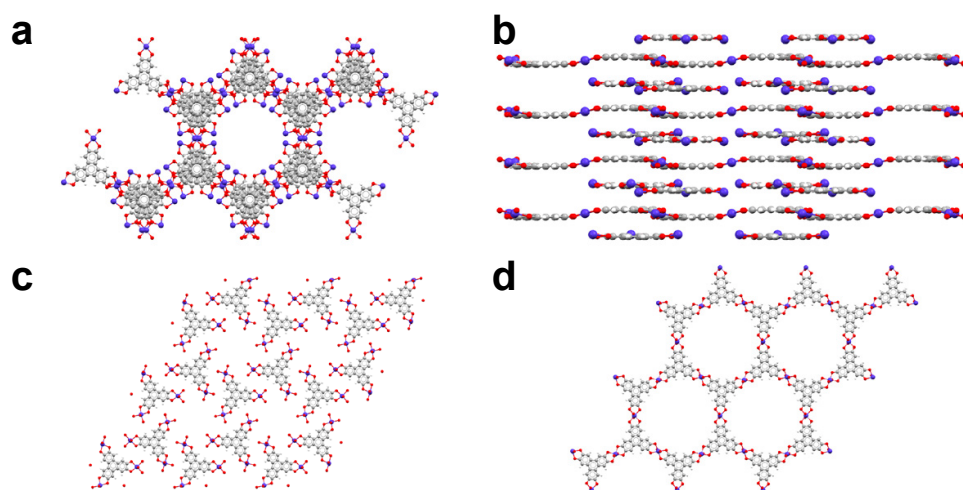


Figure 5.3 Crystal structure of CoHHTP based on single-crystal XRD data from Hmadeh et al. [36] **a:** View of the crystal structure of CoHHTP along the c -axis. **b:** View of the crystal structure of CoHHTP along the a -axis. **c:** 0D layer structure and packing. **d:** 2D layer structure and connectivity. Non-ligand water molecules were hidden in all subfigures, while ligand water was also hidden in subfigures **a** and **b** to increase visual clarity. Atom colours: C (gray), H (white), O (red), Co (blue).

5.3. Experimental

5.3.1. Materials

$\text{Co}(\text{Ac})_2 \cdot 4 \text{H}_2\text{O}$ (98.0%), $\text{Cu}(\text{NO}_3)_2 \cdot 3 \text{H}_2\text{O}$ ($\geq 95\%$), N-methylpyrrolidone (99.5%, NMP), acetonitrile ($\geq 99.5\%$, MeCN), and ammonium hydroxide solution ($\geq 25\%$ NH_3 basis, NH_4OH) were purchased from Merck Sigma. 2,3,6,7,10,11-Hexahydroxytriphenylene ($\geq 95.0\%$, HHTP) was purchased from TCI. Ethanol (99.5%, EtOH) and acetone ($\geq 99.5\%$) were purchased from Riedel-de Haën. All chemicals were used as

purchased.

5.3.2. Synthesis of CoHHTP

CoHHTP powder was produced using a protocol based on the original synthesis from Hmadeh et al. [36] $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (67 mg, 0.27 mmol, 2 eq) and HHTP (47 mg, 0.14 mmol, 1 eq) are dissolved in 10 ml of water in a 20 ml septum-capped vial. The vial is then sonicated for 30 min to homogenise the mixture. NMP (1.1 ml, 0.01 mmol, 0.08 eq) is added dropwise to the mixture. The vial is vortexed and then sonicated for 30 s. Repeat this process for 10 vials. Place the vials in a pre-heated 85 °C oven to react for 24 h. Vacuum filtrate the products using a nylon filter membrane with a pore size of 0.45 μm . Wash the solids with demiwater (6x 20 ml) and acetone (3x 20 ml). Dry the resulting powder under N_2 flow at 60 °C. Yield: 247 mg, 35% based on Co.

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5.3.3. Synthesis of CuHHTP

CuHHTP powder was synthesised based on the original synthesis from Gittins et al. [37] HHTP (0.052 g, 0.16 mmol, 0.6 eq) and water (4.1 ml) were mixed in a 20 ml septum capped vial and sonicated to homogenise the suspension. $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.064 g, 0.26 mmol, 1 eq), NH_4OH -solution (595 μl , 8.0 mmol, 30 eq), and water (1 ml) are mixed in a separate vial and added dropwise to the HHTP suspension. This process is repeated for 5 vials. The vials are screwed shut and placed in a 80 °C pre-heated oven for 24 hours. The resulting products are centrifuged at 15k RCF for 15 min to separate the solids. The solids are then washed with 3x water, 3x EtOH, and 3x acetone by resuspending the solids and centrifuging at 15k RCF for 15 min. Finally, the resulting powder is dried in a vacuum oven at 80 °C for 24 h. Yield: 382 mg, 58% based on Cu.

5.3.4. Exfoliation of MHHTP MOFs

The exfoliation procedure was inspired by the work of the Foster group on carboxylate-linked MOF exfoliation. [25–27] 5 mg of CoHHTP is placed in a 10 ml reaction vial to which 6 ml of solvent (EtOH or MeCN) is added, using 6 vials per batch. The vials are vortexed for 30 s after which they are placed in a ultrasonic bath (Fisherbrand P30H, 2.75 L, 380/350 W) equipped with a steel coil through which cooling water is run. The vials are kept in the ultrasonic bath for 12 h while applying 80 kHz ultrasound and keeping the temperature around 26 °C. The resulting suspensions were centrifuged for 1 h at 300 rcf to and split into two fractions: the bottom layer with the sedimented particles and the top layer with particles in suspension. Top fractions were collected using a pipette staying well clear of any sediment. The remaining liquid was collected as the bottom fraction, including some of the smaller sediment.

5.3.5. Characterisation

Powder X-ray Diffraction (PXRD) was performed on a Bruker Advance D8 with a Cu K α source ($\lambda = 1.5418 \text{ \AA}$) and a Ni monochromator over a 2θ range of $5\text{--}25^\circ$.

SEM measurements were performed using a JEOL JSM-IT700HR using an accelerating voltage of 5 kV and working distance of 10 mm. Samples were prepared by placing the powder onto carbon tape stuck onto an aluminium sample stub. No coating was applied. Collected images were analysed using ImageJ.

TEM measurements were performed in a JEOL TEM-1400Plus electron microscope using Cu-supported continuous carbon grids with an accelerating voltage of 120 kV. TEM samples were prepared by making a slurry using a very small amount of powder sample and grinding it together with a small amount of isopropyl alcohol using a mortar and pestle in the case of the solid samples, while the suspensions were used as-is. 10 μL of the slurry or suspension was then deposited on the grid and left to dry before measuring. Collected images were analysed using ImageJ.

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5.4. Results

Figure 5.4 shows the as-synthesised PXRD, SEM, and TEM analyses of the Co- and CuHHTP MOFs.

We can see that both CoHHTP and CuHHTP show diffraction peaks that match literature. [36, 37] The difference in which peaks are visible and their intensities can be explained by their morphology as seen in the SEM and TEM images (Figure 5.4b-e) as well as their different layer structure (Figure 5.1). CoHHTP presents as long needle-shaped crystals with a hexagonal cross-section with a large variation size. The needle crystals of CoHHTP are between 100 nm and 10 μm in length with a lateral dimension of up to 100 nm. CuHHTP, on the other hand, shows platelet-like crystals due to the inclusion of the NH_4OH as a modulator in the synthesis with a similarly large variation in size as CoHHTP. However, in CuHHTP this difference in size mainly manifests in the lateral dimension between 10 nm and up to about 5 μm with thicknesses in the order of 10 nm.

To have the highest chance of successful exfoliation, we applied some of the best practices from literature as explained in Section 5.2. This means that we used a bath sonicator with a high frequency of 80 kHz compared and power of 350 W and sonicated continuously for 12 hours. Typical bath sonicators only reach 37 kHz, while power is almost never reported. Furthermore, we used a sweeping mode to reduce hotspots and a cooling coil to keep the temperature of the bath low at 26°C . For the quantities of sample, we largely followed the example of the Foster group, using six 10 mL vials filled with 6 mL of solvent and 5 mg of MOF each. [25–27] After sonication, we combined the contents of the vials and centrifuged for 1 hour at 300 rcf. We then separated the top and bottom fraction

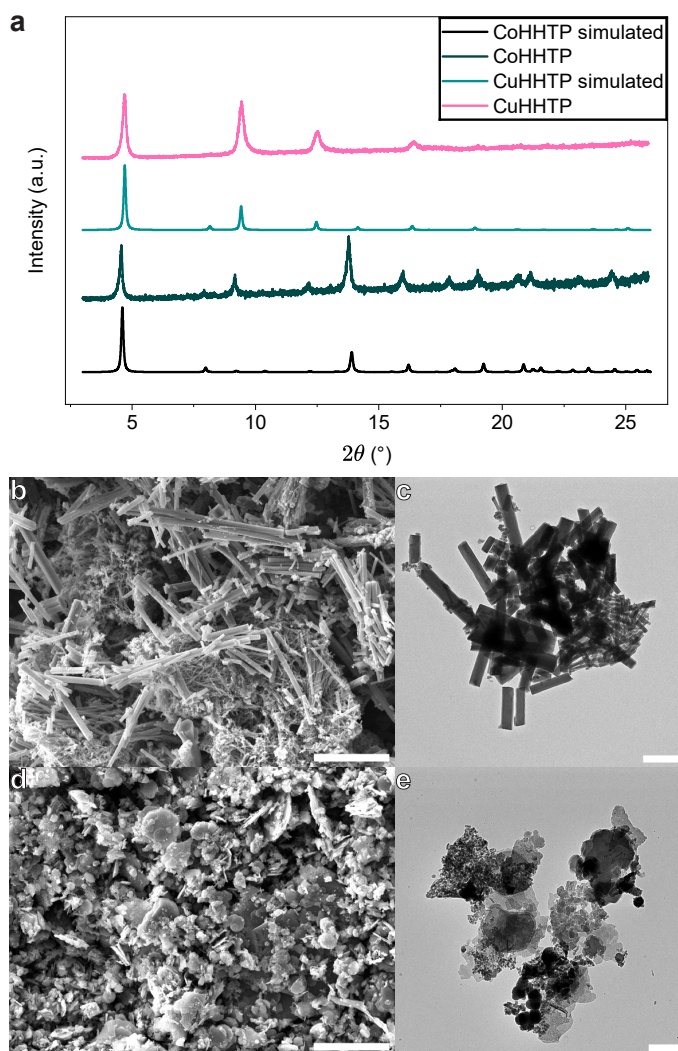


Figure 5.4 Structural characterisation of the as-synthesised Co- and CuHHTP MOFs. **a**: Normalised PXRD of CoHHTP and CuHHTP as well as simulated patterns. Simulated patterns were obtained through SC-XRD data of CoHHTP (CCDC Deposition Number: 939493) [36] and a simulated crystal structure of CuHHTP [37]. **b**, **c**: SEM and TEM images of CoHHTP. **d**, **e**: SEM and TEM images of CuHHTP. Scalebars are 5 μm and 500 nm for the SEM and TEM images, respectively.

via pipette, allowing for further analysis of the fractions through TEM.

Sonication using in EtOH, results in relatively clear solutions in which small particles float, but settle relatively quickly, leaving a dark navy powder on the

bottom of the vials. Sonication in MeCN, on the other hand, creates a dark navy suspension that remains stable over 1 month (Figure 5.5). This is an indication that the samples in MeCN contain small particles that are well-dispersed in the liquid and well-stabilised by favourable solvent-particle interaction, indicative of a good solvent for exfoliation for these MOFs.

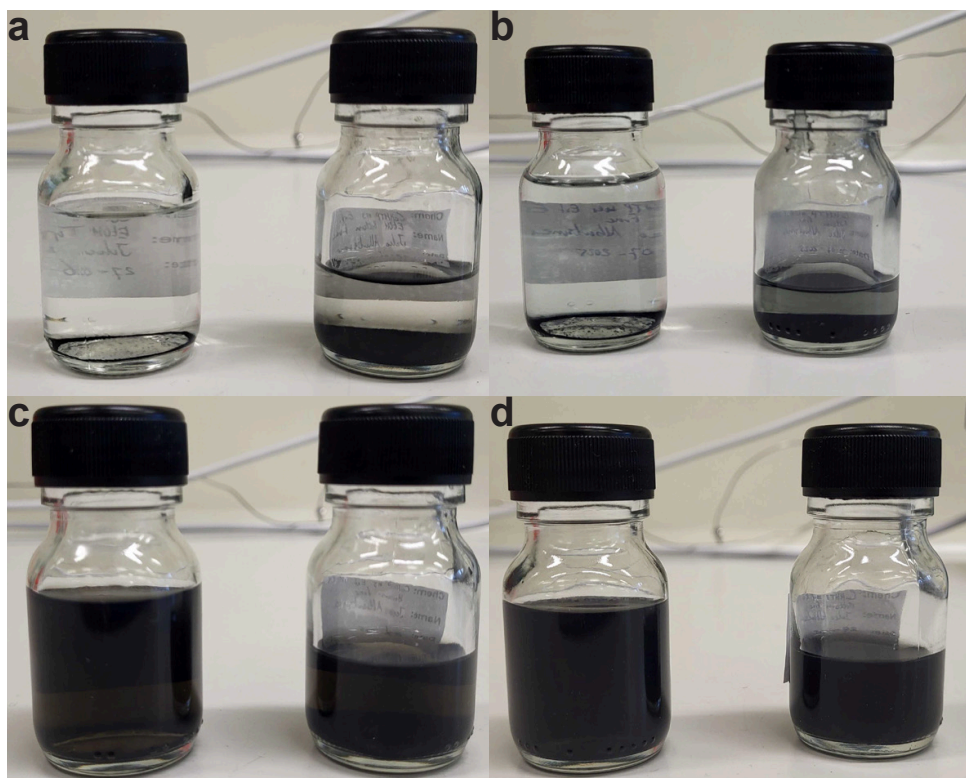


Figure 5.5 Top and bottom fractions, left and right vial on each subfigure, respectively, of sonicated HHTP MOFs after standing for >1 month. **a:** CoHHTP in EtOH, **b:** CuHHTP in EtOH, **c:** CoHHTP in MeCN, **d:** CuHHTP in MeCN.

Representative TEM images of the top and bottom fractions are shown in Figures 5.6 and 5.7, respectively. Additional TEM images can be found in Figures 5.A.1- 5.A.8.

The top fraction of CoHHTP in MeCN (Figure 5.6a, b) shows a drastic reduction in particle size compared to the original crystals observed in the SEM and TEM analyses, but retains the oblong crystal shape of the original CoHHTP (Figure 5.4b, d).

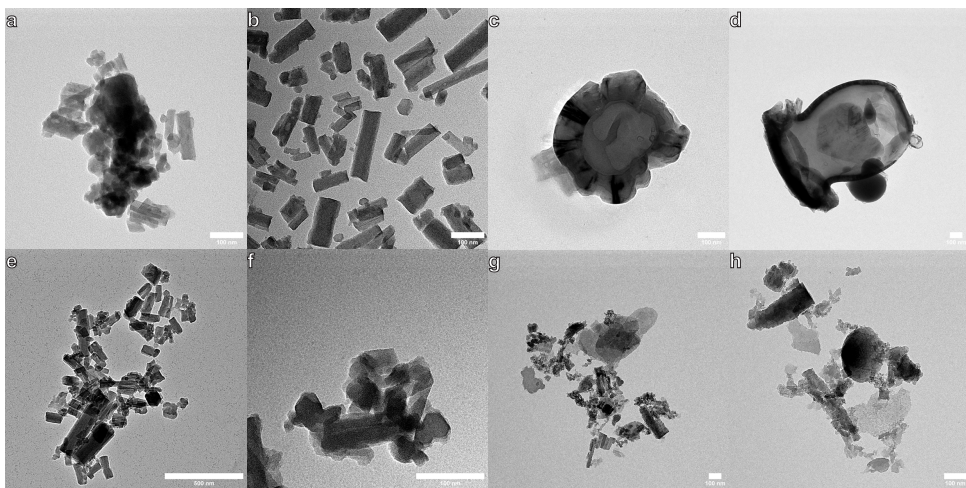


Figure 5.6 Representative TEM images of top fractions of CoHHTP and CuHHTP after LPE. **a, b:** CoHHTP in MeCN, **c, d:** CuHHTP in MeCN, **e, f:** CoHHTP in EtOH, **g, h:** CuHHTP in EtOH. Scale bar represents 100 nm.

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The top fraction of CuHHTP in MeCN shows wispy, thin, roughly spherical shapes in the TEM images (Figure 5.6c, d). The interference patterns visible in these shapes are an indication that these are not amorphous but crystalline. In terms of size, these shapes match the original CuHHTP aggregates shown in Figure 5.4e. These indications serve as cause to believe these shapes to be CuHHTP, perhaps re-stacked at an angle or (partially) curled up. However, judging by the transmittance of these particles and comparing them to the original CuHHTP, little change can be observed. This means that the overall thickness of the particles has barely changed.

Sonicated CoHHTP in EtOH, similar to sonication in MeCN, and observing the top fraction leads to size reduction of the needle-shaped crystals, but not to the formation of actual sheets, again indicating a lack of exfoliation having taken place (Figure 5.6e, f).

Lastly, in the top fraction of CuHHTP in EtOH, a mixture of stacked, thick sheets, oblong crystals, and amorphous particles can be observed (Figure 5.6g, h). This observation, again, leads us to believe no exfoliation has taken place.

The bottom fractions of all samples show similar results as the top fractions, with no visible thin sheets or other indications that exfoliation has taken place (Figure 5.7). As expected, however, the overall particle size in the bottom fractions is larger, showing the effects of the centrifugation.

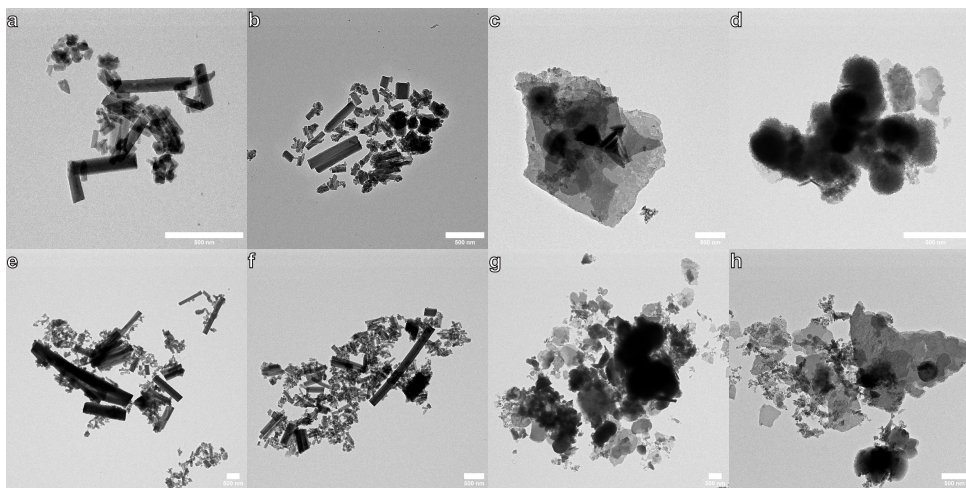


Figure 5.7 Representative TEM images of bottom fractions of CoHHTP and CuHHTP after LPE. **a, b:** CoHHTP in MeCN, **c, d:** CuHHTP in MeCN, **e, f:** CoHHTP in EtOH, **g, h:** CuHHTP in EtOH. Scale bar represents 500 nm.

5.5. Discussion

While the creation of the stable suspensions in MeCN for both CoHHTP and CuHHTP is a step in the right direction, showing that MeCN is a good solvent for MOF suspensions and should, therefore, in principle be a good solvent for exfoliation, the actual exfoliation of both CoHHTP and CuHHTP was unsuccessful. In CoHHTP, needle-shaped crystals were retained throughout all samples with no sheets visible. In CuHHTP, on the other hand, sheets were visible, but remained very thick and seemingly were only present due to the initial synthesis modulated by NH_4OH causing flake-like crystals due to the inhibition of growth along the c-axis of CuHHTP. In this discussion, we examine and hypothesise some causes for the lack of exfoliation in these MOFs, which might aid others in their exfoliation attempts.

In the introduction, the mechanism for exfoliation was introduced through the example of graphene (Section 5.2.2). [33] The main cause for the first step of exfoliation is the kink band formation, which leads ridges in the graphene along which rough flakes are cleaved. This ridge formation is caused by the inability of the stiff 2D graphene layers to disperse the energy from the sonication plastically rather than through defects. When we look at the TEM results for the HHTP MOFs, however, we do not see any flake-like structures in CoHHTP and no reduction in lateral dimensions in CuHHTP, indicating this first step in the exfoliation process has not taken place. Based on theory, three possible explanations can be given for this phenomenon: poor solvent choice, flexibility in the layers allowing plastic deformation, or the kink bands not being reactive enough to cause scission.

Poor solvent choice could explain poor performance, but not a complete lack of sheets. [33] Typically, some level of sheet formation is to be expected even under suboptimal conditions, [31] especially if the sonication time is extended sufficiently. [16, 33] On top of that, MeCN seems to be an excellent solvent considering the stability of the suspensions, while MOFs in MeCN are showing no signs of exfoliation.

One possible explanation why the first exfoliation step is inhibited is flexibility in the layer structure, allowing for plastic energy dissipation. Looking at the single crystal data from CoHHTP (Figure 5.3), we can see that the layers are not flat, due to distortions in the linker molecules, indicating some level of flexibility. Additionally, the addition of the 0D complex-layer between the 2D layers in CoHHTP allows for additional space and flexibility between the 2D layers. Lastly, there is the central pore of 1.2 nm which also allows for lateral movement of (parts) of the 2D layer, again allowing for flexibility. This flexibility has also been investigated through computational means, through which mobility was determined in three manners: slipping along the xy direction of the planes, movement perpendicular to the planes, and distortion of the linkers. [38] Similar effects were also observed in simulations of other 2D MOFs, indicating that this type of flexibility is not unique within this class of material. [39, 40]

Lastly, there is the potential of the kink bands forming, but not being reactive enough to cause scission. In the exfoliation of graphite to graphene, these kink bands form on the carbon and react with oxygen finally leading to scission. In the HHTP MOFs, these kink bands could run across not only the HHTP, which might act similarly to graphite, but also across pores and the metal-nodes which may inhibit scission. The metal-linker binding in the metal-nodes is reversible, meaning even if scission occurs the binding might spontaneously re-form if the constituent atoms are still close enough. The pores in the HHTP MOFs, on the other hand, cannot bend or form scission sites, since they are voids within the material, but may hinder the overall formation of kink bands due to allowed flexibility (vide supra).

Comparing our exfoliation results with 2D MOF structures in literature in which exfoliation was successful using the same sonicator, sonication time, and processing (Figure 5.8), [25–27] we can see a few major differences in material properties which might explain the difference in results. One of the most obvious differences between the HHTP MOFs we studied and the Cu-paddlewheel structures from Figure 5.8 is the non-typical cation-anionic radical linkage, which might be more difficult to cleave. Similarly, rigidity of the framework might also play a role, since the successfully exfoliated MOFs are all Cu-paddlewheel-based which are known to be rigid, [41] while the HHTP MOFs are flexible. [39, 40] Other factors such as the π - π interactions or the size of the pores are less likely to be of importance as the counterexamples of graphene and Cu-4,4'-dibenzoic acid MOF exist, which

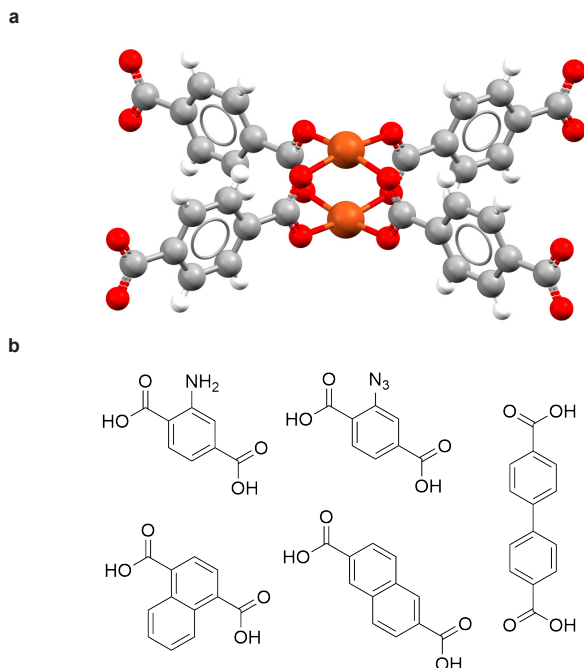


Figure 5.8 Structural elements of successfully exfoliated MOFs. **a:** General Cu-paddlewheel structure, shown with benzene-1,4-dicarboxylate anions. **b:** linkers in Cu-paddlewheel-based MOFs which were successfully exfoliated. [25–27]

have even more π - π interactions and similar pore size, respectively, compared to the HHTP MOFs.

5.6. Conclusion

We performed bath sonication-based exfoliation experiments on Co- and CuHHTP MOFs in MeCN and EtOH utilising some of the best practices recommended in literature. We were able to create stable suspensions using sonication in MeCN, while EtOH did not result in stable suspensions. In general, however, no visible exfoliation was observed in any of our samples, with the sonication only leading to size reduction of the suspended particles.

Based on theory and literature showing successful MOF exfoliation using a method similar to ours, we hypothesise that the most likely causes for the inability for these HHTP-based MOFs to be exfoliated are the relatively unique coordination environment with radical anions, as well as the flexibility of the MOF layers.

5.A. Appendix - Chapter 5

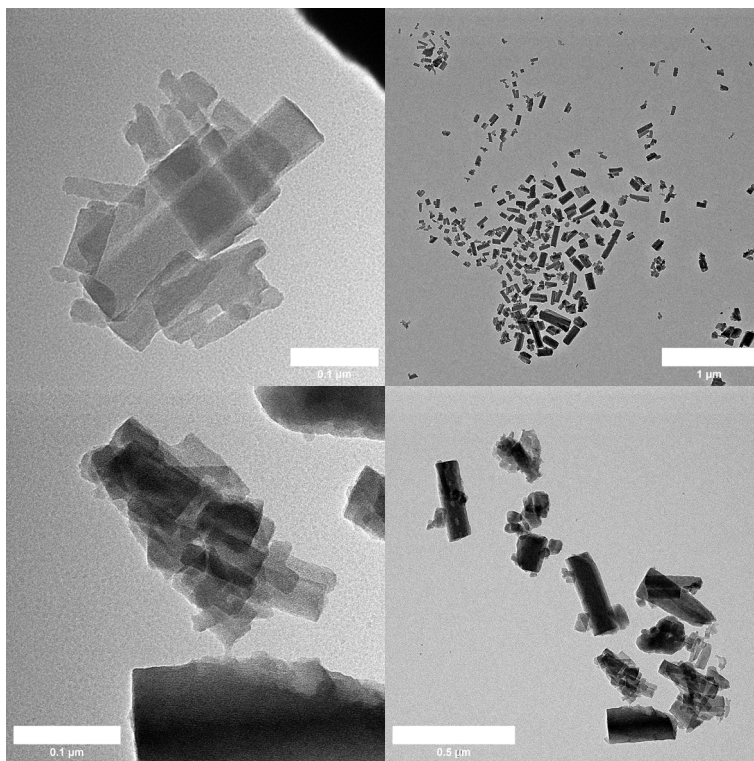


Figure 5.A.1 Additional TEM images of the top fraction of CoHHTP in MeCN.

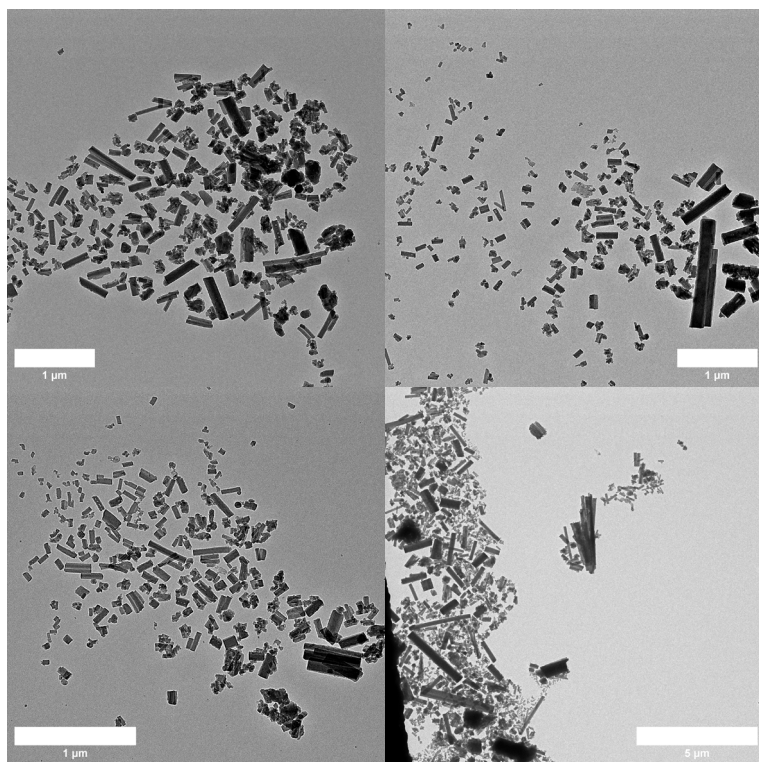


Figure 5.A.2 Additional TEM images of the bottom fraction of CoHHTP in MeCN.

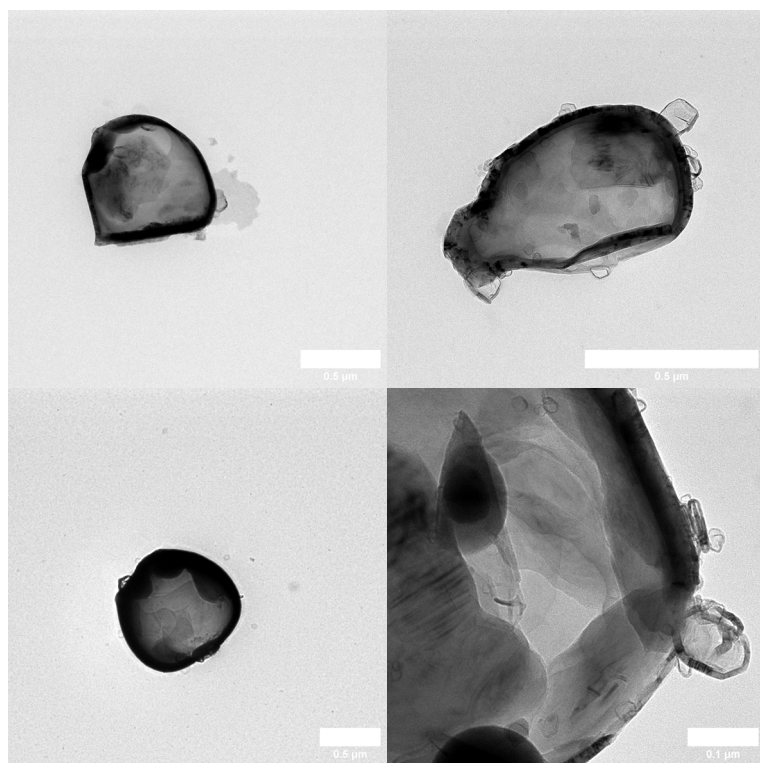


Figure 5.A.3 Additional TEM images of the top fraction of CuHHTP in MeCN.

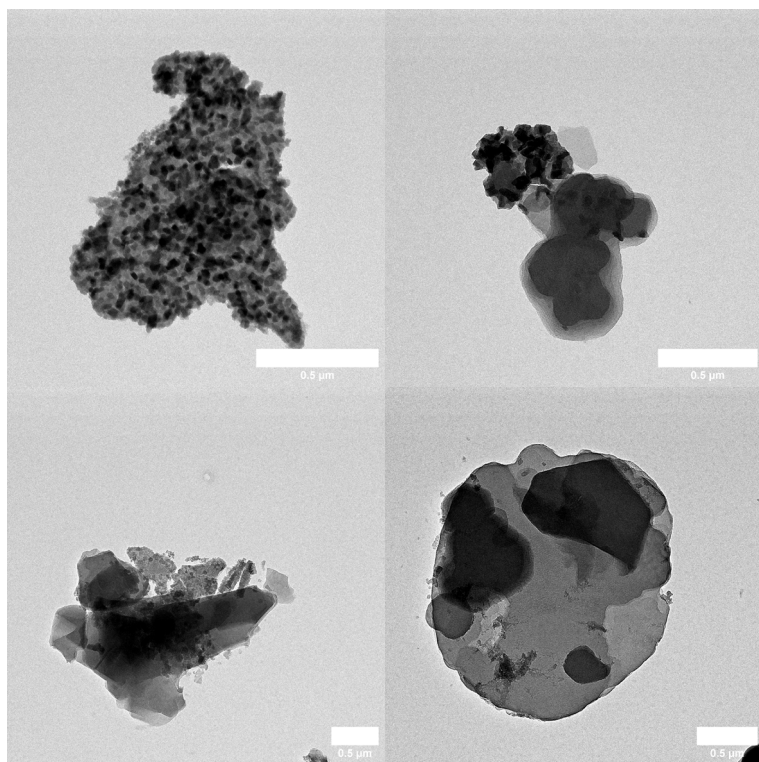


Figure 5.A.4 Additional TEM images of the bottom fraction of CuHHTP in MeCN.

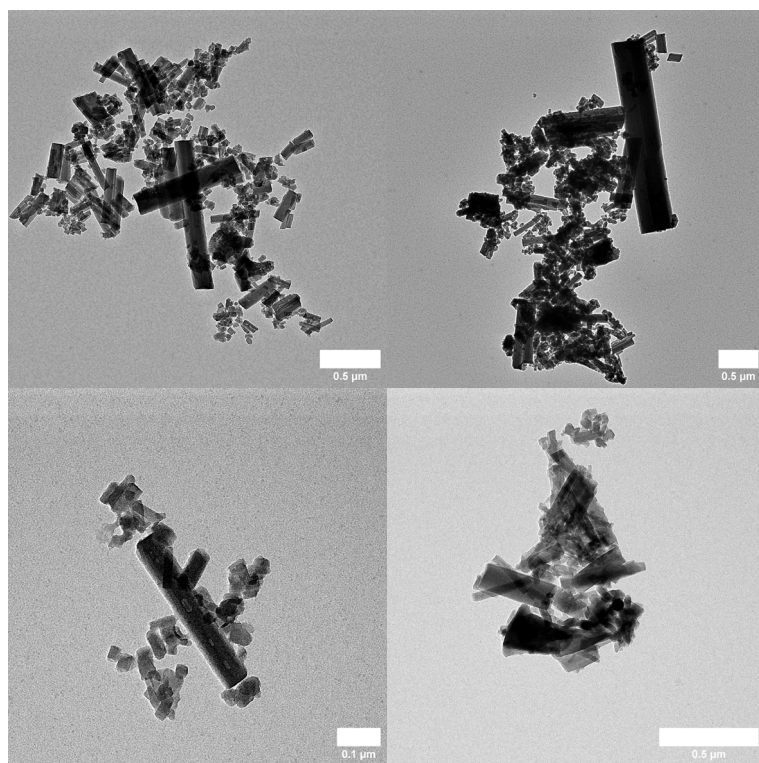


Figure 5.A.5 Additional TEM images of the top fraction of CoHHTP in EtOH.

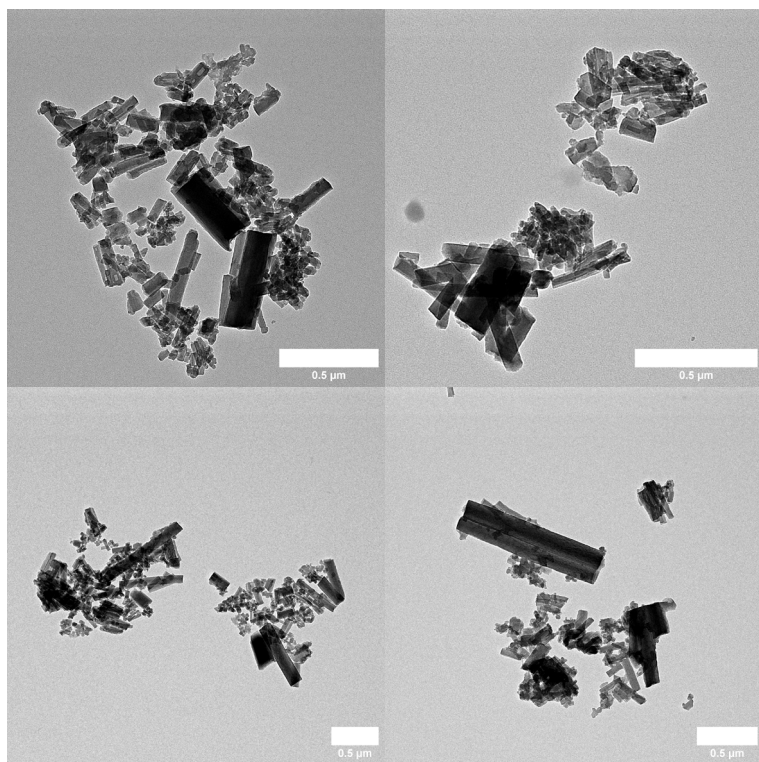


Figure 5.A.6 Additional TEM images of the bottom fraction of CoHHTP in EtOH.

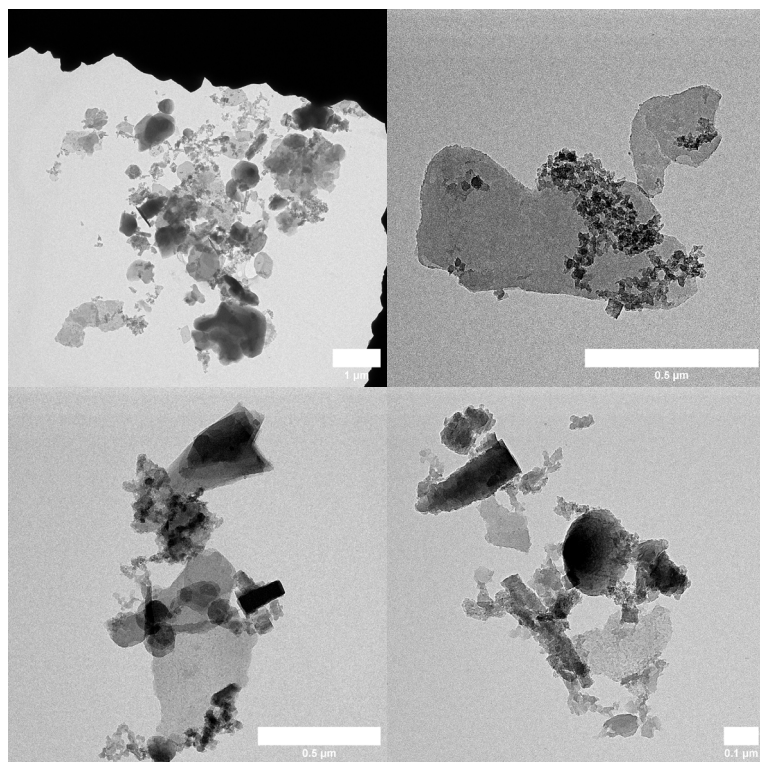


Figure 5.A.7 Additional TEM images of the top fraction of CuHHTP in EtOH.

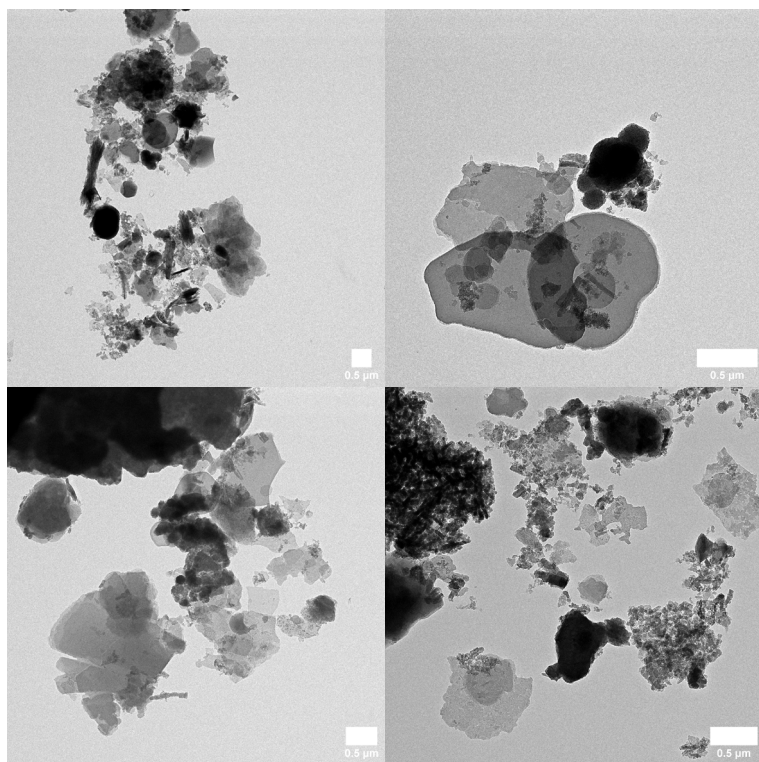


Figure 5.A.8 Additional TEM images of the bottom fraction of CuHHTP in EtOH.

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Chapter 6

Conclusion & Outlook

In this thesis, we explored the separation of CO from waste gas streams. We first highlighted the necessity of separating and reusing CO, in order to achieve a more carbon-neutral industry and reducing the output of CO₂. Secondly, we reviewed the current state-of-the-art, both industrial and academic, in the development of CO separation methods and materials needed for these separation methods. This lead us to the conclusion that the current methods of temperature and pressure swing sorption are insufficient in obtaining high-purity CO from waste gas streams and a new method is required (**Chapter 2**).

Therefore, we proposed the usage of a novel, electrochemistry-based technique: electroswing sorption. Using this technique, we are able to change the oxidation state of a metal-ion in a metal-carbonyl complex, thereby inducing a change in affinity of the complex towards CO. This allows us to 'swing' between a high-affinity and low-affinity oxidation state, effectively capturing and releasing CO when desired with minimal energy losses and on a short time scale compared to traditional pressure and temperature swing techniques.

However, to be able to utilise this new technique, new materials are needed which have redox-active open metal sites and are stable under electrochemical conditions, which was the main focus of the research that led to this thesis. For the electroswing sorption, there are two main options for material development: adsorption and absorption.

For adsorption, we focused on Prussian Blue Analogues (PBAs) (**Chapter 3**) and the exfoliation of semiconducting 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) based Metal-Organic Frameworks (MOFs) (**Chapter 5**). In PBAs, we showed the strong effects of the degassing temperature on the adsorptive behaviour, as well as the difficulties of removing water from the open metal sites in these materials with only a small percentage of the total amount of open metal sites utilisable for CO adsorption. For the HHTP MOFs, we performed exfoliation experiments to attempt to make the open metal sites accessible for CO, since they are normally blocked by the adjacent MOF layers, which was successful in achieving a stable suspension, but not in achieving thin exfoliated layers. In both materials, the underlying issue for their usability in CO electroswing adsorption is the accessibility of the open metal sites, either through competitive adsorption in the PBAs or through blocking of the sites in the HHTP MOFs.

In these materials, as well as all others tested adsorbents of which a selection are shown in Figure 6.1, the results of the cyclic voltammetry (CV) measurements in aqueous electrolyte remained unchanged when switching between N₂ and CO atmospheres, i.e., no shifts in the redox peaks were observable which indicated no interaction with CO (Section 1.4). We presumed that the main cause for this was the inaccessibility of the open metal sites either through competitive adsorption between CO and the solvent or electrolyte or through other physical metal site inaccessibility.

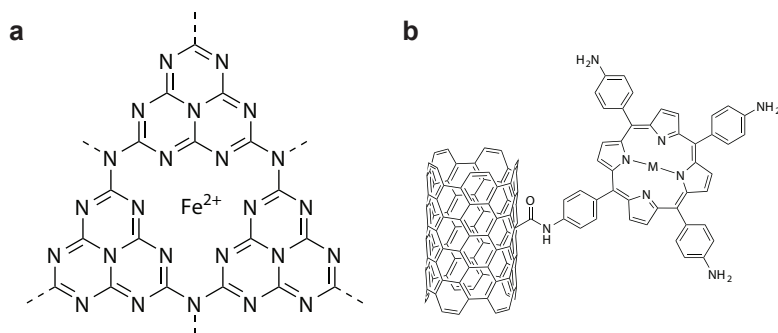


Figure 6.1 A selection of adsorbents which were tested for CO electroswinging adsorption which were not further discussed in the thesis. **a:** Fe-doped graphitic carbon nitride. **b:** Porphyrin-decorated multiwalled carbon nanotubes.

For absorption, on the other hand, there are a few examples from literature such as aqueous CuCl, [1] Ni(cyclam)Cl₂, [2, 3] and metalloporphyrins [4, 5] that do show shifts in the redox peaks when performing CVs under CO compared to under N₂. We studied Ni(cyclam)Cl₂ and aqueous CuCl [6] and found that, while they proved the concept of electroswinging absorption was scientifically feasible, improvements are still required. Specifically, using Ni(cyclam)Cl₂ can lead to the formation of highly toxic Ni(CO)₄ in a side reaction which occurs close to the Ni²⁺/Ni⁺ reduction potential required to bind CO. The concerns for CuCl, contrastingly, are of a more practical nature, with low carrier utilisation and slow kinetics partially attributable to the relatively low equilibrium constant between Cu⁺ and CO.

Herein, we sought to continue research on metalloporphyrins and metallophthalocyanines (**Chapter 4**), where we showed that DFT-based trend predictions in oxidation-state dependent affinity of coordination complexes largely hold and could be useful in exploring the material space. Additionally, we were able to show high experimental equilibrium values between iron-based macrocycles and CO which might lead to better carrier utilisation and kinetics, while not showing any dangerous side reactions, which is promising for further research.

For future research, there are still many open challenges and questions in both the adsorption and absorption-based systems. As mentioned previously, in all our tested adsorptive materials, we were unable to observe the characteristic shift in redox peak potential when CVs were done under CO. This was most likely caused by inaccessibility of the open metal sites. One possible material class that may be of interest which might avoid these accessibility issues is triptycene-based MOFs (Figure 6.2).

Triptycene-based MOFs are structurally similar to the HHTP MOFs studied in

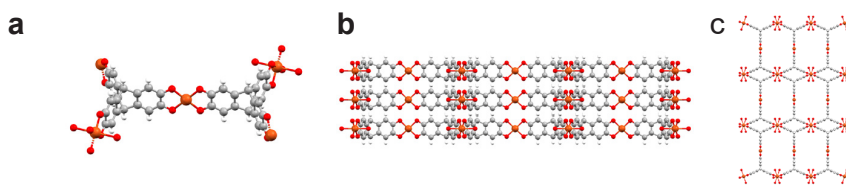


Figure 6.2 Cu-hexahydroxytriptycene (CuHHTrip) MOF. **a:** Linkage between Cu and triptycene linker. **b:** View of the crystal structure of CuHHTrip along the b-axis. **c:** View of the crystal structure of CuHHTrip along the a-axis.

Chapter 5. [7, 8] However, the open metal sites are pointed towards the pore rather than towards the neighbouring MOF layers, allowing for easy access to molecules, which should prove or disprove the potential for CO electroswinging adsorption and might also help in narrowing down the cause of the difficulties in exfoliating the HHTP MOFs.

Absorption, on the other hand, was shown to be more insensitive to the effects of competitive sorption with both Ni(cyclam)Cl₂ [2, 3, 9] and CuCl [1, 6] systems being a proof of concept in applying CO electroswinging absorption. Similarly, we showed that porphyrin- and phthalocyanine-based complexes were also capable of showing the desired shift in peak potential under CO, although an actual separation study was not performed.

The material choice, as shown by the 4 aforementioned examples, is broad with purely inorganic as well as coordination complexes in multiple solvent systems being able to perform CO electroswinging absorption which is promising for future research. In this material space, the most important features are a high equilibrium constant difference between binding and releasing oxidation states with no harmful side reactions. To achieve this, most gains can probably be attained by optimising ligands for Fe and Cu, which are the metals that have shown the most promise and have not demonstrated harmful side reactions, unlike Ni. For ease of use and handling, these future complexes should, additionally, be soluble in aqueous electrolyte and be stable under atmospheric conditions. This means that water-soluble macrocycles such as sulfonyl-functionalised metalloporphyrin are of interest, even though they tend to be expensive and relatively difficult to synthesise at scale and remain poorly soluble even with these functional groups.

Non-macrocycle options are tri- or pentadentate N-ligands, which leave open a site on the metal cation, such as N,N-bis(2-pyridylmethyl)-N-bis(2-pyridyl)methylamine [10, 11] or tris(3-tert-butyl-5-methyl-1,2,4-triazolyl)borate, [12] which have been shown to selectively bind CO in aqueous solutions. Inspiration can also be taken from the field of CO releasing molecules (CORMs) which are used to locally release CO as a medicine. These complexes are interesting since they stably bind CO until an external trigger, such as pH, solvent, or temper-

ature, causes the CO to dissociate, which may offer some additional alternatives. [13]

Lastly, it could be interesting to look at other processes that may benefit from electroswing sorption, i.e., other separations which are notoriously difficult to perform with traditional methods and can be targeted through π -backbonding. Typical examples of ligands that complexate with metals through π -backbonding are alkenes, alkynes, and NO. Of those examples, alkenes are of particular industrial interest, as olefin/paraffin separations such as C_2H_4/C_2H_6 and C_3H_6/C_3H_8 are, similar to the CO/N_2 separation, difficult, costly processes with enormous upsides if these separations could be made more effective and sustainable. [14, 15] Early work by Terry et al. [16], has already shown that aqueous CuCl is capable of performing this separation electrochemically, indicating the potential for future research similar to what was proposed and shown for the CO/N_2 separation.

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- Jelco

Curriculum Vitæ

Jelco Albertsma was born on the 15th of October 1996 in Arnhem (The Netherlands) and lived in the nearby town of Rheden during his youth. He obtained his bachelor's degree in chemical engineering in 2017 at the University of Twente, after which he continued his studies there. In 2019 he did his master's internship at the Institute for Molecular Science in Okazaki (Aichi Prefecture, Japan) in the group of Prof. dr. Makoto Fujita, where he worked on the structural elucidation of natural products using the crystalline sponge method. In 2021, he obtained his master's in chemical engineering and master's in nanotechnology, both with the distinction *cum laude*. His



thesis titled "Modelling spin crossover-induced CO adsorption behaviour in $\text{Fe}_2\text{Cl}_2(\text{bbta})$ " was performed under the guidance of Dr. ir. Sissi de Beer and Dr. Geert Brocks.

At the end of 2021, he joined Delft University of Technology (The Netherlands) to start his PhD. He was part of the section of Catalysis Engineering at the Department of Chemical Engineering supervised by Dr. ir. Monique van der Veen and Dr. ir. David Vermaas. During his PhD, he worked on the synthesis and modelling of redox-active coordination complexes for their application in CO electroswing sorption.

List of Publications

7. C. I. Koopman, J. Albertsma, Z. Zhu, M. A. van der Veen, D. A. Vermaas, "Electrolyte effects on the stability and CO binding of copper chloride complexes for electrochemical separation of CO/N₂", *Journal of Material Chemistry A*, 2026, **14**, 20261-20272.
6. C. I. Koopman, J. Albertsma, M. A. van der Veen, D. A. Vermaas, "Electrochemically Mediated Separation of Carbon Monoxide Using a Ni-Based Redox Couple", *ACS Energy Letters*, 2026, **11**, 2229-2234.
5. Y. Wang, C. Huang, J. Albertsma, M. A. van der Veen, M. Alcalde and F. Hollmann, "MOF-constrained Rh Enables Stable in Situ H₂O₂ Supply for Peroxide-Dependent Enzymes", *Molecular Catalysis*, 2026, **591**, 115702.
4. J. Albertsma, C. I. Koopman, E. Draaijer, W. Rook, D. A. Vermaas and M. A. van der Veen, "Activation of Prussian Blue Analogues: Temperature Effects on Structure, Porosity, and Open Metal Site Accessibility", *Microporous and Mesoporous Materials*, 2026, **402**, 113959.
3. C. Huang, S. A. Noorian Najafabadi, J. Albertsma, W. Rook, M. Fischer, M. Hartmann and M. A. van der Veen, "Capturing CO₂ under Dry and Humid Conditions: When Does the Parent MOF Outperform the MTV MOF?", *Inorganic Chemistry*, 2025, **64**, 18916-18924.
2. H. Veldhuizen,* M. Abdinejad,* P. J. Gilissen, J. Albertsma, T. Burdyny, F. D. Tichelaar, S. van der Zwaag, M. A. van der Veen, "Combining Nickel- and Zinc-Porphyrin Sites via Covalent Organic Frameworks for Electrochemical CO₂ Reduction", *ACS Applied Materials & Interfaces*, 2024, **16**, 34010-34019.
1. X. Ma,* J. Albertsma,* D. Gabriels, R. Horst, S. Polat, C. Snoeks, F. Kapteijn, H. B. Eral, D. A. Vermaas, B. Mei, S. De Beer and M. A. Van Der Veen, "Carbon monoxide separation: past, present and future", *Chemical Society Reviews*, 2023, **52**, 3741-3777.

