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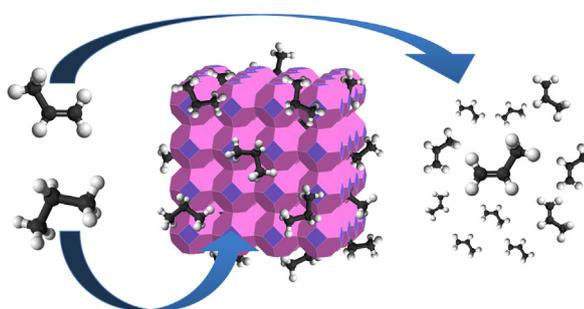
ZIF-67 as silver-bullet in adsorptive propane/propylene separation

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HIGHLIGHTS

- ZIF-67 presents constant inverse selectivity towards propane uptake.
- Cobalt promotes a more rigid framework than zinc.
- This adsorption process is dominated by kinetics.
- ZIF-67 stands out over other adsorbents such as ZIF-8 or ZIF-7.
- No previous work has been published about the role of ZIF-67 in this separation.

GRAPHICAL ABSTRACT



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ABSTRACT

The cobalt-based ZIF-67 has been evaluated for the adsorptive propylene/propane separation in a fixed bed. Characterization techniques and dynamic measurements have been performed over ZIF-67 to evaluate its potential in this defiant process. Cobalt promotes a more rigid framework than zinc in the isostructural ZIF-8. Although the adsorption affinity of ZIF-67 for both hydrocarbons is similar, the lower flexibility of the framework makes ZIF-67 behave with a clear preference towards propane. This inverse selectivity promotes the enrichment in propylene content upon breakthrough, and may simplify the separation scheme. Therefore, ZIF-67 adsorptive separation is presented as an alternative to energy-demanding distillation.

1. Introduction

Propylene/propane separation is worldwide known as one of the most challenging and energy intensive processes in chemical engineering [1]. Due to the similar physical properties of both hydrocarbons (as volatility or size), distillation is the only technique currently applied for this process [2,3]. Propylene, as feedstock PP monomer, has a growing demand, requiring > 99.5 mol% purity. Accordingly, propylene is the target product.

Adsorption based processes, such as Pressure Swing Adsorption (PSA), may present an alternative to dethrone the traditional energy-demanding methods. The tunability of the sorbents should provide a

suitable procedure to perform light alkanes/alkenes separation [2,4–6]. Zeolitic Imidazolate Frameworks (ZIFs) are a relatively new class of Metal Organic Frameworks (MOFs), combining the well-defined structures and adjustable pore sizes and the enormous surface area of MOFs with the high hydrothermal/chemical stability of zeolites. The flexibility of ZIFs is seen as an advantage in adsorptive separation, due to their gate opening effect [6–9]. In view of all this, ZIFs constitute an interesting alternative for adsorption processes [9–15]. ZIF-67 (Co(Hmim)₂) is isostructural to ZIF-8, and is formed by bridging 2-methylimidazolate anions with cobalt cations, resulting in a sodalite (SOD) topology with a pore size of about 0.34 nm [14], although due to its flexibility, the pore may reach 0.4–0.45 nm values [16]. Unlike ZIF-8,

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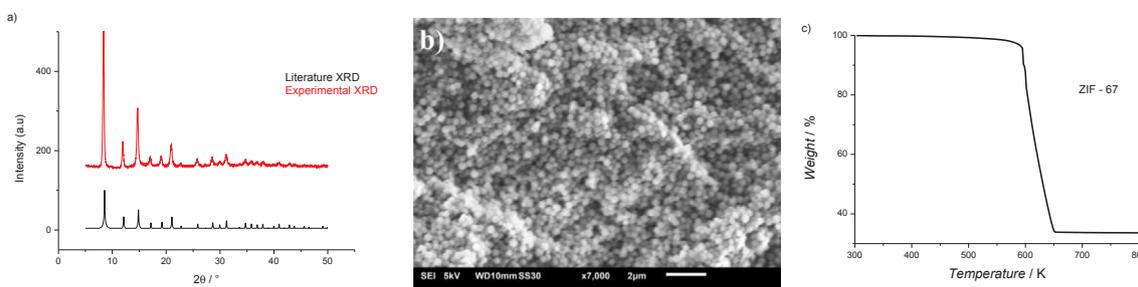


Fig. 1. ZIF-67 characterization by XRD (a), SEM images (b) and TGA in air at 5 K min^{-1} (c).

ZIF-67 has been hardly explored in adsorptive separation, and the only studies reported so far are mostly theoretical calculations and adsorption measurements—which point at ZIF-67 as an ‘interesting candidate for an unprecedented separation’ [3,17–19].

Here, we present results of an experimental study of ZIF-67 for the adsorptive separation of propane/propylene mixtures in a fixed bed. ZIF-67 shows a preferential propane uptake, enriching the propylene content at the outlet of the fixed bed. This effect is extremely rare [6,9,20,21] and this unexpected behavior may constitute a step forward in the development and implementation of this challenging separation process [22–24].

2. Materials and method

2.1. Sample preparation

ZIF-67 was synthesized according to the procedure reported by Lee et al. [25] with minor modifications. 2.93 g cobalt nitrate hexahydrate and 6.49 g 2-methylimidazole (Hmim) were dissolved separately in 200 mL methanol. These solutions were then mixed and stirred for 8 h at room temperature. The resulting purple precipitate was collected by filtration, washed with methanol, and finally dried under vacuum at 353 K for 24 h.

2.2. Sample characterization

The XRD patterns of the powders were recorded in Bragg–Brentano geometry with a Bruker D8 Advance X-ray diffractometer equipped with a LynxEye position-sensitive detector. Measurements were performed at RT by using monochromatic $\text{CoK}\alpha$ ($\lambda = 1.788970\text{ \AA}$) radiation between $2\theta = 5^\circ$ and 50° . Scanning electron microscopy (SEM) images were recorded using a JEOL JSM-6010LA with a standard beam potential of 10 kV and an Everhart–Thornley detector. Thermogravimetric Analysis (TGA) in air was carried out to check the thermal stability of ZIF-67. TGA was performed on a Mettler Toledo TGA/SDTA1 with a sample robot (TSO 801RO) and gas control (TSO 800GC1). The temperature was linearly increased from 303 to 1073 K at a heating rate of 5 K min^{-1} under air flow ($100\text{ cm}_{\text{STP}}^3\text{ min}^{-1}$).

Gas adsorption was measured by volumetric methods. Textural properties of ZIF-67 were analyzed by N_2 , propane and propylene adsorption–desorption isotherms at 77 K and 298 K, respectively, in a Tristar II 3020 Micromeritics sorptometer. Prior to the measurement, the sample was outgassed at 323 K for 16 h. High-pressure single gas adsorption isotherms of propane and propylene were measured using a BELSORP-HP, with an equilibration time of 600 s (0.1% pressure deviation) at 273 K. Prior to the measurement, the sample was outgassed overnight at 353 K.

2.3. Dynamic adsorption measurements

The Breakthrough set-up for dynamic adsorption performance determination is based on a packed adsorption column with pressure and temperature control. Upon step changes in composition the response

outlet composition is analyzed by *i*) a Mass Spectrometer (MS), and *ii*) a Compact Gas Chromatograph (CGC). Because of the fragmentation patterns of propane and propylene in the MS the most characteristic m/e intensities were used for propane (29) and propylene (40). For an improved time resolution the CGC is equipped with three parallel capillary columns with a Flame Ionization Detector (FID).

For dynamic experiments, 1.5 g ZIF-67 (pelletized (500–1000 μm) at 4 ton/m^2) was used. Temperature was set to 298 K and the pressure at 2 and 6 bara (absolute pressure). The inlet flow consisted of an equimolar hydrocarbon mixture (propane and propylene, 3.5 mL min^{-1} each, or 2.0 mL min^{-1} each) and $1\text{ mL min}^{-1}\text{ H}_2$ used as non-adsorbing tracer. ZIF-67 pellets were regenerated before every experiment in $10\text{ mL min}^{-1}\text{ He}$ flow at 1 bar and 323 K for 2 h. Time zero is set with the first detection of hydrogen.

3. Results and discussion

3.1. Sample characterization

Fig. 1 shows the characterization of the as-prepared ZIF-67. The XRD pattern of ZIF-67 (Fig. 1a) aligns with the simulated pattern from the literature [26], thus confirming the proper synthesis. Moreover, ZIF-67 consists of small crystal particles, of a fairly homogeneous size, on average around 200 nm according to SEM (Fig. 1b). The TGA of ZIF-67 in air shows this material is thermally stable up to 600 K. Above this temperature, the frameworks starts to disintegrate and it is completely decomposed at 650 K.

Fig. 2 shows the gas adsorption results carried out by volumetric methods. Low pressure N_2 adsorption-desorption analysis (Fig. 2a) highlights the high BET area ($S_{\text{BET}} = 1500\text{ m}^2\text{ g}^{-1}$) and the microporous nature ($V_{\text{micropore}} = 0.66\text{ cm}^3\text{ g}^{-1}$) of ZIF-67. Besides, the pronounced three steps (inset Fig. 2a) in the isotherm are characteristic of the flexibility of the framework for this material, exhibiting a gate opening effect [7]. High-pressure single gas adsorption isotherms (Fig. 2b) show the adsorption capacity for propane and propylene of ZIF-67. The adsorption uptake of this material for both propane and propylene is initially fairly similar above 0.5 bar, the final adsorption capacity of propylene surpasses that of the alkane. Furthermore, after converting the adsorbed vapor phase volumes to liquid phase (assuming gases adsorbed in pores behave as liquid), the hydrocarbons adsorption capacity at 1 bar (propylene ($0.36\text{ mL}_{(\text{liq})}\text{ g}_{\text{ZIF}}^{-1}$) or propane ($0.37\text{ mL}_{(\text{liq})}\text{ g}_{\text{ZIF}}^{-1}$)) [27] roughly corresponds with the adsorption uptake in the second/third step in the low pressure nitrogen isotherm ($0.35\text{ mL}_{(\text{liq})}\text{ g}_{\text{ZIF}}^{-1}$); Fig. 2c shows a detailed low-pressure adsorption-desorption isotherms for both hydrocarbons. A clear discrepancy is observed between the profiles: propylene displays an adsorption threshold pressure that is not present for propane. Differences in equilibrium times (Table A.1) show that adsorption of propylene is much slower than that of propane. Their desorption profiles, however, coincide. Such an effect has been also observed for ZIF-7 [9], and is attributed to kinetic phenomena. The saturation loading of propene is higher than for propane, what would give an entropic selectivity for propene, but that cannot be found due to diffusional impediments.

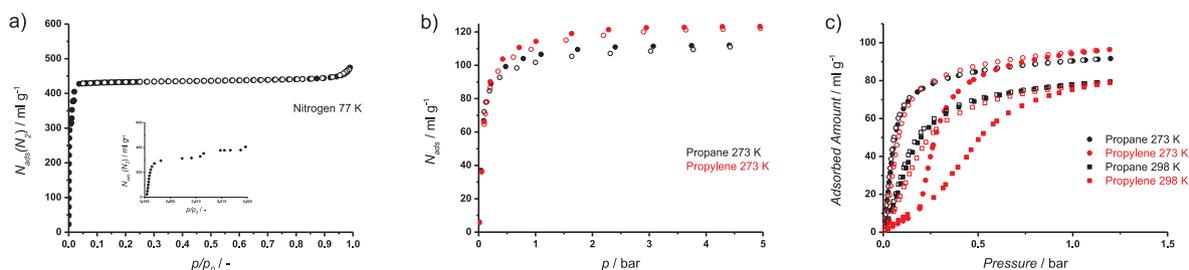


Fig. 2. a) Low pressure nitrogen adsorption/desorption isotherm at 77 K in ZIF-67; b) High-pressure adsorption/desorption isotherms at 273 K for propane (black), and propylene (red) in ZIF-67; c) Low-pressure precision adsorption/desorption isotherms at 273 K (circle) and 298 K (square) for propane (black), and propylene (red) in ZIF-67. (solid symbols for adsorption and open ones for desorption). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Pressure step sizes, equilibration conditions and instrumental settings differ for the high- and low-pressure measurements, what triggers a slight variance in the shape of the adsorption branches (Fig. 2b and c).

All these results (i) confirm the successful synthesis of ZIF-67, (ii) show its main properties regarding particle size, thermal stability, surface area and porosity, (iii) corroborate the anticipated fairly similar adsorption affinity for both hydrocarbons, and, (iv) suggest the propane adsorption in ZIF-67 is affected by kinetic effects.

3.2. Dynamic adsorption measurements

Fig. 3 shows the results of the breakthrough experiments for ZIF-67, analyzed by mass spectrometry and gas chromatography, performed at 298 K at 2 bara (Fig. 3a) and 6 bara (Fig. 3b). Hydrogen is used as a tracer to study diffusion effects; it is the first gas to break through the column and it allows tracking the mixture along the setup. Time zero is set with the first hydrogen detection by MS. Table 1 presents the calculated adsorbed amounts from both MS and CGC analyses.

Even after normalizing the flows, several effects can be observed in the breakthrough profiles (Fig. 3): (i) hydrogen is the first gas to break through, while the other gases are being adsorbed; (ii) a sharp high hydrogen elution peak produced by gas accumulation in the downstream line and the breakthrough of the following gas (propene for hydrogen), accelerating the hydrogen flow to an apparent roll-up, an artefact of the set-up; (iii) a roll-up phenomenon is observed for pure propylene, and propane elutes as last.

The MS response displays the inverse selectivity of ZIF-67, which shows a preference towards the alkane uptake. The breakthrough profiles, for hydrocarbons, analyzed by MS and CGC do concur. CGC analysis confirms the results obtained by MS, proving that propane is retained preferentially and thus, pure propylene is directly obtained during the initial hydrocarbon breakthrough, interesting for a simplified separation process scheme. This analysis allows studying the adsorption capacity of the material, using the hydrogen breakthrough

time as reference, as this gas is assumed not to be adsorbed and can be used to track the flows through the system. By integrating the area between the tracer MS signal appearance and that of the hydrocarbons, the adsorbed amounts have been calculated. The calculated difference between the adsorbed amounts, a selectivity indicator, matched reasonably for both analysis methods. The capacities are lower than those obtained in the isotherms, similarly as can be deduced from other works [20,28]: static adsorption measurements generally provide higher values than dynamic ones; equilibrium is reached under static conditions, while in these dynamic experiments the time is shorter and the adsorption is competitive, while kinetic effects interfere. Adsorption separation ratios (in blue in Table 1) have been calculated by dividing the adsorbed amounts, relative to their respective feed flow ratio.

In the first breakthrough stage, studied by MS, only hydrogen is observed, while both hydrocarbons (propane and propylene) are being adsorbed in ZIF-67. As expected, the breakthrough time for hydrocarbons is longer at higher pressure (Fig. 3b), due to the void space in the system and, to a larger adsorbed amount. In the following stage propane and propylene show a different breakthrough time at both pressures, but more pronounced at 2 bara. Contrary to what is expected for most other MOFs and sorbents, propylene breaks through first, followed by propane after some time. The exact mechanism for this selectivity is not directly obvious. Single component gas adsorption isotherms showed similar affinities and capacities for both hydrocarbons, but the low pressure equilibrium data indicated that kinetic - mass transport - effects interfere in this process. It is known that cobalt promotes a more rigid framework than zinc – through a stiffer Co-N bond [17]. Accordingly, the small changes in the pore size and flexibility are likely able to make the difference and reverse the selectivity of ZIF-67 if compared to the isostructural ZIF-8.

The rigidity of this framework results in an earlier breakthrough for propylene that has difficulties entering the ZIF-67, while propane hasn't. The isotherms indicate a slower uptake of the alkene; therefore, diffusivity controls entrance or the transport through the pores in this

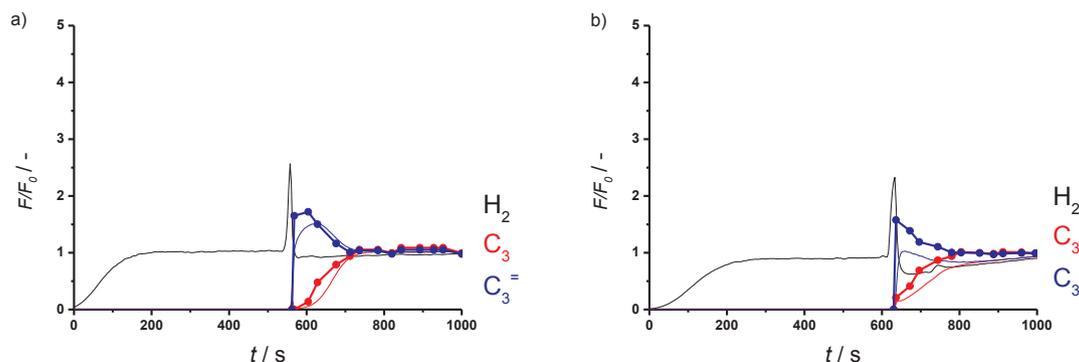


Fig. 3. Breakthrough normalized exit flow rates vs. time for $C_3:C_3^-:H_2$ (3.5:3.5:1) on ZIF-67 at 298 K and 2 bara (a) and 6 bara (b). Time zero is set with the first detection of hydrogen. (CGC analysis (lines and symbols) over MS analysis (lines)).

Table 1

Adsorbed amounts and separation parameters determined from breakthrough profiles for $C_3:C_3^=:H_2$ (3.5:3.5:1) on ZIF-67 at 298 K and 2 bara (left) and 6 bara (right). (MS analysis and CGC analysis, see text).

	2 bara				6 bara			
	propane	propylene	Δ ads.	ratio	propane	propylene	Δ ads.	ratio
MS [mL/g]	26.3	21.0	5.3	1.32	30.0	27.1	2.8	1.10
CGC [mL/g]	26.2	19.8	6.4	1.25	26.2	22.9	3.3	1.15

more rigid structure. Size only considerations do not yield an explanation: the ‘kinetic diameter’ of propylene is larger than that of propane (0.45 nm against 0.43 nm), on the contrary, the ‘Van der Waals diameter’ and ‘critical molecular diameter’ show the opposite relationship (0.40 nm and 0.27 nm from propylene, versus 0.42 nm and 0.28 nm from propane; respectively) [29–31]. For ZIF-7 a similar effect has been observed, claiming that propylene adsorption at the outside of the crystals blocks its own entrance [9]. It is noticed that both components are adsorbed in the ZIF-67. Krokidas’ computational work and adsorption isotherms [17], support our results. However, a larger propylene diffusivity in ZIF-67 was predicted, what does not match with the threshold pressure observed in the propylene adsorption isotherm, suggesting an entrance effect. An [18] and Kwon [3,32] based their research on ZIF-67 in membranes. Those membranes yielded, however, a high propylene/propane selectivity. Their adsorption measurements also correspond with our work. Further analysis is needed to be able to explain the propane adsorption selectivity of ZIF-67 in this separation. Higher pressures (Fig. 3) reduce this; at increasing pressure (and so loading) the influence of kinetics decreases, reducing the sieving effect of the framework.

In order to corroborate the dominating effect of kinetics in this adsorptive separation process, both hydrocarbon inlet flows were modified for the breakthrough experiments, as shown in Fig. 4 and in Table 2 (from $C_3:C_3^=:H_2$ (3.5:3.5:1) to $C_3:C_3^=:H_2$ (2:2:1) and to $C_3:C_3^=:H_2$ (0.5:3.5:1)).

In both situations, the pure propylene breakthrough period is longer. Lower partial pressures and a lower propane/propylene feed ratio results in a better separation performance. Unfortunately, the high propylene concentration at the inlet in this experiment (Fig. 4b) is far from industrial conditions [33]. However, it can be envisaged as a second step in a network of breakthrough steps in series, or as a supporting sidestep debottlenecking a distillation process, in order to reach the demanded high propylene purity.

Do other ZIF-type adsorbents perform to obtain similar results? ZIF-8, isostructural to ZIF-67 but based on zinc instead of cobalt, is by far the most studied member of the ZIFs family. Some publications claim it as paraffin-selective material, while other attribute its propylene uptake to kinetics control through a gate opening effect [28,34,35]. Thus, the global behavior of this structure is not clear. ZIF-7 is also a zinc-based

isostructural framework, but in this case the benzimidazole linker also differs. Here, an inversion in the selectivity of ZIF-7 towards propane occurs with an increase in temperature [9]. ZIF-4 has also been studied on alkanes/alkenes separation, showing paraffin selectivity in high olefin-concentrations in binary mixtures [20]. ZIF-67 has a unique behaviour. This study has demonstrated its constant selectivity towards propane (2–6 bar, 298–323 K), providing a purified propylene flow, even at equimolar conditions. Regeneration is successfully performed at mild conditions. ZIF-67 stands out its competitors for the adsorptive separation of propane/propylene mixtures.

4. Conclusions

ZIF-67 is another member of the ZIF family displaying inversed propane/propene selectivity. Under dynamic conditions, propane preferentially adsorbs over propylene, thus providing an enriched propylene flow at the outlet in the adsorptive separation of a mixture of both hydrocarbons. Propylene is usually adsorbed over propane due to the specific interaction of its double bond with a sorbent, but in this case, kinetics has an overriding role. Cobalt promotes a more rigid framework and slightly smaller windows. These small changes are able to make the difference and inverts the selectivity of ZIF-67, although a clear explanation is still to come.

Overall, the results confirm that ZIF-67 is a promising adsorbent for designing simpler propane/propylene PSA-based separation schemes, requiring less cycles and energy.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2018.11.118>.

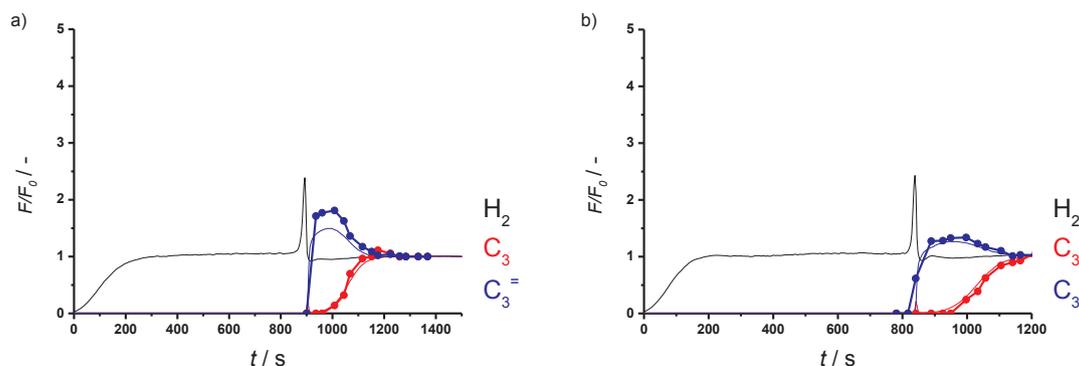


Fig. 4. Breakthrough normalized exit flow rates vs. time, at 298 K and 2 bara on ZIF-67 at 298 K and 2 bara, for $C_3:C_3^=:H_2$ (2:2:1) (a), and $C_3:C_3^=:H_2$ (0.5:3.5:1) (b). Time zero is set with the first detection of hydrogen. (CGC analysis (lines and symbols) over MS analysis (lines)).

Table 2

Adsorbed amounts and separation parameters determined from breakthrough profiles for $C_3:C_3=H_2$ on ZIF-67 at 298 K and 2 bara with different hydrocarbons flows: (left) $C_3:C_3=H_2$ (2:2:1) and (right) $C_3:C_3=H_2$ (0.5:3.5:1). (MS analysis and CGC analysis).

	2:2:1				0.5:3.5:1			
	propane	propylene	Δ ads.	ratio	propane	propylene	Δ ads.	ratio
MS [mL/g]	23.9	18.5	5.4	1.29	5.9	31.6	–25.7	1.30
CGC [mL/g]	25.0	22.6	2.4	1.11	6.0	31.1	–25.1	1.35

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