# Hydrogen Storage in Porous Materials and Magnesium Hydrides

PROEFSCHRIFT

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Cover: Hydrogen adsorption in metal-organic framework MOF-5 and structure of  $Mg\mathrm{H}_2$ 

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Dedicated to my parents Grazyna and Grzegorz and my husband Piotr

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## Chapter 1

### Introduction

The energy demand increases with the increase of the world population and economic development. The energy consumption is related to a wide variety of activities including e.g. the production of consumer goods, house heating and transportation. Global population densities grow and worldwide reserves of energy in the form of fossil fuels are depleting. In 2011 86.5 % of the world's energy consumption was related to the fossil fuels natural gas, oil and coal (Figure 1.1). With current energy consumption and production techniques the known easily recoverable national reserves of natural gas, oil and coal last only for 61, 43 and 148 years, respectively.<sup>1</sup> Such alarming short term forecast is forcing humanity to develop alternative, renewable energy sources and carriers that can be applied on the required large scale to sustain respectively improved living standards. Apart from the fossil fuel limitations and demand the second important issue related to our energy supply is environmental pollution. It is now indicated by United Nations (UN) organizations such as the Intergovernmental Panel of Climate Change (IPCC) that global warming effects are induced with high probability by the anthropogenic  $CO_2$  emissions to the atmosphere. The global warming cause the sea level to raise, polar ice to melt, permafrost defrosting, and the increase of extreme weather phenomena like tornadoes or heavy rains.

In view of the above, especially developing countries which release the largest amounts of greenhouse gases to the atmosphere are expected to minimize  $CO_2$  emission and at the same time improve the share of "clean" energy in total energy consumption. The "clean" and renewable energy sources like wind, water and solar radiation are not constant, but vary in seasonal or day and night interval. The sun shines only during the day and the wind is not constantly blowing. As the production of renewable energy is intermittent the produced energy surplus has to be stored in order to be released in high demand and low production periods. Two

energy carriers that are considered for energy storage on a large scale and that are not based on fossil fuels are batteries (electricity) and hydrogen (fuel). New Li-ion and Ni-MH batteries were introduced in recent years, however, there is still much to improve. Still low energy density, high cost, and long recharging times limit their application mainly to computers and mobile phones while larger applications require further significant progress. Hydrogen, whose energy can be transformed into mechanical or electrical energy with high efficiency (50-60%) when used in a fuel cell, is considered as a next-generation energy carrier for large scale mobile application and also for stationary power.<sup>23</sup> Significant benefit of hydrogen is that the combustion of hydrogen in order to extract energy can be a very clean process resulting only in energy with water vapor as by product. When produced from a renewable source this fuel can thus be environment friendly and CO<sub>2</sub> emission free.<sup>4</sup>



Figure 1.1 World energy consumption by fuel.5

#### 1.1 Why hydrogen?

The choice for hydrogen as main future energy carrier has important advantages related to its fundamental properties. Hydrogen is the lightest most abundant element in the Universe and is highly abundant on the surface of the earth as part of a number of compounds including water, hydrocarbons and biomass. H<sub>2</sub> is

colourless, odourless, tasteless and nontoxic under normal conditions. The diatomic  $H_2$  gas molecule can be easily produced from various sources. Currently the most popular hydrogen production method is steam reforming of methane or natural gas, which, however, additionally generates undesirable CO2. Alternatively hydrogen can be obtained from water dissociation during electrolysis. This "clean" hydrogen production from sustainable energy sources is a fully reversible process. Currently around half of the total amount of produced hydrogen is used for the production of ammonia mainly for fertilizers, a large part is utilized in oil refineries. Hydrogen is also employed for synthesis of various intermediate chemical products. Because of its light mass hydrogen has a very large energy density per mass of about 39 kWh kg<sup>-1</sup>, which is three times higher than the most common fuel used nowadays - gasoline However, to drive a car with combustion engine for a distance of 400 km about 8 kg of hydrogen is required which at room temperature and atmospheric pressure occupies a volume of around 100 cubic meters.<sup>6</sup> Therefore for reasonable and practical applications the low hydrogen density in the gas phase must be increased by compression and temperature decrease, or other high hydrogen density storage methods have to be designed. Some general properties of hydrogen gas are given below (Table 1.1).

 Table 1.1 Properties of molecular hydrogen.7

Properties	Values
Boiling point (T <sub>b</sub> )	-252.87°C
Melting point (T <sub>m</sub> )	-259.14°C
Density at 0°C	0.090 kg/m³
at T <sub>b</sub>	70.8 kg/m³
at T <sub>m</sub>	70.6 kg/m³
Inflammability limits	4.65 – 94 %
Explosion limits	4 – 74.5 %
Molecular weight	2.015 g/mol
Heat of combustion	241 – 285 kJ/mol

In the next section a list of the requirements and different methods of hydrogen storage will be presented.

#### 1.2 General requirements and methods for hydrogen storage

It is clear that for application on large scale hydrogen storage methods should be safe, compact, light, long lasting, economical and should preferably not contain poisonous or polluting materials.

More specific criteria have been established by the U.S. Department of Energy<sup>8</sup> for commercial application of hydrogen storage systems:

- High gravimetric capacity the amount of hydrogen, is expected to be stored in a relatively light container leading to a high wt% of hydrogen in the whole system. Target is 1.8 kWh kg<sup>-1</sup> (5.5 wt%) by 2017.
- High volumetric capacity avoiding excessive volume of the system. Target is 1.3 kWh L<sup>-1</sup> (0.040kg L<sup>-1</sup>) by 2017.
- Reversibility and cyclability it should be possible to load and unloaded in the storage system many times (preferably 1500 cycles) without any significant loss and changes in the system.

- Loading/unloading time the system should be reloadable at high rate (5 kg within 3 minutes) to reduce the consumer waiting time, and also unload sufficiently fast to supply an engine or fuel cell with the desired gas flow and pressure.
- Operating conditions should be close to ambient conditions; operating temperature range -40 °C to 60 °C and maximum delivery pressure of 100 bars.
- Cheap and environmental friendly storage the materials used for manufacturing of the hydrogen storage system should be cheap, abundant and nontoxic for the environment. The storage method should have a long lifetime with the possibility for materials recycling and with high energy efficiency.
- Safety aspect the risk of explosion, leakage, radiation or pollution should be considered and completely excluded by designing a safe system.

The last aspect related to the systems safety is very important since it is connected to the establishment of societal acceptance.

The investigation of the methods for potential hydrogen storage is conducted very intensively over the last few decades. Nevertheless none of the currently available materials can completely fulfill all DOE requirements.

Two conventional ways to store hydrogen are to use high pressure or low cryogenic temperatures. Hydrogen can be pressurized in stainless steel containers up to a pressure of 200 bars and in tanks made of composite materials up to 800 bar.<sup>6</sup> Such a hydrogen compression costs a significant amount of energy (2.21 kWh kg<sup>-1</sup>)<sup>9</sup> and the volumetric storage density remains relatively small. The process is expensive and using hydrogen pressurized tanks onboard and nearby densely populated area requires safety measures. The alternative applied method is to use hydrogen in its liquid form. This option seems to be more attractive since the liquefied hydrogen occupies much less space than in pressurized form. The volumetric density of liquid hydrogen is around 70 kg m<sup>-3</sup> which is twice as much

as pressurized at 800 bar gas. The disadvantages are the energetically expensive liquefaction process (15.2 kWh kg<sup>-1</sup>)<sup>9</sup> and the requirement of thermal insulation to keep hydrogen at the very low temperature of 20 K. In addition some amount of the stored hydrogen in liquid form will be lost due to evaporation or "boil off", especially when small tanks with large surface to volume ratio are used.



**Figure 1.2** Various hydrogen storage technologies with different operating temperatures as illustrated in <sup>10</sup>.

Because none of these two methods meet DOE requirements and the energy costs and maintenance issues are huge, those conventional brute force methods may be unpractical to be used on large scale. In the Figure 1.2 next to the above described methods a couple of alternative methods are presented. The novel hydrogen carriers like porous materials and metal hydrides are believed to allow for departure from the way hydrogen as transportation fuel is delivered today. Such hydrogen storage materials can be divided in two main groups: adsorbents and absorbents, depending on the type of interaction between hydrogen and chosen material.

In the next chapters the two mechanisms: hydrogen physisorption and chemisorption in specific examples of materials will be discussed.

#### 1.3 Physisorption

Physisorption is a process during which hydrogen molecules are bound with weak van der Waals interactions to the surface of the adsorption material.<sup>11</sup> The hydrogen stays in its molecular form and no chemical reaction like dissociation occurs. In this view physisorption can be an extremely fast process and fully reversible. Hydrogen gas can be adsorbed and desorbed during several cycles without any losses. With this characteristics part of the imposed requirements for onboard application can be already fulfilled. Since the strength of adsorption interaction is very weak low, cryogenic temperatures must be applied to obtain reasonable hydrogen storage capacity. Even at low temperature, usually ~77 K, only a monolayer of hydrogen can be adsorbed. For this reason materials with very big specific surface area are specifically desirable. In the last decade porous materials with huge characteristic surface areas are subjected to intensive research. Different types of porous compounds were investigated like light porous carbon materials<sup>12</sup>, silica based materials<sup>13</sup>, zeolites<sup>14</sup> and metal-organic frameworks (MOFs).<sup>15-18</sup>

In this thesis two types of surface adsorption materials, metal-organic frameworks and silica based materials, were studied with regards to specific characteristics that are important for their use as potential hydrogen storage materials.

#### 1.3.1 Microporous Metal-Organic Frameworks

Depending on the size of the pores the porous materials are classified in three groups: microporous (d<2 nm), mesoporous (2 nm<d<50 nm) and macroporous (d>50 nm).<sup>19</sup>

Metal-organic frameworks (MOFs) are crystalline and highly porous, mainly microporous, compounds with often very large surface area per gram and very low density. MOFs were chosen as potential candidates for hydrogen storage based on physisorption for the reason of their potentially simple preparation, adjustable chemical functionality, and structural rigidity. The structure of MOFs consists of two basic building blocks: light metal ions or metal oxide clusters with coordinated organic ligands in a three dimensional lattice. Depending on the components used

for construction of the framework different types of crystal structures can be obtained.<sup>20</sup> Various sizes, shapes and volumes of pores can be achieved. In the well defined structures with open pores very fast diffusion of hydrogen can take place. It should be emphasized that the effective surface area, and the size of the pores are highly correlated with the observed hydrogen storage capacity.<sup>21,22</sup> MOFs can also be successfully applied for adsorption of other gases like methane and carbon dioxide, and also for gas separation<sup>23</sup> and purification<sup>24</sup> by selecting appropriate pore size. Besides those applications they are widely researched for application in catalysis and drug delivery.<sup>25</sup>

#### 1.3.2 Mesoporous materials

Mesoporous materials are those materials which exhibit pores with diameters in the range between 2-50 nm. With such a big pore size the pore volume of those materials is also big; therefore in theory they can contain a large amount of hydrogen by volume depending on the applied pressure. Representatives of the mesoporous materials group are some of the carbon materials, silica porous materials and also several types of MOF materials like MIL-101, which possess mesopores in their structures. Moreover very often mesoporous silica materials like MCM-48, SBA-15 and MSU-1 serve as templates for synthesis of well-tailored carbon materials.<sup>26</sup> The presence of well-defined, ordered and connected pore systems can enhance the dynamics of the gas diffusion in the material and in combination with high specific surface area offer great potential for hydrogen storage. The very important advantageous characteristics of mesoporous materials are their very low density (SiO<sub>2</sub>, C), and potentially cheap and safe production. However, due to weak adsorption interactions those materials cannot store more hydrogen than microporous MOFs. Therefore many investigations are conducted on modification of the surface area of these materials like metal doping<sup>13,27</sup> in order to increase adsorption interactions and at the same time hydrogen storage capacity. Looking from different point of view mesoporous materials can be used as a host or template material in which metal particles can be confined to control their growth. Another application is drug delivery in porous cavities.<sup>28</sup>

#### 1.4 Chemisorption in a metal hydride

In comparison with physisorption, chemisorption of hydrogen in a metal hydride is a more complex process involving more steps. The hydrogen absorption mechanism starts as previously with physisorption of hydrogen molecules at the metal surface. Due to strong interactions between the metal surface and the hydrogen molecules dissociation of hydrogen molecules and surface absorption occurs under certain temperature and pressure conditions.<sup>11</sup> In the next steps hydrogen atoms penetrate the surface, diffuse into the bulk material to finally nucleate and grow a metal hydride phase. The kinetics of this process is much slower in comparison to the adsorption of molecular hydrogen in porous materials, but atomic hydrogen in metal hydrides binds via chemical bonds with an around 10 times stronger enthalpy of formation. This fact implies that higher temperatures are required in order to break the bonds and remove absorbed hydrogen from the structure. Since the hydrogen absorption reaction is a highly exothermic process an onboard application will also need a cooling system attached to the tank with the chemical hydride inside which removes the excess of generated heat. Nevertheless some of these materials can store higher energy density than liquefied or pressurized hydrogen.

#### 1.4.1 Metal hydrides

A metal hydride is the combination of a metal or metallic compound with hydrogen. Crucial advantage of these materials is that they possess the unique ability to absorb hydrogen and desorb it later when it is needed. During absorption hydrogen binds to metal via covalent, ionic or metallic bonds, forming binary or higher hydrides. This process often causes a lattice expansion which is proportional to the concentration of the inserted hydrogen. In order to release absorbed hydrogen simply higher temperature than that during absorption must be applied to the system and/or a reduced pressure.

Metal or metallic compounds suitable for efficient hydrogen storage should have light weight and the ability to store a large amount of hydrogen by weight.

Unfortunately, for light metal hydrides the loading of hydrogen does not occur spontaneously at room temperature and ambient pressure conditions. Depending on the applied pressure and temperature conditions different amounts of gas can be stored. Additionally the time of the loading and unloading of hydrogen is different for different hydride systems. Very often metal hydrides, mainly binary hydrides with only one type of metal in the structure like  $AlH_3$  or  $TiH_2$  are either unstable or too stable. The hydrides are unstable when the pressure of hydrogen absorption and desorption is too high in other words the enthalpies of formation and decomposition are too high (small negative or even positive values). The hydrides are too stable when they require too low pressure or when their characteristic enthalpies of hydride formation are too negative. In the situation when two or more metallic elements are combined, one which forms a very stable hydride and a second which forms a very unstable one, the intermetallic or alloy can form hydrides of intermediate stability. These compounds are classified as complex hydrides like NaAlH<sub>4</sub> and LiBH<sub>4</sub>. They possess high theoretical hydrogen gravimetric capacity of 5.4 wt% and 18.5 wt%, respectively and could be used in onboard applications, however, issues like two step desorption at high temperature and rather slow kinetics have prevented application of those compounds.<sup>29,30</sup> For NaAlH<sub>4</sub> an important breakthrough has been the discovery of Ti compounds that catalyze the reversible hydrogen sorption.<sup>31</sup>

Because in many metal hydrides the density of hydrogen is higher than that of liquid hydrogen, after skillful improvement of the (un-)loading conditions these materials can become promising for hydrogen storage applications. Therefore recent studies concentrate on modification of metal hydrides in order to improve the hydrogen sorption kinetics and obtain more favorable thermodynamics while keeping high gravimetric and volumetric storage capacities.

#### 1.5 Scope of the thesis and scientific questions

• Increase the strength of van der Waals interactions in MOFs

For hydrogen storage using an internal surface adsorption process three factors are of major importance. First there needs to be sufficient interaction strength to make adsorption possible at reasonable temperatures and pressures. Second, there need to have a large amount of surface per gram of material, and third the internal surface should be easily reachable for hydrogen molecules.

The weak dispersive interactions that hold H<sub>2</sub> molecules (resulting in a shallow physisorption well) require cryogenic temperatures, typically around 77 K, and/or high pressures in order to realize a significant storage capacity. These thermodynamic conditions imply stringent cryogenic requirements for on board application, which makes that the system requires more components, such as insulation, which increases the system size and weight. Therefore, the main goal here is to devise ways for strengthening the hydrogen adsorption interactions without causing the molecular dissociation, in order to bring forward adsorption at higher temperatures and/or reduced pressures.

There are several possible ways to increase hydrogen uptake capacity in porous materials. MOFs for hydrogen storage applications should have small pores - micropores, preferably with around 6 Å diameter which is the size of two kinetic diameters of a hydrogen molecule (2 x 2.89 Å).<sup>32</sup> In such small pores the potential of opposite pore walls overlap resulting in stronger adsorption interactions. Following this rationale the idea of two or more interpenetrating frameworks was proposed. However, in the interpenetrated structure the accessible volume for the hydrogen molecules is reduced thus the total hydrogen storage capacity at high pressure is also reduced.<sup>33</sup> It was observed that hydrogen molecules can bind stronger to the metallic parts of the framework, especially to uncoordinated open metal sites, than to the organic part. However the interactions are in general weak in the range of 3-10 kJ mol<sup>-1</sup> of H<sub>2</sub>.<sup>34</sup> Therefore one of the tasks is to obtain sufficient interaction strength between hydrogen and the porous structure to make adsorption possible

at closer to ambient temperature and pressure conditions. In *Chapter 3* of this thesis the influence of the organic linker modification with the different functional groups on the hydrogen storage properties is analyzed. More specifically the answers on the following questions were sought:

What is the influence of the linker modification with different functional groups possessing different size and electronic properties on the MOFs structure and their hydrogen storage capacity? How does the strength of the van der Waals adsorption interactions change upon structure modification? Does the modification of the organic part of the MOFs structures have an influence on the mobility of the hydrogen molecule? How to protect the structure of moisture-sensitive MOFs from damage in ambient air conditions?

• Cu<sub>3</sub>(BTC)<sub>2</sub> for metal nanoparticles space confinement

The problem of slow kinetics and difficult thermodynamic conditions is well known in the metal hydrides research. Scientists put a lot of effort in order to improve the hydrogen uptake mechanisms in metal hydrides. The most common ways are nanostructuring, adding effective catalysts or encapsulation of metal particles inside the cavities of porous materials. This last method becomes recently very popular and many different materials were already tested for this purpose.<sup>3537</sup> The idea is to confine the small metal particles that potentially have ability to store hydrogen in small well defined pores which will restrict the growth of the metal hydride particles. The good dispersion of the nanoparticles within the porous framework makes that they are more accessible for the hydrogen. Since the growth of the hydride particles during cycling is always an issue this solution seems to be very promising. However not all of the porous materials are appropriate for encapsulation of the nanoparticles. The potential host material must possess suitable size of apertures and pores but also thermal and chemical stability. It must be stable in the certain temperature ranges at which metal particles will absorb and desorb hydrogen. In addition the density of the porous host should be very low in order to not compromise the overall gravimetric hydrogen storage capacity. Therefore in *Chapter 4* results on a highly porous MOF with open metal sites tested as a potential matrix for metal particles are presented. The main question is whether the structure of the chosen metal–organic framework Cu<sub>3</sub>(BTC)<sub>2</sub> maintains its high temperature stability under the applied hydrogen pressure and sorption temperatures for representative metal hydrides. Does hydrogen form chemical bond with some parts of MOF structure?

• Investigation of the long range van der Waals forces

The physisorption mechanism is based on very weak van der Waals interactions between hydrogen molecule and adsorbent. It is clear that an as big as possible specific surface is desirable because it gives a large number of adsorption sites. Furthermore it has been noticed that for some types of materials like MOFs, porous carbons and zeolites, a linear relationship between specific surface area and hydrogen uptake can be presented for those materials. The question arises whether this type of correlation can be found for porous silica materials, which are also tested for their ability to store hydrogen. In addition it is interesting to know what happens with the long range van der Waals interaction that keeps hydrogen molecules adsorbed in very large pores. Trying to answer these questions, in *Chapter 5*, a characterization of more fundamental interest is carried out on the mesoporous silica materials: MCM-41, HMS, and an aerogel with three different size of pores 2.3 nm, 3.9 nm and 20 nm respectively. Especially very large mesopores give information on the long range van der Waals interaction.

• Microstructure of MgH<sub>2</sub>-0.05TiF<sub>3</sub>

It is clear that until now none of the available metal hydrides or complex metal hydrides with high gravimetric storage capacity meets the required conditions for onboard application. Thus it is a reasonable idea to choose one compound which is able to absorb relatively large amount of hydrogen and try to improve its kinetics and thermodynamics. Techniques such a ball milling and adding proper catalyst are implemented successfully to improve the sorption kinetics.<sup>41,43</sup> By reducing particle and grain sizes more surface area is accessible for the hydrogen and the

diffusion path becomes shorter, therefore the speed of the absorption process can increase. Additives that contain usually transition metal elements are believed to have the role of hydrogen molecule splitter.<sup>44</sup> Thanks to adding the appropriate catalyst to the certain metal hydride systems the kinetics and reversibility can be improved. The conditions of pressure and temperature at which loading and unloading processes occur can be more desirable for applications. An additional function of the catalyst is to act as additive that leads to nano scale grain refinement.<sup>45</sup> This means that certain additive to the hydride can form compounds which will work as abundant nucleation centers for the hydride. Furthermore, by having an analogous crystal structure with similar lattice parameters new compounds can control the growth of the hydride particles. This function of the catalytic additive was discovered in the previous research of the MgH<sub>2</sub>-TiF<sub>3</sub> system, next to the occurrence of alterations of the phase behavior induced by the nanoscale. To get insight on the atomic scale the investigation of that system was continued in this work using microscopic probes. Detailed microstructural analysis of the MgH<sub>2</sub>- $TiF_3$  system is performed in order to answer the questions: How is the catalyst distributed over the compound? Which crystallographic phases are present in the sample? What is the reason for improved hydrogen sorption kinetics in MgH<sub>2</sub>? How do the structure and sorption capability change over time?

In *Chapter 6* microstructural analysis of the MgH<sub>2</sub>-TiF<sub>3</sub> system is presented and complete models of the morphological and structural features of the dehydrogenated and hydrogenated system are designed.

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# Chapter 2

## Methods

In this work both experimental as well as computational methods were applied in order to characterize and understand the hydrogen sorption mechanisms in different hydrogen storage materials.

#### 2.1. Experimental methods

#### 2.1.1 Synthesis of Metal Organic Frameworks (MOFs)

Several methods to synthesize MOFs have been reported including: solvothermal, hydrothermal, vapor diffusion, microwave heating and electrochemical methods.<sup>1-5</sup> The most applied methods for the synthesis of the compounds investigated in this thesis are the solvothermal methods.

The MOF starting materials consist of metal salts and organic ligands, which in the solvothermal synthesis route are dissolved in an organic solvent such as DMF or DMSO. The metal-organic framework structures are formed by self-assembly at the temperatures between room temperature and up to 200 °C in a few hours. In the assynthesized MOFs, solvent remaining in the pores need to be exchange with other solvents with low boiling points such as CHCl<sub>3</sub>, MeOH or EtOH. Subsequent removal by heating and evacuating in vacuum yields the porous MOF structure. This sample activation by removing environmental adsorbents or residues of the synthesis process from the pores and the external surface is a very important step in the synthesis procedure. It should be pointed out that filtering and drying of metal-organic compounds must be carried out with great care because of their high porosity and large specific surface area that can easily retain some occluded solvent. Depending on the used reagents and synthesis conditions, produced MOF

compounds form rigid structures or sometimes flexible breathing structures, having a wide variety in possible architectures.

Within a joint project all the metal-organic framework compounds, except  $Cu_3(BTC)_2$  which was purchased from Sigma-Aldrich, have been synthesized by Jie Yang from Department of Aerospace Engineering of Delft University of Technology.

#### 2.1.2 Ball-milling

The ball-milling technique is applied in order to achieve nanostructured metal hydride particles. During this process grinding balls crush and disintegrate the starting material to small sizes. There is some control over the size reached by the speed of the rotation, amount of the sample, size and number of grinding balls and grinding time. The result also strongly depends on the material itself, where brittle materials can be grinded more easily. For this reason the brittle hydrides are grinded rather than the metals.

The particle size of the starting material decreases by utilizing alternately opposing centrifugal forces caused by the rotation of the ball-milling bowl and its supporting disc in opposite directions (Figure 2.1). The grinding balls are running along the inner wall of the grinding bowl causing the frictional effect. The reduction of the particle size is also due to impact effect when the balls are impacting against the opposite wall of the grinding bowl. The fraction of fine particles increases when the ball milling time is increased. The homogeneity of the sample can be also improved by increasing the number of grinding balls and when the powder to ball mass ratio is increased.

A Fritsch Pulverisette 6 planetary monomill was employed to obtain nanostructured material. During ball-milling powders were contained in an 80 ml airtight stainless steel bowl, with 32 grinding balls with diameter of 10 mm and weight around 4 g each. Every time around 2.6 g of the powder was milled in order to keep a ball to powder weight ratio 50:1. The powder was grinded for a total period of 60 min. with 15 min. break after 15 min. of milling with rotational speed 400 rpm.

After the second 15 min. period, the material which stuck to the bowl's side walls was returned to the center of the bowl. The powder sticks to the walls when the surface forces begin to dominate for smaller particle sizes. Due to the fact that the used material is air sensitive the handling of the powders was done in the Ar glovebox with  $H_2O$  and  $O_2$  levels below 0.1 ppm.



**Figure 2.1** Illustration of ball-milling bowl showing the movement directions and the involved forces.<sup>6</sup>

#### 2.1.3 Thermogravimetric Analysis (TGA)

Thermogarvimetric analysis is a method to characterize the stability and the release of volatile components in materials by measuring the weight change of the material as a function of temperature and time, in a controlled environment. The investigated MOF materials very often contain some moisture or solvent remains. With the TGA technique a bit of the material is heated with a controlled heating rate, while the sample mass is recorded as a function of temperature. When the material is heated the volatile components will evaporate. When the material reaches its stability limits the sample decomposes and the weight drops quickly until the material has released all volatile fractions completely. The weight can also remain constant for some intermediate times before the next component starts release or disintegration. Such process provides characteristic weight release patterns for each material. With such method the thermal stability and volatile composition of the material is analyzed, both qualitatively and quantitatively.

Thermogravimetric analysis is very useful to investigate the thermal stability of a material, or to investigate its behavior in different atmospheres (e.g. inert or oxidizing). It is suitable for use with all types of solid materials, including organic and inorganic materials.

Thermal stability of the samples was evaluated by thermogravimetric analysis on a TG/DTA-7 Pyris Diamond (PerkinElmer) under a dry nitrogen flow at a heating rate of 10 °C per min.

#### 2.1.4 Powder X-ray Diffraction (PXRD)

X-ray diffraction is a universal and non-destructive technique for characterizing crystalline materials. The method is used to obtain information about crystallographic structures, chemical composition and some physical properties of the investigated samples. In X-ray diffraction, electromagnetic radiation with wavelength in the order of typically 1.54 Å elastically scatters on the electron cloud of the atom in a crystal. The wave-like character of the X-rays causes the scattered X-rays to interfere constructively or destructively, depending on the X-rays wavelength  $\lambda$  and the distance between lattice planes of atoms, in the crystal structure. The interference of these waves follows Bragg's law (Figure 2.2):

$$n\lambda = 2d_{kl}\sin\theta \tag{2.1}$$

where: n – integer,  $\lambda$  – wavelength,  $2\theta$  – angle between the transmitted and scattered beam directions,  $d_{hkl}$  – lattice spacing for a particular set of Miller (hkl) indices.



Figure 2.2 Schematic description of Bragg's law.

By varying the incidence angle of the X-ray incoming beam by  $\theta$  and scattering angle by 2 $\theta$  the scattered intensity is measured as a function of the latter. In our laboratory the Bragg-Brentano setup is used where the sample remains in a fixed position while both X-ray source and detector rotate by  $\theta$ , clockwise and anticlockwise, respectively. These precise movements are performed by a goniometer which is a main part of the diffractometer.<sup>7</sup>

The amplitude of the wave which is reflected by an atom is proportional to the number of the electrons in the atom. The strength of the scattering is expressed as a scattering length or scattering cross-section and is dependent on the number of the electrons surrounding the nucleus. The heavy elements like lead scatter stronger than that light elements with few electrons in the atom. Therefore X-ray scattering by hydrogen can be disturbed by the scattering strength of heavier surrounding atoms. The amplitude of the scattered wave is described by the atom form factor  $f(\theta)$  (Equation 2.2) and varies with the scanning angle  $\theta$ . For  $\theta=0^\circ$  when incident and scattered beam have the same path the atomic form factor only depends on the charge distribution and yields the number of electrons of the atom Z.

$$f(\theta) = \sum_{i=1}^{4} a_i \exp\left[-b_i \frac{\sin^2 \theta}{\lambda^2}\right] + c$$
(2.2)

where:  $\theta$  – scanning angle,  $\lambda$  – wavelength of the radiation,  $a_{i\prime}$   $b_{i\prime}$  c – scattering coefficients  $^8$ 

Regarding the scattering form factor one important aspect has to be introduced, which is the effect of thermal vibrations. Oscillations of the atoms in the solid affect the phase coherence in the scattered beam, which results in reflections intensity loss.

For this purpose temperature dependent Debye-Waller factor  $B = 8\pi u^2$  is imposed with  $\overline{u^2}$  as mean square amplitude of the temperature vibrations. The temperature dependent form factor can be rewritten as:

$$f_T(\theta) = f_0 \exp\left[-8\pi u^2 \frac{\sin^2 \theta}{\lambda^2}\right]$$
(2.3)

If the structure is more than one atom per unit cell calculations must be performed for all the atoms and the total charge distribution of the unit cell must be taken into account. Interference of the waves scattered from all different atoms in the crystalline unit cell is summed up and described by structure factor *F* (Equation 2.4). The intensity of the peaks obtained in the experimental pattern is then proportional to  $|F(hkl)|^2$ . As the mathematic form of the structure factor is a discreet Fourier transform in principle it would be possible to obtain the atomic positions in the unit cell from the peak intensity after reverse transformation. However in powder diffraction this procedure is not used because of loss of critical information.

$$F(hkl) = \sum_{n} f_n \exp(-i\Phi_n) = \sum_{n} f_n (\cos\Phi_n + i\sin\Phi_n)$$
(2.4)

where:  $f_n$  – scattering form factor,  $\Phi_n$  –phase factor

The phase factor is specified by fractional coordinates of each atom n within the unit cell and Miller indices h, k, l of the lattice planes giving rise to the corresponding reflections:

$$\Phi_n = 2\pi \left(hx_n + ky_n + lz_n\right) \tag{2.5}$$

The number of the crystallographic planes which contributes to the diffraction has influence on the diffraction peak width. For sufficiently small crystallites, at some small deviation from the Bragg angle  $\theta$ , constructive interference can still occur. However, when the crystallites become larger only very small deviations from the  $\theta$  angle are possible and therefore narrow peaks appear in the pattern.

The crystallite size L can be estimated with the expression for the full-width-halfmaximum (FWHM) of the diffraction peak:

$$L = \frac{K\lambda}{B(2\theta)\cos\theta}$$
(2.6)

where: K – Scherrer constant,  $\lambda$  – wavelength of the radiation, B(2 $\theta$ ) – FWHM in radians

The Scherrer constant (*K*) is related to the shape of the crystallites and with the assumption of a spherical powder K = 1. For e.g. a flat polycrystalline film with a constant small thickness it can equal 0.89. For powder samples with different crystallite shapes about 20 % variation of K can be expected.

Appropriate data collection is very important and it has influence on the later data analysis. The factors as diffractometer geometry, instrument calibration quality, slit sizes, thickness of the sample and its preparation and finally the counting time. The powder sample should be pressed with smooth flat surface exposed to X-rays with preferably randomly oriented crystal planes. Thickness of the sample is an issue if it contains only light elements. In the reflection geometry the X-ray beam is usually completely absorbed by the specimen, however with only light elements in the sample this assumption might be unfulfilled. This will result in lack of the part of intensities at high angles. On the other hand for a sample containing mostly heavy elements problems can occur during measurement in the transmission setup because the incident beam will not be able to penetrate whole sample. The counting time should be long enough to obtain good signal to noise or peaks to background ratio especially at high angles where the peak intensities are lower. More time should be spent on data collection if the sample scatters not very well. Higher counting statistics are needed when the sample consists of small particles because then XRD pattern contains lowered and broadened peaks which can also overlap. The structures of all materials were determined by powder X-ray diffraction (PXRD) using a PANalytical X'Pert Pro PW3040/60 diffractometer with Cu Ka ( $\lambda = 1.54$  Å) radiation operating at 45 kV and 40 mA. The scans have been taken in the 20 range from 5° to 150°, with step size of 0.0167°. All the samples were loaded into an airtight sample holder covered with Kapton in an Ar containing glovebox.

#### **Rietveld refinement**

Detailed information regarding microstructure of the investigated sample and its phase composition is obtained by the analysis of the X-ray diffraction data with Rietveld refinements.

The Rietveld analysis is a least squares method and its goal is to match the positions and the intensities of the peaks in the observed diffraction pattern to a known pattern of peaks from a standard sample or from a model calculation. The fitting is done in iterative cycles. During the iteration the parameters are changed in order to minimize the difference between the calculated and measured diffraction patterns. The refinement is considered finished when the  $R_{wp}$  (Equation 2.7) parameter which is the weighted residual of the minimization function is generally as low as possible or below a certain threshold. Most informative are the profile plots for monitoring the refinement.

As a consequence the experimentally obtained XRD pattern is modeled with proper concentration of all the components of the sample. All the components in the sample must be identified before the refinement proceeds, and afterwards the parameters describing the structural information of the existing phases are determined.

$$R_{wp} = \sqrt{\frac{M}{\sum w_i y_i (obs)^2}} = \sqrt{\frac{\sum_i w_i (y_i (obs) - y_i (calc))^2}{\sum w_i y_i (obs)^2}}$$
(2.7)

where:  $w_i$  – weight given to point *i* determined from number of counts,  $y_i(obs)$  – measured X-ray pattern,  $y_i(calc)$  – model function for the powder profile.

During this study the General Structure Analysis System (GSAS) programme was used in conjunction with EXPGUI, a graphical user interface.<sup>9</sup> The parameters are fitted sequentially with the most important ones at the start.

The first step of the fitting is background refinement which is very crucial in order to get acceptable end result. There are currently seven polynomial functions available in GSAS with thirty-six coefficients used for this purpose. The function "shifted Chebyschev" was selected to fit the background in all examples presented in this work. Later refinement of the scale factors for the diffraction peaks intensities can be performed. Further the sample position error and subsequently lattice parameters and atomic positions for all existing phases in the sample can be fitted. When the peak positions of the measured and calculated patterns match well the peak shapes are refined.

The shape of the peaks can be properly fitted with pseudo-Voigt profile function which is weighted sum of Lorentzian and Gaussian profiles:

$$F = \eta L(\Gamma) + (1 - \eta)G(\Gamma)$$
(2.8)

where:  $\eta$  – mixing factor (function of  $\Gamma$  and Lorentzian coefficient),  $\Gamma$ - total full width at half maximum (FWHM) of the peak, L( $\Gamma$ ) – Lorentzian function , G( $\Gamma$ ) – Gaussian function.

There are two sources of peak broadening in the XRD pattern. The broad peaks indicate that the size of the particles in the powder sample is relatively small and can be determined from the modified Scherrer equation 2.6 with use of the Lorentzian broadening profile factor X of the fitted sample as determined in GSAS:

$$g = \frac{18000K\lambda}{\pi(X - X_0)}$$
(2.9)

where:  $\lambda$  – wavelength of the incident radiation, K – Scherrer's constant, grain shape related, X - peak broadening factor, X<sub>0</sub> – instrumental contribution to X.

The shape and the positions of the peaks can be also changed by the internal strains present in the structure. When strains occur in a non-uniform manner in the specimen the strain distributions gives contribution to peak broadening. This microstrain can be calculated from the profile factor Y from GSAS with the equation:

$$s = \frac{\pi}{18000} (Y - Y_0) \tag{2.10}$$

where: Y - peak broadening factor, Y<sub>0</sub> - instrumental contribution to Y

The parameters like peak asymmetry, site occupancy and temperature factor are usually refined later in the sequence and might be sensitive to details of sample preparation and background corrections.

#### 2.1.5 Hydrogen sorption

Considering the type of interactions between hydrogen and materials we can distinguish two kinds of materials for hydrogen storage widely discussed in the literature:

- a) materials which adsorb hydrogen on the surface of an adsorbent
- b) materials which absorb hydrogen after dissociation in the bulk

Materials of both types are investigated and described in this work. The most important properties of physical and chemical storage in materials are: amount of ad(ab)sorbed and desorbed gas, sorption kinetics, the temperature and pressure conditions at which the processes occur, reversibility and cyclability. Amounts are most often described in terms of the weight percentage of hydrogen in the material. Additional important factors are cost and safety of the materials.
#### 2.1.5.1 On the surface

Weak dispersive forces called van der Waals interactions are responsible for the adsorption of the molecular hydrogen on the surface. The hydrogen molecules form monolayer on the surface of porous materials which can be described with Langmuir isotherms or type I isotherms according to the IUPAC classification (Figure 2.3). The Langmuir equation which describes the Langmuir isotherm can be derived with the assumption that the number of molecules (*n*) that hits the surface per second is captured and stays at the surface for a certain average time called residence time (*r*).<sup>10</sup> Then the number of adsorbed molecules per unit area of surface is:

$$\sigma = n\tau \tag{2.11}$$

It is important to notice that in the model the residence time ( $\tau$ ) is dependent on the heat of adsorption (Q<sub>ads</sub>) and the temperature (T) as:

$$\tau = \tau_0 e^{\frac{Q_{ads}}{kT}} \tag{2.12}$$

The additional assumption to Langmuir theory states that if the molecule strikes the surface at an already occupied position it will immediately return to the gas phase. Therefore if the total available number of surface sites is  $\sigma_0$  the fraction of the adsorption sites still available for molecules is  $1 - \frac{\sigma}{\sigma_0}$  and the equation 2.11 can be modified to:

$$\sigma = n \left( 1 - \frac{\sigma}{\sigma_0} \right) \tau \tag{2.13}$$

To determine surface coverage ( $\theta$ ) which is the ratio of  $\frac{\sigma}{\sigma_0}$ , the above equation can be remodeled to:

$$\theta = \frac{n\tau}{\sigma_0 + n\tau} = \frac{\frac{n\tau}{\sigma_0}}{(1 + \frac{n\tau}{\sigma_0})}$$
(2.14)

Finally the Langmuir equation can be written as:

$$\theta = \frac{kp}{(1+kp)} \tag{2.15}$$

where: p – gas pressure and  $k = \frac{N}{\sqrt{(2\pi MRT)}} \times \frac{\tau}{\sigma_0}$ 



Figure 2.3 Langmuir (type I) adsorption isotherms at different temperatures.

Multilayer formation of hydrogen does not occur because the adsorption energies are too weak at the temperature above the critical hydrogen temperature. Therefore a crucial parameter for the hydrogen adsorption is the effective surface area. Extraordinarily large surface area of porous material provides many adsorption centers which correlates with high hydrogen uptake results. The information about surface area but also pore textural properties like pore volume and pore size distribution can be obtained from nitrogen adsorption experiments at 77 K. The second parameter which determines the hydrogen capacity is the adsorption interaction strength which has a relation with the pore size. Pores with diameter < 2 nm are defined as micropores, 2-50 nm pores are classified as mesopores and > 50 nm are macropores. The most desirable for effective hydrogen storage are materials containing large micropore volume composed of pores with small size. In small pores the hydrogen can interact relatively strongly with more than one surface, which enhances the interaction. Very large pores are not favorable for hydrogen storage, because hydrogen molecules near the center of the pore are unlikely to experience any attraction from the potential surface of the pore walls.

The properties of the hydrogen adsorption process can be determined using the volumetric Sievert techniques (Figure 2.4). Because of the weak interactions only small amounts of hydrogen can be adsorbed at room temperature and therefore generally low temperature measurements are performed. First the clean sample under vacuum in an airtight container is cooled down to 77 K by immersion in Dewar vessel filled with liquid nitrogen. Then known volumes of hydrogen with e.g. a pressure of 1bar are applied. The pressure drops down very fast in the case of MOF materials with well defined crystalline structure and after it reaches equilibrium another 'shot' of hydrogen pressure can be applied. The adsorption process is fully reversible with fast kinetics and long term stability. Hydrogen can be easily released by evacuation or by heating the system up to room temperature. Because the storage mechanism is based predominantly on physisorption, there are no large activation energy barriers to be overcome when liberating the stored hydrogen.



**Figure 2.4** Schematic of volumetric Sievert type apparatus for hydrogen sorption experiments.

According to the ideal gas law the amount of the adsorbed hydrogen can be evaluated from the pressure difference. The hydrogen capacity is then calculated as a gravimetric uptake (Equation 2.15), expressed in wt%. Referring to the mass of the sample ( $m_s$ ) and mass of the adsorbed hydrogen ( $m_{H2}$ ) the wt% is

$$wt\% = \frac{m_{H_2}}{(m_{H_2} + m_s)} \cdot 100\%$$
(2.15)

At low pressure the adsorption isotherm presents a step increase in the hydrogen uptake whereas at higher pressures the storage capacity reaches a plateau. Further increase in hydrogen pressure does not cause an increase in the storage capacity. This isotherm describes the total storage capacity which is adsorbed in the porous material without considering the gas phase present between the material. However, more often in the literature the 'excess adsorption capacity' is indicated and this value is used for comparisons. The excess adsorption isotherm does not possess a plateau at high pressure but a maximum and with further increase of hydrogen pressure the excess uptake decreases. This is happening because the gas in the pores saturates but at the same time the external gas density is still increasing. So the excess storage capacity can be defined as the difference in the amount of gas stored at certain temperature T and pressure p in the volume which contains adsorbent and the amount of gas which would be kept at exactly the same conditions but without gas-solid interactions. In order to obtain the excess adsorption capacity the volume of non-adsorbed gas ( $V_{ref}$ ) or so called skeletal density of the sample is measured at room temperature with a non-adsorbing gas, e.g. helium.<sup>11</sup>



Figure 2.5 Definition of the total gas adsorption volume.

The total volume illustrated on the Figure 2.5 is equal to:

$$V_{total} = V_{solid} + V_{ads} + V_{gas}$$
(2.16)

where:  $V_{\text{solid}}$  – solid adsorbent volume,  $V_{\text{ads}}$  – adsorbed phase volume,  $V_{\text{gas}}$  – gas phase volume.

The reference mass ( $m_{ref}$ ) of the gas phase H<sub>2</sub> that can be present in the system, can be calculated by subtracting the volume of the not accessible  $V_{solid}$  as determined by using the non-adsorbing He gas (at room temperature):

$$m_{ref} = \rho_H (V_{total} - V_{solid}) \tag{2.17}$$

where:  $\rho_H$  – density of hydrogen

The excess hydrogen adsorption can be obtained (Equation 2.18) from the difference between total mass of hydrogen accumulated in the sample during measurement ( $m_{system}$ ) and estimated mass of the hydrogen which would be present in the compound if the adsorption would not occur:

$$m_{excess} = m_{system} - m_{ref} \tag{2.18}$$

The hydrogen adsorption measurements of MOF compounds described in this work were carried out on an in house designed Sieverts apparatus. A Sieverts apparatus is a system of pressure transducers, capillaries, and valves, with known calibrated volumes, connected to a vacuum turbo pump and connected to a highly pure hydrogen source (Figure 2.4). Two pressure transducers attached to the capillaries allow to measure in low 0-2.5 bar and high 0-200 bar hydrogen pressure ranges. The transducer is selected by closing off the ball valve to the second transducer. The experiments were performed at room temperature and 77 K as well as some other selected temperatures.

Initially the airtight sample holder filled with the sample in the glovebox was connected to the Sieverts setup. Then, in order to remove the solvent residues, the sample was heated, depending on the sample stability, at temperature up to 180 °C and evacuated until a vacuum of 10<sup>-6</sup> mbar was reached. After sample activation the adsorption measurement at room temperature and pressures up to 2 bars was performed by applying subsequent shots of 1 bar of hydrogen. For the low temperature measurement the sample was desorbed by evacuation and subsequent immersion of the sample container in a Dewar vessel filled with liquid nitrogen. Small portions of hydrogen were loaded with 5 min. equilibrium waiting time. Two kinds of measurement were conducted at 77 K: low pressure adsorption up to a pressure of 2 bars and high pressure adsorption up to pressure of 60 bars.

At low pressure a correction of the total adsorption was made for the free volume of the capillary and the empty volume in the sample container by subtracting the amount of hydrogen measured subsequently at room temperature and at 77 K in a sample holder filled with a volume of non-adsorbing material corresponding to the crystallographic volume of the sample. For high pressure measurements the excess adsorption isotherms were constructed by subtraction a non-adsorbing volume deduced from the helium experiment from the total hydrogen uptake.

The adsorption of hydrogen on the surface is an exothermic process during which heat is released. Because the van der Waals interactions are very weak the heat of adsorption values are also very low typically between 3-10 kJ mol<sup>-1</sup> of H<sub>2</sub>. That is also the reason for low hydrogen capacity measured at room temperature. To obtain significant adsorption amounts usually the measurement is performed at the boiling temperature of liquid nitrogen ~77 K. Yildirm and Hartman in their work<sup>12</sup> on MOF-5 have reported that adsorption energies are not equal for whole framework but specific adsorption sites exist which interact stronger with hydrogen molecules. This was also predicted by calculations.<sup>13</sup> Stronger adsorption sites are those located around metal oxide parts whereas the organic parts adsorb weaker. The values of the heat of adsorption for specific sites can be calculated from the computer simulations which will be described in the computational section. In order to estimate the average values of the isosteric heat of adsorption for the whole system experimentally, the hydrogen adsorption measurement for at least two different low temperatures have to be performed. The measurements are conducted only in the low pressure regime since only in that regime the adsorption energies have influence on the hydrogen capacity. The experiments must be corrected for the hydrogen dead volume which is present in the capillaries and partially in the container and also for the density of the gas at different temperatures.

The adsorption energy values for certain concentration are obtained from the slope of the graphical expression of Clausius–Clapeyron equation:

$$\left(\frac{\partial \ln p}{\partial T}\right)_{\vartheta} = \frac{Q_{ads}}{RT^2}$$
(2.19)

where: p – equilibrium pressure,  $Q_{ads}$  – isosteric heat of adsorption, T – adsorption temperature, R – gas constant



Figure 2.6 Picture of the cryostat for accessing temperatures between 50 K and RT.

The measurements were carried out at the temperatures: 55 K, 64 K and 100 K and the pressure up to 2 bars in the in house cryostat design at the Reactor Institute (Figure 2.6). The cryostat constitutes 10 L Dewar vessel with stainless steel tube in which sample holder is placed on the sample stick. The lid of the vessel has access to a main channel for the sample stick, connections for vacuum pump and contact gas (e.g. He) and also tubes for liquid nitrogen filling, a vacuum pump connection and a tube with safety spring. The low temperatures 55 K and 64 K were easily obtained by pumping on the liquid nitrogen for certain periods of time. The 100 K

was achieved by heating up the sample holder, surrounded by the heating element, positioned on the metal sample stick in the cryostat. At the same time a He contact gas pressure of 0.3 bar was kept for better temperature control. A heating element is connected via a copper wire to the Oxford Instrument ITC 4 temperature controller. The temperature was regulated with Allen-Bradley resistor which works very well in the temperature range 4.2-300 K. The resistor positioned in the cavity drilled in the sample holder and connected via manganin wire (d = 0.25 mm) to the Oxford Instrument ITC 4 controller was calibrated using the standard method at three well defined temperatures: 273 K (ice), 195 K (dry ice CO<sub>2</sub>) and 77 K (liquid nitrogen). Manganin wire is a Cu-Mn-Ni alloy and it was chosen because it can minimize heat transfer between points which need electrical connections.

Like in the case of hydrogen uptake experiments at 77 K the blank experiment for each temperature was performed and the dead gas volume was subtracted from the total adsorbed value. The three values of the pressure logarithm (lnp) for chosen small hydrogen concentration (wt%) in the sample were plotted as a function of inverse temperature (1/T) and isosteric heat of adsorption was derived from the slope.

# 2.1.5.2 Hydrogen absorption in a metal hydride

Kinetics and thermodynamics are two important aspects that have to be considered when discussing about hydrogen storage in metal hydrides. Kinetics in metal hydrides is much slower than in porous materials. Transport of hydrogen in the gas phase, physisorption, dissociation, chemisorption on the surface and penetration in the bulk material and possibly the nucleation of a new phase are steps before the hydride phase is created. The kinetics measurements are simply performed by adding the hydrogen pressure dose at the chosen temperature and analyzing the pressure drop over time.

The operating temperature and pressure range are dependent on thermodynamic properties of the absorbing material. Those properties are the enthalpy of formation ( $\Delta$ H) and entropy ( $\Delta$ S) of formation, which can be evaluated from Pressure-Composition-Isotherms (PCI). These PCI are also obtained to observe the reversible

storage capacity. For a binary hydride like MgH<sub>2</sub> absorption and/or desorption experiments, for at least three different temperatures, have to be conducted (Figure 2.7) during which equilibrium H<sub>2</sub> pressures (p) are measured for different hydrogen concentrations ( $c_H$ ) in the sample. At low concentration hydrogen exist as a solid solution  $\alpha$ -phase randomly distributed in the crystal structure of the metal. When the concentration of hydrogen in the lattice increases the hydride  $\beta$ -phase starts forming and coexists with the  $\alpha$ -phase, which gives at certain temperature a constant pressure plateau. Further increase in hydrogen pressure and concentration results in saturation of the material where only the hydride  $\beta$ -phase remains. As the temperature rises the phase diagram approaches its critical point (T<sub>c</sub>) and the plateau region can be narrower with also a lower reversible absorption capacity in the  $\beta$ -phase.

The van't Hoff plot, which is a graphical visualization of van't Hoff equation (Equation 2.20), can be constructed by plotting plateau pressures  $p_{eq}$  versus 1/T. The  $\Delta$ H and  $\Delta$ S values can be extracted from the slope and the intercept of the plot, respectively.

$$\ln p_{eq} = \frac{\Delta H}{RT} - \frac{\Delta S}{R} \tag{2.20}$$

where:  $p_{eq}$  – equilibrium pressure, T- temperature, R-gas constant,  $\Delta H$  – enthalpy,  $\Delta S$  entropy of hydride formation.



**Figure 2.7** Pressure-Composition-Isotherms (left hand side) and van't Hoff plot (right hand side) as obtained for a typical two phase metal hydride system.<sup>14</sup>

The pressure composition isotherms were not measured in this project. It is known from the literature that for MgH<sub>2</sub> catalyzed with TiF<sub>3</sub> the enthalpy and entropy of formation differ with the hydrogen concentration<sup>15</sup>, and for the middle of the plateau are close to the values obtained for uncatalyzed MgH<sub>2</sub><sup>16</sup> and equal to -74 kJ mol<sup>-1</sup> and 130 J mol<sup>-1</sup>K<sup>-1</sup>, respectively.

In this work samples of MgH<sub>2</sub>-0.05TiF<sub>3</sub> were prepared by means of ball milling. They were desorbed in the Ar glovebox with the water and oxygen levels < 0.1 ppm at elevated temperature from 50 °C up to 300 °C within 3 hours. Directly after desorption each sample was loaded into a sample holder of the Sieverts apparatus and hydrogen was re-absorbed up to concentration of e.g. MgH<sub>1.5</sub> at 150 °C with a few shots of hydrogen, with pressures ranging from 1-20 bars. Absorption kinetics measurements reported in the literature show that the TiF<sub>3</sub> catalyzed MgH<sub>2</sub> compound can be loaded with 5 wt% of hydrogen within 30 s at 573 K.<sup>17</sup>

## 2.1.6 Fourier Transform Infrared spectroscopy (FT-IR)

FT-IR is a very useful method for identification of materials without long range crystalline order. Additionally this method is relatively fast, inexpensive and often straightforward in application.

Each molecule possesses distribution of energy which is defined as a sum of the contributing energy terms:

$$E_{total} = E_{electronic} + E_{vibrational} + E_{rotational} + E_{translational}$$
(2.21)

One portion of the total energy, vibrational energy, is related to energy absorption within the infrared region of electromagnetic spectrum. In infrared spectroscopy, IR radiation passes trough the sample. During that process part of the radiation is absorbed by the sample and another part is transmitted. As a consequence the infrared spectrum with frequency usually between 4000 cm<sup>-1</sup> and 400 cm<sup>-1</sup> is recorded by the instrument.<sup>18</sup> The frequency of the absorbed radiation matches the frequency of the bond or the group that vibrates in the investigated compound. The vibrational spectrum is unique and characteristic for each molecule therefore can be

used as a fingerprint for identification of the unknown structure by comparison with previously recorded reference spectra.

The IR spectroscopy can also be analyzed quantitatively. The intensity of absorption bands assigned to certain functional groups increases with the density of this group in the material.

FT-IR Spectroscopy was performed on a FT-IR Spectrophotometer Perkin-Elmer Spectrum 100 series, with measuring range of 7800 to 370 cm<sup>-1</sup>. The sample was transferred for the IR measurement without exposure to air.

## 2.1.7 Electron Microscopy

Electron microscopy has been developed because of the limitations of the magnification and resolution of the optical microscope.

# 2.1.7.1 Transmission Electron Microscopy (TEM)

Transmission electron microscopy is a very practical tool for the characterization of structure and morphology of a sample. It provides information about crystallinity of the sample, phase analysis, presence of the defects in the structure and particle size.

In a conventional TEM electron beams generated by the electron gun are accelerated to an energy of 50 – 300 keV, highly focused and directed on the specimen. Electrons interact strongly with atoms by the elastic and inelastic scattering; therefore the sample must be very thin usually around 200 nm to allow transmission. Behind an objective lens, an objective aperture is placed in the back focal plane. By the positioning of the objective aperture on specific positions in the back focal plane two kinds of images can be obtained. In the situation where the aperture allows only the transmitted electrons to pass through a bright-field (BF) image is formed. If the aperture is positioned to pass only diffracted electrons a dark-field (DF) image is obtained. The transmitted or diffracted signal from the sample is magnified by a system of electromagnetic lenses and finally is visible as an image on the fluorescent screen or with CCD camera.<sup>19</sup>

Except diffraction and spatial imaging the inelastically scattered high-energy electrons produced in TEM cause electronic excitation of the atoms in the investigated sample. Therefore it is possible to obtain information about the chemical composition of the specimen. With a small focused electron beam, an energy-dispersive electron spectroscopy (EDS), characteristic X-ray spectrum of the elements present in the sample is acquired. The lateral resolution of EDS is dependent on the width of the electron beam, as radiation is emitted from the entire area illuminated by electrons.<sup>7</sup>

In this study, a FEI Tecnai Transmission Electron Microscopy in the bright field mode was used with an accelerating voltage of 200 kV which allows resolutions of the orders of Angstroms. Before measurement samples were dispersed in hexane and transferred on the 3 mm copper grid with carbon film on top to the TEM airtight sample holder. The entire sample preparation was carried out in the glovebox.

## 2.1.7.2 Scanning Electron Microscopy (SEM)

A scanning electron microscope (SEM) is a scientific instrument which allows examining the surface topography, morphology and composition of the specimen. It provides also crystallographic information about the sample. The electron beam generated from the tungsten element is focused by several magnetic lenses, hits the sample and electrons from the beam collide with the electrons from the specimen. As a result of elastic scattering highly energetic (>50 eV) back scattered electrons (BSE) are reflected back in back scattered mode. Due to inelastic collisions secondary electrons (SE) with lower energy (2-50 eV) are emitted. Additionally characteristic X-rays are produced by excited electrons in the sample that relax to lower binding states. The detected signals are amplified and transferred to the computer. As a consequence an image of the chosen area is obtained with typical resolution between 1 nm and 10 nm.<sup>20</sup>

In the backscattered mode incident electrons are elastically scattered with higher energy by the specimen. The brightness of the image formed by backscattered electrons depends on the atomic number of the element which is present in the sample. Darker parts of the image are visible on the screen when the light elements are present in the specimen whereas heavier elements appear bright. Therefore this mode can provide information about distribution of the different elements in the sample.

One of the differences between TEM and SEM is that in conventional TEM a stationary incident beam is used whereas in SEM the sample is scanned horizontally in two perpendicular directions. Additionally with SEM relatively thick so called bulk sample can be investigated because SEM is not transmission limited.

For the imaging of the aerogel topology in *Chapter 5* the SEM FEI/Philips XL30 SFEG was utilized in a secondary electron mode.

# 2.1.8. Solid-state Nuclear Magnetic Resonance (NMR)

The Nuclear Magnetic Resonance technique is suitable to study the electronic and magnetic environment of specific isotopes of elements that are present in the sample. That specific method can be applied to crystalline solids as well as to amorphous materials which make it complementary to many other spectroscopic techniques.

When an external magnetic field  $\mathbf{B}_0$  along the *z* direction is applied to the sample and the nuclei in the sample, a nuclear spin net magnetization arises. The nuclear spin precesses in the fixed **B** field with a frequency which is called Larmor frequency ( $\omega_0$ ).<sup>21</sup>

The nuclear magnetic moment  $(\mu_i)$  related to nuclear spin  $(I_i)$  interacts with the applied field, which results in splitting of the nuclear spin energy level (Figure 2.8) into 2I+1 possible energy levels (the Zeeman effect):

$$\Delta E = \hbar \omega_0 = \gamma \hbar B_0 \tag{2.22}$$

where:  $\gamma$  – gyromagnetic ratio, constant for given type of nucleus,  $\hbar$  – reduced Planck constant.

The energy which is required for a transition between two energy levels corresponds to radio frequency (r.f.) waves with a frequency depending on the

magnetic field applied. If the radio frequency matches with the energy for a nuclear spin transition between the two levels, absorption of energy will occur. The r.f. pulse ( $\omega_{rf}$ ) in the NMR experiment is applied in such a way that its magnetic field oscillates along a directions perpendicular to *z* and **B**<sub>0</sub>. The net effective field (**B**<sub>eff</sub>) is the vectorial sum of the components along *x* and *z* directions. When so called  $\pi/2$  pulse is applied the magnetization is rotated 90 degrees and lies in the plane perpendicular to **B**<sub>0</sub>. This magnetization will thus subsequently precess and the conducting RF coil placed in the precession plane registers an induced current. In this way the free induction decay (FID as a function of time is recorded), which can be e.g. a sinusoidal exponential damped function. Fourier transformation of the FID results in a final frequency dependent spectrum. Depending on the frequency of the r.f. pulse different nuclear isotopes can be detected. The NMR spectra and lineshapes provide much information on chemistry, structure and dynamics in the solids.<sup>21</sup>



Figure 2.8 Schematic of the energy levels of a nuclear spin  $\frac{1}{2}$  in a static magnetic field **B**<sub>0</sub>.

The applicable interactions between the sample and internal magnetic fields like: chemical shielding (CS), dipole coupling (DC) and quadrupole coupling (QC) can be described by Hamiltonian operator:

$$H = H_{CS} + H_{DC} + H_{QC}$$
(2.23)

Not only the nucleus but also the electrons surrounding them react in magnetic field. As a result of this interaction a secondary magnetic field is produced, which contributes to the total magnetic field interacting with nucleus. This specific interaction is called shielding interaction and it has a form:

$$H_{CS} = -\gamma \hbar \mathbf{I} \cdot \mathbf{\sigma} \cdot B_0 \tag{2.24}$$

where: I – spin,  $\sigma$  – second-rank tensor (chemical shielding tensor)

This shielding interaction effectively causes an alteration of the field registered by the nucleus, i.e. a shift in frequency in the NMR experiment known as a chemical shift. During NMR experiments the spectra and their chemical shifts are recorded relative to a chosen reference sample frequency.

Two experimental methods in NMR have been used in this thesis:

a) Magic angle spinning (MAS)

MAS technique is used to reduce large line-width caused by chemical shielding anisotropy and also nuclear dipolar interactions. The sample is placed in the zirconia rotor, as it is visible on the Figure 2.9, at the magic angle  $\theta_m = 54.74^\circ$ , which describes the orientation of the shielding tensor with respect to static magnetic field **B**<sub>0</sub>. It is rotated with a high spinning rate at that specific angle since then anisotropic parts of the interactions that depend on the crystalline orientation in the magnetic field are averaged, while the dipolar interaction which is proportional to  $(3\cos^2 \theta m - 1)$  may average to zero, and disappear. Additionally if the spinning rate is lower than the static line width spinning side bands appear at intervals of the spinning frequency.<sup>22</sup>



Figure 2.9 Magic angle spinning experiment.

## b) 2D exchange NMR experiments

In this method the  $\pi/2$  pulse is applied to the sample causing that the spins start their precession evolution during the variable  $t_1$  time at  $\omega_1$  frequencies. At the end of the  $t_1$  evolution time the magnetization is accumulated using a -  $\pi/2$  along the z axis for a so called mixing time  $\tau_m$ . During this mixing time the nuclear spins interact and spin diffusion can take place. After this mixing time another  $\pi/2$  pulse rotates the magnetization perpendicular to the applied field and spin precession takes place for the  $t_2$  evolution time at  $\omega_2$  frequencies. The evolution of this signal is recorded as a FID for increasing  $t_1$  times as a 2D dataset (Figure 2.10).

The two-dimensional two evolution times dependent dataset yields after a 2D Fourier transform a two-dimensional frequency ( $\omega_1$ ,  $\omega_2$ ) correlation spectrum. In our case the spin exchange is visible in the 2D spectrum as off-diagonal cross peaks. If there is no spin-exchange during the  $\tau_m$  mixing time the characteristic spectral intensity appears only along the diagonal of the 2D spectrum. Therefore with this experiment the proximity of the same chemical elements in different chemical environments can be studied.



Figure 2.10 2D NMR experiment pulse sequence.

During this research <sup>1</sup>H MAS NMR was used to describe the structure of the metal organic framework  $Cu_3(BTC)_2$  after it was decomposed in a hydrogen atmosphere. Furthermore <sup>1</sup>H MAS NMR, <sup>19</sup>F MAS NMR and 2D <sup>19</sup>F - <sup>19</sup>F spin diffusion experiments were carried out on the MgH<sub>2</sub>-0.05TiF<sub>3</sub> dehydrogenated and rehydrogenated materials.

All experiments were performed on a Bruker DMX500 spectrometer operating at a <sup>1</sup>H NMR frequency of 500 MHz and equipped with a 2.5-mm MAS probe head. As a reference (0 ppm) for the chemical shift calibration tetramethylsilane (TMS) for <sup>1</sup>H and -196 ppm of PTFE for <sup>19</sup>F MAS NMR were used. All samples were transferred in air-tight bottles under Ar and packed in a MAS sample holder and closed inside an Argon glove box with oxygen level below 1 ppm. The sample holders were rotated inside the probe head using a dry nitrogen flow at a sample spinning rotation rate of 15 kHz and 20 kHz for the metal hydride sample.

## 2.2 Calculation methods

Many characteristic parameters that are important for porous materials, like pore volume, adsorption energies or hydrogen diffusion coefficients, can be determined from computational simulations using (commercially) available computer codes. The structural models of all MOFs discussed in this thesis have been built in the Materials Studio Modeling 4.2 program.<sup>23</sup> Materials Studio 4.2 is a complete modeling environment for structure design as well as an interface to simulation codes for determining the behavior of the models under different imposed conditions. The X-ray diffraction patterns for the experimental data measured on our chemically synthesized structures were calculated with the Reflex module as implemented in Materials Studio 4.2. This facilitates e.g. a comparison between the structures of as synthesized and activated samples.

In this chapter the simulation approaches will be briefly described.

## 2.2.1 Free pore volume calculation

The solvent accessible voids were estimated in the program PLATON, which was written by A.L. Spek from Utrecht University.<sup>24</sup> The free volume within the structure is calculated by finding and fitting a spherical probe with given probe radius (Figure 2.11). The probe radius default value is set to 1.2 Å and can be modified depending on the user needs and objectives.<sup>25</sup> For the purpose of this work 1.8 Å was used as the probe value, however, it was noticed that for the structure containing big, open pores, such as MOF-5, there is only 3-5% difference in the free pore volume calculated with probe radius 1.2 Å and 2 Å. Nevertheless when the porous structure consist of narrow and not completely open pores the value of the probe radius become very important factor which can affect the calculation.



**Figure 2.11** Visualization of the method of free solvent volume calculation in PLATON.

# 2.2.2 Ab initio calculation

Ab initio, meaning "from the beginning", or "first principles calculation" is a calculation method which gives information about the physical properties of an investigated system starting from the basic input of types and positions of the atoms in the structure. The electronic structure of the chemical structures is calculated from quantum mechanical principles, but some basic approximations are applied for computational efficiency. The Born-Oppenheimer approximation assumes that the mass of the nuclei in comparison to the mass of the electrons is much larger so that nuclei can be considered stationary in the electronic structure calculation steps. The electronic energies are calculated by solving the time independent Schrödinger equation (Equation 2.25) for the fixed nuclear configuration.

$$\hat{H}\psi = E\psi \tag{2.25}$$
 where:  $\hat{H}$  – Hamiltonian operator,  $\psi$  – wave function, E – energy eigen values

The calculations of the full quantum mechanical electronic wave functions and electronic energies for systems which contain more than one nucleus with one electron are computationally highly time demanding, and therefore usually the density functional method for approximating local electron densities needs to be used.

#### 2.2.2.1 Density Functional Theory

The density functional theory (DFT) concerns of the calculation of the ground state of a many particles system, where the electron probability density function  $\rho(x,y,z)$ takes into account the electron density at position (x,y,z). That represents a probability of finding electron in the certain volume with the coordinates x, y, z. The physical foundation to that theory, which says that all the properties of a molecule in a ground electronic state are determined by the ground state electron density function, was given by Hohenberg and Kohn<sup>26</sup> and further developed by Kohn and Sham.<sup>27</sup>

According to Hohenberg and Kohn the functional of the ground state electron density function can be considered as a sum of the Coulomb interactions of electrons with the external potential  $V_{ex}$ , and a part which is the sum of kinetic energy of electrons and interelectronic interactions<sup>26</sup>:

$$E_0[\rho(\mathbf{r})] = \int V_{ex}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + F[\rho(\mathbf{r})]$$
(2.26)

The equation could not be solved because the functional  $F[\rho(r)]$  was unknown until 1965 when Kohn and Sham introduced the new approximation:

$$F[\rho(\mathbf{r})] = E_{K}[\rho(\mathbf{r})] + E_{C}[\rho(\mathbf{r})] + E_{XC}[\rho(\mathbf{r})]$$
(2.27)

where:  $E_K$  – kinetic energy,  $E_C$  – electron-electron Coulomb interaction,  $E_{XC}$  – exchange and correlation energy of an electron system with electron density  $\rho(r)$ .

Further, electron density has to be calculated from equation:

$$\boldsymbol{\rho}(\boldsymbol{r}) = \sum_{i=1}^{N} \left| \boldsymbol{\psi}_{i}(\boldsymbol{r}) \right|^{2}$$
(2.28)

All terms from the equation 2.27 can be expressed in a formal theoretical manner, except the exchange and correlation functional. To express that part another approximation indicated with e.g. local density approximation (LDA) or generalized gradient approximation (GGA) must be implemented.

#### 2.2.2.2 VASP

Density functional methods employ a plane-wave basis set for the valence electrons, and the pseudopotential (PP) approximation for the potential representing the atomic core electrons, to solve the Kohn-Sham (KS) equation (2.27). Energy minimization to the ground state energy for the certain system can be completed in the Vienna Ab-initio Simulation Package (VASP).<sup>28</sup> Two standard pseudopotentials which describe interactions between ions and electrons are available in VASP: ultrasoft Vanderbilt pseudopotentials (USpp) and projector augmented wave (PAW). In the case of PAW two main approximations to the exchange-correlation functional can be used: LDA and GGA. The GGA method is considered as more accurate since it includes density and the gradient of the density whereas LDA takes into account only density at any point in space. In this work the Perdew-Wang '91 method in generalized gradient approximation was used for the electron exchange and correlation potential.<sup>29</sup>

To calculate ground-state energies for a certain molecular or crystalline system four main input files have to be defined in VASP: POSCAR, POTCAR, KPOINTS and INCAR. POSCAR includes information about lattice parameters, number and type of atoms and their coordinates within the unit cell. Depending on the type of calculation the volume of the cell can be optimized by calculating the minimum energy of the cell as a function of the cell parameters, or atomic positions can be frozen for e.g. density of states calculations. The POTCAR file used in VASP contains pseudopotentials for all elements corresponding to the atoms in the POSCAR file. It stores also more detailed atom specifications such as mass, valence electron numbers, or energy of the reference configuration which was used for the pseudopotentials generation.

The third file called KPOINTS contains the k-point coordinates and mesh size, which define the k-point grid, for sampling the Brillouin Zone. The number of k-points is an important parameter which depends on the nature of the system. For example for metals a larger number of KPOINTS is needed than for semiconductors or insulators. Last key file for setting up calculations is the INCAR file in which calculation parameters must be specified and the type of calculation is defined. The minimization algorithm consists of two loops: outer loop where the ionic positions are optimized in order to minimize the total free energy, and an inner loop in which the electronic wavefunctions are modified to minimize the electronic energy for a fixed ionic configuration. When the calculation for a chosen system is completed output files like OSZICAR, CONTCAR, CHGCAR and DOSCAR are generated, which include information about total free energy, relaxed atomic coordinates and cell parameters, density of charges and density of states.

## 2.2.3 Force fields method

Quantum mechanical methods such as DFT give reasonably fast and accurate results for relatively small systems with not too large numbers of atoms (or valence electrons). For large systems, e.g. organic biological molecules with large number of atoms, this method is not recommended because it is exceedingly time-consuming. For such systems instead of quantum mechanical methods, molecular mechanics (force fields methods) are applied since they are faster while they still can enable adequate comparison with experimental data. Also thermodynamic parameters, diffusion processes and structure dynamics are usually calculated with force fields methods. Force field methods do not consider the electronic motions, but the energy of the given system is calculated based only on the position of the nuclei. This estimated energy is called molecular mechanics energy ( $E_{\rm MM}$ ) and only within some approximations and calibrations the change in this energy ( $\Delta E_{\rm MM}$ ) can be equivalent to changes in free energy ( $\Delta G$ ). The molecular mechanics energy is calculated by summing up the strain in all the bonds present in the investigated system and van der Waals and Columbic interactions for all the atoms<sup>30</sup>:

$$E_{MM} = E_{bonds} + E_{angles} + E_{vdW} + E_{torsion} + E_{charge} + \dots$$
(2.29)

The first two terms of the equation 2.29,  $E_{\text{bonds}}$  and  $E_{\text{angles}}$ , are related to stretching (pushing and pulling) and bending of the bonds.  $E_{\text{vdW}}$  is an energy contribution from non bonded attraction and repulsion interactions, and can be modeled by implementing a Lennard-Jones 6,12 type potential.<sup>31</sup>  $E_{\text{torsion}}$  is associated with the energy barriers for molecules to rotate around defined single bonds and  $E_{\text{charge}}$  describes charge - charge Coulomb interactions. If the investigated system is more complicated other extra terms can be introduced which allow obtaining better results, therefore the equation 2.29 is not complete (e.g. hydrogen bonds).

Before the calculation starts the complete molecular structure has to be described. In the force field method the atomic coordinates of each atom, atoms description, and a list of the bonds and their bond type connecting the atoms, are needed.

Because force field calculations are much faster than ab initio methods they can be successfully utilized in molecular dynamics to simulate the movement of the molecules on extended time scales. In this way a complex simulation as e.g. molecules in solution or hydrogen diffusion in MOFs at different temperature can be performed. When the simulation starts each atom obtains some kinetic energy, causing the movement of the whole molecule. Depending on the temperature used in the simulation the atoms will therefore move faster or slower. The desired step size and simulation length are set balancing speed of calculation and the stability of the calculations. From the results the time evolution can be directly observed in the form of a molecular dynamics movie.

Alternative force fields as e.g Universal, COMPASS, Dreiding have been developed for all types of molecular systems and different kinds of problems. For the purpose of this thesis the Dreiding force field implemented in Materials Studio 4.2 package was employed for simulation of hydrogen diffusion in MOFs. In several instances the output was also compared to the COMPASS force field.

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# Chapter 3

Hydrogen storage capacity of modified MOF-5: An experimental and computational approach.

Water stability of methyl modified MOF-5.

The chapter is based on the submitted and published articles:

Yang, J.; Grzech, A.; Mulder, F. M.; Dingemans, T. J., accepted to *Microporous and Mesoporous Materials* 

and

Yang, J.; Grzech, A.; Mulder, F. M.; Dingemans, T. J., Chem Commun 2011, 47, 5244



Despite that metal-organic frameworks (MOFs) are widely investigated as potential hydrogen storage materials, there is only limited systematic information available on the effect of small functional groups introduced on the phenyl ring, on the stability of the crystal structure and the hydrogen storage properties of the framework. Therefore in this work MOF-5 modified with the simple functional groups bromine (-Br), chlorine (-Cl) and methyl (-CH<sub>3</sub>) having different sizes and electronic effects are investigated. All synthesized MOFs were characterized by means of powder X-ray diffraction, nitrogen and hydrogen sorption techniques, as well as modeled in the Materials Studio 4.2 and VASP programs. Additionally the stability against moisture of MOFs modified with one or two hydrophobic methyl groups is tested.

The modified MOFs possess in general the same cubic structure as the unmodified MOF-5 but different crystal qualities are obtained. The specific surface area (BET) of the samples ranges from 680 to 2750 m<sup>2</sup> g<sup>-1</sup>, illustrating the difficulty to obtain activated and perfectly porous structures. Hydrogen uptake capacities measured at 1 bar and 77 K are 1.42, 1.08,  $0.99 \pm 0.05$  wt% for CH<sub>3</sub>-MOF-5, Br-MOF-5 and Cl-MOF-5, respectively. Introduction of functional groups does not have significant influence on the isosteric heat of adsorption at low hydrogen pressures. Molecular dynamics simulations demonstrated that the hydrogen self-diffusion coefficient is slightly reduced in the modified MOF-5s. Methyl modified MOF-5 appeared to be highly water resistant and maintains its hydrogen storage capability after 4 days exposure in air, unlike ordinary MOF-5 which looses it completely.

## 3.1 Introduction

Metal-organic frameworks (MOFs) are a new class of highly crystalline porous materials consisting of metal ions or metal oxide clusters and organic ligands as linkers. MOFs possess typically extraordinary low densities, large surface area and adjustable pore size which make them interesting for a wide range of applications including gas storage and separation, catalysis, drug delivery and sensing.<sup>17</sup> Already the first MOF reported as hydrogen storage material in 2003 by Yaghi's group<sup>8</sup> containing Zn<sub>4</sub>O clusters coordinated to terephthalic acid appeared to be a

very good candidate for this purpose. Named as MOF-5 (IRMOF-1) the porous structure has an excess hydrogen uptake capacity of 7.1 wt% at 77 K and 40 bar. Total  $H_2$  uptake of that MOF reaches 10 wt% at 100 bar corresponding to a record volumetric storage density of 66 g L<sup>-1</sup>. Since then more and more MOFs with different porous structure were discovered and tested as potential candidates for effective hydrogen storage.<sup>9-12</sup> However, many of the MOFs are moisture-sensitive and easily decompose in ambient air; therefore the additional challenge is to design MOFs with enhanced water resistance. This can be successfully achieved by introduction hydrophobic functional groups into the framework structure.<sup>13</sup> Several factors such as specific surface area, pore volume, pore size, and adsorption strength can influence the hydrogen uptake of MOFs. For this reason scientists make effort to modify those parameters in order to obtain higher hydrogen adsorption capacities under more favorable conditions. Following this track in 2004 Yaghi et al. published MOF-177 which exhibits a large surface area of 4500 m<sup>2</sup>g<sup>1</sup> and a pore volume of 1.61 cm<sup>3</sup> g<sup>-1</sup>, but it adsorbs 'only' 1.25 wt% of hydrogen at 1 bar and 77 K, similar to other MOF's.14,15

Another strategy to obtain high hydrogen storage capacity is to increase the rather weak strength of the van der Waals interactions between hydrogen molecule and adsorbent. Two popular strategies are by pore size reduction and by the formation of interpenetrating structures. Decreasing the pore size of the framework allows hydrogen molecules to interact more effectively with pore walls because the attractive potentials of opposite walls overlap.<sup>16</sup> This approach can be achieved by employing rather short ligands, which are still sufficiently long to build porous structure organic ligands. Much longer ligands promote the generation of interpenetrating structures which is an alternative way to decrease the pore size of the resulting structure. It was reported that hydrogen uptake capacity in the interpenetrating structures increases in the low pressure regime, due to increase of isosteric heat of adsorption. However, at high pressure the hydrogen capacity is reduced because of the accessible volume reduction.<sup>17</sup>

The isosteric heat of adsorption of hydrogen in the framework can also be enhanced by introduction of coordinatively unsaturated metal sites or functional ligands to the aromatic linker.<sup>18,19</sup> According to results of neutron powder diffraction experiments unsaturated metal sites possess the strongest affinity towards hydrogen among all other adsorption sites present in the MOF.<sup>20,21</sup> Introduction of the functional group to the organic ligand is a very interesting strategy because it may be realized without changing the basic structure of the MOF topology. It was shown that chemical modification of the organic part by substitution of hydrogen atom on the benzene ring of the MOF-5 structure with  $-NH_2$ , -Br,  $-C_2H_4$  groups improve hydrogen storage capacity at 77 K and 1 bar on a molar basis, which was explained by the pore narrowing.<sup>22</sup> Based on computer simulations it was suggested that especially electron-donating groups have the ability to enhance the affinity of the framework towards the hydrogen molecule. However, no improvement in the hydrogen sorption ability by replacement of hydrogen with -F or  $-CH_3$  was observed in pillared MOFs.<sup>16</sup> To design and optimize the structure which would effectively adsorb larger amounts of hydrogen, a better understanding of influence of the different pendant groups on the MOF structure needs to be gained. Therefore in this work functional groups of various size and polar effect (-CH<sub>3</sub>, -Br and -Cl) were introduced to the benzene ring and their influence on the structure stability and hydrogen storage capability were investigated. For the modified MOFs structures designed in the program the heat of hydrogen adsorption and hydrogen self-diffusion coefficients were evaluated. Additionally the moisture stability of MOF-5 modified with one and two hydrophobic methyl groups was tested.

# 3.2 Materials and methods

# Materials preparation

All the compounds: MOF-5 and modified MOF-5 with –Br, -Cl, –CH<sub>3</sub> functional groups were prepared, with the methods reported in literature, by Jie Yang from Aerospace Engineering TU Delft. Within the project she was responsible for the synthesis efforts and microstructure characterization of the compounds.

# Materials characterization

Powder X-ray diffraction (PXRD) characterization was performed by use of a PANalytical X'Pert Pro PW3040/60 diffractometer with monochromatic Cu  $K_{\alpha}$ 

radiation operating at 45 kV and 40 mA within a 20 range of 5-60°. Air sensitive samples were loaded in the Ar glove box into an airtight sample holder with a Kapton<sup>®</sup> window. Pore volume and BET surface area analysis was registered at 77 K on Micromeritics ASAP 2010 adsorption analyzer. Before the measurements the samples were heat treated at 135 °C in a vacuum to remove e.g. adsorbed water. Hydrogen uptake experiments were conducted on a calibrated volumetric Sieverts type apparatus at the temperatures 64 K, 77 K and 100 K in the pressure range 0-2 bar. Excess hydrogen uptake measurements were performed for all the samples at 77 K and pressures up to 60 bars. Samples were loaded into the stainless steel containers with copper O-ring and connected to the setup with a thin capillary for hydrogen access. Prior to the adsorption measurements the samples were heated at 150 °C under vacuum for a period of three days. Pressure of hydrogen gas of ultrahigh purity (99.999%) was applied in doses and was monitored with pressure transducers. For the low pressure range experiments, a correction was made for the free volume of the capillary and the dead volume in the sample container by subtracting the amount of hydrogen measured at 77 K in a sample holder filled with a volume of non-adsorbing material corresponding to the volume of the sample. The non-adsorbing volume of each sample for excess hydrogen uptake measurements was determined with He gas at room temperature and pressure of 1 bar. The isosteric heat of hydrogen adsorption for each compound was estimated according to Clausius - Clapeyron equation:

$$\left(\frac{\partial \ln P}{\partial T}\right)_{\vartheta} = \frac{Q_{ads}}{RT^2}$$
(3.1)

The equation 3.1 can be written as:

$$\ln(\frac{p_2}{p_1}) = \frac{Q_{st}}{R} (\frac{1}{T_1} - \frac{1}{T_2})$$
(3.2)

where: p – pressure, T – temperature,  $Q_{ads}$  – isosteric heat of adsorption, R – universal gas constant,  $\vartheta$ -coverage.

#### Computational simulations.

Empty voids accessible for the solvent were calculated using the PLATON program written by A.L. Spek from Utrecht University.<sup>21</sup> The empty space or voids within the model structures of MOFs can be calculated based on finding and fitting spherical probes of a given radius in the empty voids. The calculation uses the atomic van der Waals radii to define the space occupied by the probe molecules and then searches the remaining space for other potential voids that meet the probe dimension criteria. The probe radius can be modified, while the default value is 1.2 Å. If a framework contains large and open pores the value of the probe radius ranging from 1.2 to 2 Å does not make a large difference (2-3 %). However, in case of narrow and not completely open pores, the value of the probe radius becomes an important parameter to estimate the correct empty void volume in the structure. The obtained value can be compared to experimental values measured using N<sub>2</sub> as a probe. The kinetic diameter of N<sub>2</sub> is 3.6 Å; therefore in this study calculations were performed with a probe radius of 1.8 Å using a low symmetry space group.<sup>14</sup>

To obtain hydrogen adsorption energies Density Functional Theory (DFT) calculations were performed in the generalized gradient approximation (GGA) with Perdew-Wang '91 functionals, describing electron exchange and correlation potential, as implemented in the VASP plane wave pseudo-potential code. DFT has been used before to obtain adsorption energies that appear consistent with experiment.<sup>23,24</sup> First, a primitive cell of MOF-5 with 106 atoms was built using the program Materials Studio 4.2. Further the initial structure was relaxed to its ground state in the VASP program with kinetic energy cutoff of 400 eV and the Brillouin zone sampled with, since it is a large cell, a 1×1×1 Monkhorst-Pack k-point mesh. Relaxed MOF-5 possesses a cubic structure with the symmetry group *Fm-3m* and it reaches the minimum energy for the lattice parameter a=25.46 Å. In the next step one of the hydrogen atoms of each phenyl in the MOF-5 structure was replaced with a -Br, -Cl, or -CH<sub>3</sub> group, respectively. Subsequently the structures of the new compounds were relaxed and the energies of the minimized configurations were calculated. In order to calculate hydrogen adsorption energies, hydrogen molecules were placed in the primitive cell and relaxed at four special positions which have been confirmed as hydrogen adsorption sites in MOF-5 by computational and

experimental methods.<sup>25</sup> The adsorbed molecules in modified MOFs structures still find the same positions as minimum energy adsorption sites. The adsorption energies for four different sites of each of the modified MOFs were calculated from the difference in energy of the minimized structure with and without a specific adsorbed H<sub>2</sub>, and corrected for the energy of a free H<sub>2</sub> molecule in the same empty cell. The adsorption energies can be evaluated using Equation 3.3:

$$\Delta E_{ads} = E(H_2 + MOF) - E(H_2) - E(MOF)$$
(3.3)

In order to investigate the mobility of hydrogen in the obtained compounds hydrogen diffusion coefficient calculations were performed using force field calculations. First *ab initio* calculations were performed in the VASP simulation package to find a minimum state of energy for the structures. Then using this model for relaxation calculations of the structures with 10 H<sub>2</sub> and 32 H<sub>2</sub> in the unit cell were executed with the program Materials Studio 4.2, using the Dreiding force field. The relaxed structures did not deviate much from the VASP calculations which may indicate that the force field closely represents what is determined from DFT in VASP. For calculating electrostatic interactions, the Ewald summation method was used and the short-range interaction was estimated with a cut-off distance of 12 Å. Molecular dynamics simulations at three different temperatures with simulation times of 10 ps were then performed using the Materials Studio 4.2 suite in the NVT ensemble (NVT = constant number of molecules, volume, temperature) and Berendsen thermostat. The self-diffusivity characterizes the motion of individual, chosen particles. In a three-dimensional isotropic material, the self-diffusivity is related to the mean-squared displacement (MSD) of the center of mass of the diffusive molecules after time *t* by the Einstein relation (Equation 3.4). From the slope of the mean square displacement against time a diffusion coefficient can be extracted.

$$D = \frac{1}{6} \lim_{t \to \infty} \frac{d}{dt} (MSD)$$
(3.4)

$$MSD = \left\langle r^{2}(t) \right\rangle = \left\langle \frac{1}{N} \sum_{i=0}^{N} \left( r_{i}(t) - r_{i}(0) \right)^{2} \right\rangle$$

where:

*N*-corresponds to number of hydrogen molecules and  $r_i(t)$  gives the vector positions of the diffusing molecules.

#### 3.3 Results and discussion

3.3.1 Hydrogen storage capacity of modified MOF-5s: An experimental and computational approach.

#### 3.3.1.1 Powder X-ray diffraction analysis of the structures.

Four as synthesized compounds MOF-5, CH<sub>3</sub>-MOF-5, Br-MOF-5, Cl-MOF-5 (Figure 3.1) were activated, by removing solvent from pores, and characterized by means of powder X-ray diffraction. The structures of all the samples were also designed in the Materials Studio 4.2 program. The diffraction patterns for those structures were calculated and compared with experimental ones. The diffraction pattern obtained for MOF-5 sample is in good agreement with the calculated pattern (Figure 3.2) and that reported in the literature.<sup>26</sup> The structure of MOF-5 is cubic with space group *Fm-3m* and lattice parameters a = 25.46 Å. Such big lattice parameters results in diffraction peaks positioned at low angle  $2\theta = 6.9^{\circ}, 9.7^{\circ}, 13.8^{\circ},$  $15.4^{\circ}$ . CH<sub>3</sub>-MOF-5 as modeled has a structure with *Pa-3* space group, due to the  $CH_3$  group substitution, which is subgroup of the space group *Fm-3m* with lower symmetry. Since the lattice parameters are the same all the peak positions in the powder diffraction of CH<sub>3</sub>-MOF-5 are identical with simulated results, and CH<sub>3</sub>-MOF-5 thus possesses the same cubic topology as MOF-5. However, for both compounds the ratio of the peak intensities at 13.8° and 6.9° is higher when compared to the simulated results (Figure 3.2). This fact was already observed by researchers and it was interpreted as presence of interpenetrating structures.<sup>27-29</sup> Therefore a twofold interpenetrated MOF structure was designed and an XRD pattern of the obtained structure was calculated (Figure 3.2). Effects on the peak intensities can also be related to the anisotropic temperature factors caused by the rotational motions of the benzene rings around the axis formed by the two COO groups, multiplied by the random substitution of CH<sub>3</sub> groups on the sides of the benzene rings. The two other samples denoted as Br-MOF-5 and Cl-MOF-5 are modeled with the same cubic (*Pa-3*) structure, showing sharp peaks located at angle 2 $\theta$  of 6.9° and 9.7° but not all the peaks fit well with the calculated patterns. Therefore it is suggested that some impurities are present in the samples. In addition it is known that the splitting of the first peak at low 2 $\theta$  angle in the PXRD pattern of Cl-MOF-5 is the result of a distortion of the cubic symmetry.<sup>28</sup> Increase of lattice parameter *a*, *b* or *c* of the Cl-MOF-5 structure by only 1Å indeed results in peak splitting in simulated XRD pattern present in the Figure 3.2.



Figure 3.1 MOF-5 modified with different functional groups.



**Figure 3.2** PXRD patterns of as activated samples MOF-5, CH<sub>3</sub>-MOF-5, Br-MOF-5, Cl-MOF-5 and simulated in Materials Studio 4.2.
## 3.3.1.2 Specific surface area and pore volume determination.

The specific surface area (SSA) and pore volume of the samples accessible for hydrogen was evaluated from nitrogen sorption measurement. Theoretical pore volumes of the simulated structures were computed (Table 3.1) in the PLATON program. Since all the investigated compounds possess micropores (d<2 nm)  $N_2$ sorption measurements show type-I isotherms according to IUPAC isotherm classification.<sup>30</sup> The specific surface area and pore volume of MOF-5 are 2750 m<sup>2</sup> g<sup>-1</sup> and 1.15 cm<sup>3</sup> g<sup>1</sup>. These results are comparable to the previously reported and calculated results obtained by PLATON (Table 3.1). CH<sub>3</sub>-MOF-5 gives a BET specific surface area of 1685 m<sup>2</sup> g<sup>-1</sup> and a pore volume of 0.69 cm<sup>3</sup> g<sup>-1</sup>. The almost two times smaller experimental pore volume of that compound than that of MOF-5 is smaller than expected from the presence of the CH<sub>3</sub> groups. This can be related to the partial structure interpenetration. The specific surface areas and pore volumes of Br-MOF-5 (840 m<sup>2</sup> g<sup>-1</sup> and 0.36 cm<sup>3</sup> g<sup>-1</sup>) and Cl-MOF-5 (675 m<sup>2</sup> g<sup>-1</sup> and 0.28 cm<sup>3</sup> g<sup>-1</sup>) are also lower than those of CH<sub>3</sub>-MOF-5 and MOF-5. The experimentally obtained values are much lower than the calculated ones, which implies that DEF solvent and uncoordinated ligands, apparently block the pores (see also TGA results below).



Figure 3.3 TGA curves of MOF-5, CH<sub>3</sub>-MOF-5, Br-MOF-5, Cl-MOF-5 measured with heating rate of  $10 \,^{\circ}$ C min<sup>-1</sup> and in a nitrogen atmosphere.

Samples	SSA <sub>Lang.</sub>	SSABET	$\mathbf{V}_{p ext{total}}$	$\mathbf{V}_{p ext{total}^{\mathbf{a}}}$	$N_{H2}^{b}$	$N_{H2}^{c}$
	(m <sup>2</sup> g <sup>-1</sup> )	(m <sup>2</sup> g <sup>-1</sup> )	(cm <sup>3</sup> g <sup>-1</sup> )	(cm <sup>3</sup> g <sup>-1</sup> )	(wt%)	(wt%)
MOF-5	3058	2750	1.15	1.22	1.33	4.7
CH <sub>3</sub> -MOF-5	1855	1685	0.69	1.09	1.42	3.6
Br-MOF-5	947	840	0.36	1.00	1.08	2.0
Cl-MOF-5	751	675	0.28	0.86	0.99	1.9

**Table 3.1** Specific surface areas, pore volumes, low and high pressure hydrogen uptake capacities of MOF-5 and modified MOF-5s.

 $^{\rm a}$  Calculated by PLATON,  $^{\rm b}$  at 77 K and 1 bar,  $^{\rm c}$  at 77 K and 60 bar

#### 3.3.1.3 Hydrogen adsorption.

Hydrogen adsorption isotherms for the samples measured at 77 K and the pressure below 1.3 bar by the volumetric method are presented in the Figure 3.4. MOF-5 and CH<sub>3</sub>-MOF-5 can store 1.33 wt% and 1.42 wt% of hydrogen, respectively. Although CH<sub>3</sub>-MOF-5 possesses lower specific surface area (SSA) it has higher hydrogen uptake capacity below 1.3 bar. For Br-MOF-5 and Cl-MOF-5 lower hydrogen uptake capacities of 1.08 wt% and 0.99 wt% were found. Additionally, all MOF-5s possess very poor hydrogen storage capacities (less than 0.04 wt%) at room temperature and 1 bar, and they follow the same trend as that at 77 K (Figure 3.4). It was reported that reducing the pore size by the introduction of pendant groups can result in increase of the interaction between hydrogen molecules and pore walls at low pressure and moderate temperatures.<sup>31</sup> Therefore it was suspected that functional groups with different size and also different electronic effect (electrondonating or electron-withdrawing) would affect the interactions between hydrogen and modified organic linkers. As can be noticed the value of hydrogen uptake capacity of methyl modified MOF-5, which is the largest, and which is an electrondonating group, is higher than the values of the uptake measured for MOFs possessing electron-withdrawing groups on organic linker. According to PXRD patterns MOF-5 and CH<sub>3</sub>-MOF-5 possess high crystal quality in contrast to Br- and Cl- modified MOF-5s. This indicates that the introduction of the functional group with different electronic character has an effect on the coordination ability of the linker to zinc (II), in this case resulting in poorer crystal quality of Br-MOF-5 and Cl-MOF-5. Additionally the large span of specific surface areas and pore volumes can affect the hydrogen storage capacity. As can be noticed the presented hydrogen uptake capacities for all MOFs (Figure 3.4) are calculated per weight (gravimetric) of the sample. Therefore obviously introduction of the heavy elements into the structure of the framework will decrease gravimetric capacity of the compound. Additionally presence of partially interpenetrated structure in the case of CH<sub>3</sub>-MOF-5 sample, resulting in smaller total pore volume than calculated one, may have influence on the hydrogen storage capacity at low pressure. In the interpenetrating structures the pore size, which in non-interpenetrating MOF-5 is ~ 12 Å, is significantly reduced but the hydrogen accessible internal surface from the interpenetrated cell may still be available.

In order to gain information on the adsorption interaction strengths measurements of the isosteric heat of adsorption ( $Q_{ads}$ ) were performed. Hydrogen uptake measurements at three different temperatures 64 K, 77 K and 100 K (Figure 3.5) were conducted and values of the  $Q_{ads}$  were determined from the slope of the plot  $\ln(p)$  versus T<sup>-1</sup> at a fixed coverage (Figure 3.6). Because the functional groups, especially Br, possess larger mass, which will reduce the hydrogen uptake capacity per gram, the adsorption measurements are presented per mol of the sample to be able to compare the effects of the substituents. As can be seen in Table 3.2 at very low coverage (1 mol of H<sub>2</sub> per mole of the sample) average  $Q_{ads} \sim 3kJ/mol$  and no significant differences in the values of isosteric heat of adsorption for all MOFs (Figure 3.5) is recorded. The strongest adsorption interactions between hydrogen and the framework can be found at low coverage, while at increasing hydrogen loading these more favorable sites are saturated first, leading to a decrease in adsorption energy for the remainder of sites.

Interestingly for methyl modified MOF-5 the heat of adsorption decreases at a bit higher hydrogen loading of 2 or 3 moles which can be related to  $H_2$ - $H_2$  attractive interactions at low coverage (Figure 3.7).



**Figure 3.4** Hydrogen uptake for MOFs measured at 77 K (left) and at room temperature (right).



**Figure 3.5** Hydrogen storage capacities measured at different temperatures of 64 K, 77 K, 100 K for MOF-5, CH<sub>3</sub>-MOF-5, Br-MOF-5, Cl-MOF-5 calculated per mole of the sample.



**Figure 3.6** Estimation of the isosteric heat of adsorption for MOF-5 with 1, 2 and 3 moles of  $H_2$  loaded in the framework. The slopes of the lines and resulting isosteric heat of adsorption are about equal.

 $\label{eq:Table 3.2} The istosteric heat of hydrogen adsorption on MOFs calculated at a coverage of 1 mol H_2 loaded into 1 mol of the compound (unit: kJ mol-1 H_2)$ 

Sample	MOF-5	CH <sub>3</sub> -MOF-5	Br-MOF-5	Cl-MOF-5
Heat of adsorption	-2.8	-2.8	-3.0	-3.0



Figure 3.7 Isosteric heats of adsorption MOF-5, CH<sub>3</sub>-MOF-5, Cl-MOF-5 and Br-MOF-5 at different  $H_2$  loading.

The excess hydrogen uptake, which is obtained after subtraction of the amount of non-absorbed hydrogen gas present in the sample cell at certain pressure, is demonstrated in Figure 3.8. Evaluation of excess uptake is common practice in the literature and it is normally used to compare adsorption properties of microporous materials. MOF-5 almost reaches its saturated uptake capacity of 4.7 wt% at around 60 bars. CH<sub>3</sub>-MOF-5 exhibits 3.6 wt% of hydrogen uptake capacity at 60 bar and still does not reach the saturated uptake capacity. The excess hydrogen uptake capacities of the Br-MOF-5 and CI-MOF-5 samples are 2.0 wt% and 1.9 wt% at 60 bar, respectively. These values are much lower than those obtained for CH<sub>3</sub>-MOF-5 and MOF-5. It is clear that excess hydrogen uptake capacities of all the samples are related to their surface areas and pore volume, which is in agreement with previous results.<sup>32,33</sup>



Figure 3.8 Excess hydrogen storage capacities measured at 77 K.

Table 3.	3 Heats of a	dsorption c	alculated for	or four ads	orption site	es in MOFs	(units: kJ
mol-1)							

Sample	Cup	ZnO <sub>3</sub>	ZnO <sub>3</sub> ZnO <sub>2</sub>	
MOF-5	-6.6	-7.6	-7.0	-4.4
CH <sub>3</sub> -MOF-5	-6.7	-7.7	-6.3	-3.9
Br-MOF-5	-6.9	-8.5	-6.8	-5.1
Cl-MOF-5	-7.0	-9.5	-7.6	-6.0

The effect of the functional groups (-CH<sub>3</sub>, -Br, -Cl) on hydrogen storage capability was investigated computationally. In general weak long range van der Waals interactions are described with limitations with density functional theory (DFT). However, when the generalized gradient approximation (GGA) is implemented good agreement between experiment and simulations can be achieved.<sup>34,35</sup> As was

predicted with inelastic neutron scattering the metal-oxide cluster is predominantly responsible for the adsorption and those sites are occupied first whereas the organic linkers play a secondary role.<sup>8,25</sup> Therefore the values of heat of adsorption (Table 3.3) obtained for Cup, ZnO<sub>3</sub> and ZnO<sub>2</sub> within range 6.3-9.5 kJ mol<sup>-1</sup> for all the MOFs are significantly higher than adsorption energies for benzene ring site. Unfortunately the strongest adsorption sites are saturated very fast because of the limited number of available sites.

The computational study on MOF-5 showed that the role of the organic linkers in the adsorption process increases with rising pressure.<sup>36</sup> As presented in Table 3.3, Cl-MOF-5, according to the calculations, possesses a higher adsorption energy on its adsorption sites; it is 0.4-1.9 kJ mol<sup>-1</sup> higher than those of MOF-5. This calculated outcome may be related to the higher electronegativity of –Cl which reaches 3.16 on a Pauling scale, where the other functional groups -H, -CH<sub>3</sub> and -Br reach 2.20, 2.28 and 2.96, respectively. This apparently leads to a somewhat stronger polarizing power and interaction. Still the presence of the highly electronegative group results in only small improvement of the heat of adsorption and it should not cause large difference in hydrogen uptake capacities measured in the low pressure range. It must be noticed that computational calculations were performed for perfect structures, without defects and at very low coverage (one hydrogen molecule at specific adsorption site).

Experimentally larger coverages were used to reach sufficient sensitivity. The calculated absolute value of the adsorption energies is larger than the experimental one. However, there is only a small difference between the experimental adsorption energies of the materials which is consistent with the calculations. A factor which may also play a role is that ground state relaxation calculations are necessarily performed at 0 K and not at 77 K which reduces impact of the thermal motion of the H<sub>2</sub> on the adsorption energy. Experimentally it is observed that hydrogen already moves through the structure at 77 K, which will average the adsorption interaction to lower absolute values<sup>37</sup> whereas at 15 K most of the molecules remain captured at their sites.<sup>23</sup> Moreover due to steric hindrance from the different hydrogen molecules not all adsorption sites can be occupied simultaneously, lowering the average adsorption energy for higher coverage.

Since the organic linkers were modified with different functional groups, which occupy some space in the framework, it is important to investigate whether such modification has influence on the diffusion of the hydrogen in the framework. In order to do that molecular dynamics simulations with  $10 H_2$  and  $32 H_2$  at 38, 77 and 298 K for MOF-5 and modified MOFs were performed and self-diffusion coefficients were calculated (Table 3.4). The simulation duration after equilibration that was used for the calculation was always 10 ps, which according to Figure 3.8 appears to be long enough for accurate determination of hydrogen self-diffusion coefficient. Hydrogen diffusion coefficients for MOF-5 with 32 H<sub>2</sub> are 6.0x108 m<sup>2</sup> s<sup>-1</sup> and 9.1x10<sup>8</sup> m<sup>2</sup> s<sup>-1</sup> at 38 K and 77 K, respectively and they are similar to previously obtained results.<sup>23</sup> The order of magnitude of the determined self-diffusion coefficient is comparable with experimental results obtained on diffusion of hydrogen in nanostructured carbons like nanotubes where  $D = 2 \times 10^8 \text{ m}^2 \text{ s}^1$  at 38  $K^{38}$  It can be deduced from Table 3.4 that hydrogen self-diffusion coefficients for modified MOF-5s for the different temperatures are slightly lower than that for ordinary MOF-5. It is also clear that the diffusion coefficients decrease with increasing the size of the functional group. CI-MOF-5 having the smallest functional -Cl group shows the highest diffusion coefficient among the three modified MOF-5s at all temperatures. Additionally a concentration dependence of the self-diffusion coefficients was observed for 32 H<sub>2</sub> and 10 H<sub>2</sub>, showing a moderate decrease with increasing hydrogen concentration. This behavior is one of the most common forms of concentration dependence detected in nanoporous materials and arises as a natural consequence of steric hindrance between diffusing hydrogen molecules. The obtained results on the hydrogen self-diffusion coefficient indicate that the pore size of all the MOFs is large enough for free hydrogen transport throughout the porous systems.



Figure 3.9 Mean square displacement for  $32 H_2$  in the MOF-5 at 77 K.

Sample	38 K(10 <sup>8</sup> m <sup>2</sup> s <sup>-1</sup> )		77 K(10 <sup>-8</sup> m <sup>2</sup> s <sup>-1</sup> )		298 K(10 <sup>-8</sup> m <sup>2</sup> s <sup>-1</sup> )	
	32H <sub>2</sub>	10H <sub>2</sub>	32H <sub>2</sub>	10H <sub>2</sub>	32H <sub>2</sub>	10H <sub>2</sub>
MOF-5	6.0	8.5	9.1	22	25	37
Br-MOF-5	5.3	2.2	6.2	14	15	17
Cl-MOF-5	5.4	6.6	7.1	16	22	40
CH <sub>3</sub> -MOF-5	4.6	6.7	6.8	12	13	15

**Table 3.4** Calculated diffusion coefficients of hydrogen on MOF-5 and modifiedMOF-5 at different temperatures.

# 3.3.2 Water stability of methyl modified MOF-5.

One of the important issues when considering MOFs as potential hydrogen storage materials is their sensitivity against moisture. MOF-5 is very sensitive to moisture due to the potential hydration of the -COO group, breaking the bond between the Zn and O in the inorganic unit. The structure distortion caused by only 2.3 % of water molecules in the structure was already observed in the computational study of MOF-5.39 Weak water stability of these compounds causes difficulties in obtaining pure structures and lowers the gas sorption capabilities of the MOFs structure when working with imperfectly dry gas. Recently it was reported that by introducing water repellent functional groups higher water stability in the MOF structure can be reached.<sup>40</sup> Therefore by introducing one or two hydrophobic methyl groups to the organic linker of MOF-5 the structural stability against moistures was investigated in this work. Successfully synthesized materials denoted as CH<sub>3</sub>-MOF-5 and DiCH<sub>3</sub>-MOF-5 were analyzed by means of powder Xray diffraction directly after activation at 160 °C for 24 h in vacuum and after 4 days of exposure to the ambient air. Figure 3.10 demonstrates clearly that the structures of methyl modified MOFs-5 are well retained after 4 days of air exposure whereas the structure of ordinary MOF-5 decomposed already after 1 day in ambient air. This finding shows that hydrophobic methyl groups effectively enhance stability of the MOF-5 structure.

The hydrophobicity is illustrated by TGA, since according to the TGA results MOF-5 modified with two methyl groups adsorbed only 1 % of water after 4 days exposure to air which is about 2 % less that MOF-5 modified with only one – $CH_3$  on the benzene ring. This implies that more hydrophobic groups introduced on the framework more efficiently repels water molecules and can thus also keep the crystal structure intact.



**Figure 3.10** PXRD patterns of CH<sub>3</sub>-MOF-5, DiCH<sub>3</sub>-MOF-5 and MOF-5 before and after exposure to air.

In the next step hydrogen uptake capabilities of the methyl modified MOFs exposed in air were examined. For that first the samples were reactivated at 160 °C for 24 h to remove adsorbed water. As can be seen in the Figure 3.11 the hydrogen storage capacity of CH<sub>3</sub>-MOF-5 after air exposure decreases only about 30 %, in the studied pressure range, compared to the unexposed sample. This result shows that the limited amount of water (about 3 wt%) in the CH<sub>3</sub>-MOF-5 structure still leads to some distortions of the MOF structure. The reactivated DiCH<sub>3</sub>-MOF-5 shows almost the full hydrogen storage capacity of the fresh sample, whereas ordinary MOF-5 lost its hydrogen adsorption ability completely. It can be concluded that substitution of larger amounts of –CH<sub>3</sub> groups results in a remarkably improved water resistance.



**Figure 3.11** Hydrogen storage capacities of CH<sub>3</sub>-MOF-5, DiCH<sub>3</sub>-MOF-5 and MOF-5 before and after (indicated by -4d or -24h) exposure to air.

## **3.4 Conclusions**

Experimental and computational studies on structural and hydrogen storage properties of mono-substituted MOF-5 derivatives were performed. Three different functional groups -CH<sub>3</sub>, -Br, -Cl were introduced on the organic linker of MOF-5. Crystal structure quality and hydrogen adsorption capability of the modified MOFs were significantly altered. MOFs modified with electron-withdrawing groups (-Br, -Cl), result in relatively poor crystal quality and associated lower hydrogen storage capacity at low and at high pressure, in contrast with MOF-5 and CH<sub>3</sub>-MOF-5. Methyl modified MOF-5 showed the highest hydrogen storage capacity at 77 K and pressures below 1 bar. In general modification of the organic linker does not have significant effect on the average experimental heat of adsorption of the analyzed structures. Also computational results demonstrate that strong electronegativity of the -Cl and -Br has only limited impact on adsorption energies calculated at very low coverage. Diffusion of the hydrogen in the MOFs is influenced by spatial hindrance by larger side groups or by increasing the hydrogen loading which makes the self-diffusion coefficient decrease. Water stability of MOF-5 was successfully improved by introducing hydrophobic methyl groups on the benzene ring. This is an important finding for applicability of these materials, which allows for better protection of moisture sensitive MOFs structures from unwanted decomposition.

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# Chapter 4

# Irreversible high-temperature hydrogen interaction with the metal organic framework Cu<sub>3</sub>(BTC)<sub>2</sub>

The chapter is based on the published article: **Grzech A.**, Yang J., Dingemans T.J., Srinivasan S., Magusin P.C.M.M., Mulder F. M., *J. Phys. Chem. C*, **2011**, *115* (43), 21521.



Unsaturated metal coordination sites in metal organic frameworks (MOFs) offer preferential hydrogen adsorption sites. In addition MOFs can be applied as scaffolds for nano metal hydrides operating at elevated temperatures. For these reasons the thermal stability of the framework with unsaturated Cu<sup>2+</sup> coordination sites in a hydrogen atmosphere has been investigated in Cu<sub>3</sub>(BTC)<sub>2</sub>. It is found that Cu<sub>3</sub>(BTC)<sub>2</sub> irreversibly binds 1.1 wt% of hydrogen at the temperatures between 323 – 423 K and 2 bar H<sub>2</sub> pressure, which corresponds to three hydrogen atoms per BTC ligand. In accordance, FT-IR and NMR spectroscopy show that the BTC linkers are converted into their acid form, while XRD reveals the presence of reduced Cu<sup>0</sup> metal particles and decomposition of the framework. When designing more strongly interacting MOFs for H<sub>2</sub> storage applications or as template for light metal hydrides one has to take possible reduction of the metal centers and the stability of the lattice into account.

# 4.1 Introduction

Porous metal-organic framework (MOF) materials are capable of fast reversible adsorption of hydrogen at low temperature (~77 K), with volumetric storage densities that reach at pressures of 100 bar up to 80 % of that of liquid hydrogen at 20 K.<sup>1</sup> The volumetric density of hydrogen stored as molecules in a MOF is lower than that of, for example, atomic hydrogen in metal hydrides but the advantage is that the hydrogen is stored and released quickly. In fact, much research in the area of hydrogen storage in MOFs is devoted to enhance the adsorption interaction with hydrogen, such that the operating temperatures and pressures can be closer to ambient conditions. The low adsorption heat (typically 3 - 7.5 kJ mol<sup>-1</sup> H<sub>2</sub>)<sup>2 3</sup> would preferably be increased towards 15 - 20 kJ mol<sup>-1</sup> H<sub>2</sub>.<sup>4</sup> Interestingly, in this respect, molecular hydrogen binds relatively strongly to exposed metal ions with incomplete coordination in metal organic frameworks.<sup>5</sup> <sup>6</sup> Such is the case in, for example, Cu<sub>3</sub>(BTC)<sub>2</sub>. This is a metal-organic framework that consists of Cu<sup>2+</sup> ions, which together with oxygen atoms create a so-called paddle-wheel unit as a secondary building unit (SBU). This unit is connected through the 1,3,5benzenetricarboxylate (BTC) ligands into a cubic network with open pores. In the as-synthesized compound the residual axial coordination sites are filled by weakly bound water molecules, which can easily be removed by heat treatment under vacuum. In contrast to other MOFs, like MOF-5,  $Cu_3(BTC)_2$  has open metal sites which are able to interact as strong hydrogen adsorption sites. The Lewis acid copper (II) sites polarize the hydrogen molecule and as a result increase the interaction between the copper (II) ions and hydrogen. In the present investigation the reactivity of such interaction sites is studied. Here it will be shown that such enhanced interaction enables the dissociative chemisorption of the hydrogen to the BTC linkers, thereby resulting in the collapse of the metal organic framework. The experimental hydrogenation process of the metal-organic framework  $Cu_3(BTC)_2$  at temperatures up to 423 K is studied. The results can be rationalized by the notion that  $Cu^{2+}$  with electronic configuration d<sup>9</sup> is capable of splitting H<sub>2</sub> molecules followed by hydrogen transfer to the BTC linkers. In the past reduction of pure CuO to Cu was observed in hydrogen atmosphere at the temperature of 553 K.<sup>7</sup>

As an alternative to surface adsorption materials, light metal hydrides as storage medium generally have slower kinetics of hydrogen sorption<sup>8</sup> <sup>9</sup> and are only reversibly operated at elevated temperatures. They have significant absorption heat required or expelled during sorption (50-80 kJ mol<sup>-1</sup>  $H_2$ ). In order to improve the light metal hydride operating conditions one aims at lowering enthalpies of formation down to  $\sim 40 \text{ kJ}$  mol<sup>-1</sup> H<sub>2</sub>. In this respect hybrid materials consisting of a porous framework with small light metal hydrides incorporated are an alternative approach, which might have improved operating conditions. Recently there has been a growing interest in using porous carbons, silica and metal-organic frameworks as a template for metal nanoparticles in order to investigate the potential application in hydrogen storage, catalysis and sensing. So far a number of well-known metal-organic frameworks such as MOF-5, MOF-177, MIL-101 and Cu<sub>3</sub>(BTC)<sub>2</sub> have been reported as support for metals such as Pd, Ru, Cu, Au, Pt and Au with different incorporation techniques.<sup>10 11 12 13 14 15 16 17</sup> In the hydrogen storage field improvement of the hydrogen capacity at room temperature was achieved by, for example, Pd incorporation into MOF-5<sup>11</sup> or Pt into MOF-177.<sup>11,18</sup> The porous host materials can impose a space confinement of the metallic particles, allowing the formation of nanoparticles with specific sizes and shapes controlled by the pore

structures of the framework. This approach may limit the growth of the nanoparticles trapped inside the pores by preventing Ostwald ripening of the metals and/or hydrides. The nanoscale of the metal hydrides is known to alter thermodynamic properties as well as to enhance the reversible hydrogen uptake.<sup>19</sup> Similar effort was also taken to confine NaAlH<sub>4</sub> particles into Cu<sub>3</sub>(BTC)<sub>2</sub>.<sup>20 21</sup> However, previous research in this field is limited to the synthesis of the metal particles incorporated in the Cu<sub>3</sub>(BTC)<sub>2</sub> framework and dehydrogenation process in case of NaAlH<sub>4</sub>. To the best of our knowledge there is no research which indicates reversible storage of hydrogen in those systems. However, in view of the present study one has to realize that an important issue of the space confinement in such porous host is the thermal and chemical stability of the framework itself at the operating conditions applied. The result will be that the idea of using MOF with unsaturated metal sites for space confinement of metal hydrides (MgH<sub>2</sub>, NaAlH<sub>4</sub>) which absorbs hydrogen at relatively high temperature appears rather unreasonable.

# 4.2 Materials and methods

Cu<sub>3</sub>(BTC)<sub>2</sub> was purchased from Sigma-Aldrich and further cleaned from adsorbed water and activated in an Ar glovebox with H<sub>2</sub>O and O<sub>2</sub> levels below 0.1 ppm by heating for 4 hours at the temperature of 473K. The structure of the material after activation was determined by powder X-ray diffraction (PXRD) using PANalytical X'Pert Pro PW3040/60 diffractometer with Cu Ka radiation operating at 45 kV and 40 mA. The measurements were performed at room temperature with an airtight Kapton covered sample holder. Thermal stability of the sample was evaluated by thermogravimetric analysis on a TG/DTA-7 Pyris Diamond (PerkinElmer) under a dry nitrogen flow at a heating rate of 10 °C min<sup>-1</sup> and also by long-term temperature dependent X-ray diffraction measurement performed in vacuum. Volumetric hydrogen uptake measurements were performed on a Sievert apparatus on an activated sample at temperatures from 77 up to 423 K. Activated Cu<sub>3</sub>(BTC)<sub>2</sub> was loaded in the glove box under Ar atmosphere into sample container made of stainless steel with a copper O-ring, and connected with a thin capillary for

hydrogen access. Additional degassing and Ar removal was performed at elevated temperature (423 K) under high vacuum (down to  $10^{6}$  mbar). The sample container was immersed in liquid nitrogen to reach the temperature of 77 K. The sample was loaded gradually up to the hydrogen pressure of 2 bar. The amount of hydrogen loaded was determined volumetrically from the pressure drop in a calibrated volume at room temperature. Correction was made for the free volume of the capillary and the empty volume in the sample container by subtracting the amount of hydrogen measured at 77 K in a sample holder filled with a volume of non-adsorbing material corresponding to the volume of the sample. The airtight sample holder filled with the sample in the glove box was heated up to 423 K in three steps starting at 323 K. At each step:  $323 \pm 2$  K,  $373 \pm 2$  K and  $423 \pm 2$  K a hydrogen pressure of 2 bar was applied to the system and hydrogen uptake was measured. After the hydrogen uptake measurements the hydrogenated sample was analyzed with X-ray diffraction.

To obtain information about the location of chemisorbed hydrogen in the structure, FT-IR Spectroscopy was performed on a FT-IR Spectrophotometer Perkin-Elmer Spectrum 100 series, with measuring range of 7800 to 370 cm<sup>-1</sup>. The hydrogenated sample was transferred for the IR measurement without exposure to air while during the IR measurement the exposure to air was kept short, therefore contamination with water is not expected and (also not visible in FT-IR spectrum).

<sup>1</sup>H MAS NMR measurements of ordinary and hydrogenated Cu<sub>3</sub>(BTC)<sub>2</sub> were performed on a Bruker DMX500 spectrometer operating at a <sup>1</sup>H NMR frequency of 500 MHz and equipped with a 2.5-mm MAS probe head. As a reference (0 ppm) for the chemical shift calibration tetramethylsilane (TMS) was used. All the samples were transferred in air tight bottles under Ar and packed in a MAS sample holder and closed inside an Argon glove box with oxygen level below 1 ppm. The sample holders were rotated inside the probe head using a dry nitrogen flow at a sample spinning rotation rate of 15 kHz.

#### 4.3 Results and discussion

#### 4.3.1 Thermal stability of Cu<sub>3</sub>(BTC)<sub>2</sub>



**Figure 4.1** Thermogravimetric analysis (TGA) of  $Cu_3(BTC)_2$ . The thermogram was obtained in a nitrogen atmosphere and using a heating rate of 10 °C min<sup>-1</sup>.

In order to determine the thermal stability and the required activation temperature of the as purchased Cu<sub>3</sub>(BTC)<sub>2</sub> thermogravimetric analysis (TGA) (Figure 4.1) and temperature dependent Powder X-ray diffraction (PXRD) were evaluated. The TGA results indicate that at the temperature of 473 K water molecules (23 wt.%) was already removed from the framework, which is in agreement with previously reported data.<sup>22</sup> The second weight loss event was observed at 593 K indicating that above this temperature framework decomposition occurs.



Figure 4.2 Temperature dependent PXRD of Cu<sub>2</sub>(BTC)<sub>3.</sub>

PXRD experiments performed on previously activated  $Cu_3(BTC)_2$  (Figure 4.2) with elevated temperatures from room temperature up to 573 K show that the compound does not decompose under the given conditions. This result is consistent with the above interpretation of the TGA results and confirms thermal stability of the activated compound. These two individual measurements, TGA and PXRD, show that thermal treatments up to 573 K do not cause irreversible or other changes in the structure of the framework. These results from TGA and PXRD are in good agreement with data reported in literature for this compound.<sup>22</sup>



## 4.3.2 Hydrogen loading at 77 K and above room temperature

Figure 4.3 Low temperature hydrogen adsorption of Cu<sub>3</sub>(BTC)<sub>2</sub>.

Figure 4.3 shows the low pressure adsorption isotherm collected on the volumetric Sievert apparatus at 77 K, with a hydrogen capacity of 2.55 wt% at a pressure of 1 bar. This result is similar to that of 2.6 wt% at 77 K and pressure of 1.01 bar obtained previously by Rowsell and Yaghi.<sup>2</sup>



Figure 4.4 High temperature hydrogen sorption of Cu<sub>3</sub>(BTC)<sub>2</sub>.

The same sample was subjected to initially a 2 bar hydrogen pressure at temperatures higher than room temperature in the Sievert apparatus. At 323 K this results in a reduction of the pressure with time, i.e. a small hydrogen uptake as can be seen in Figure 4.4. Another two doses of 2 bars of hydrogen were applied at 373 K and 423 K. The result is a total uptake at temperatures above room temperature of 1.1 wt% over the complete adsorption measurement during three days. The recorded amount of around 1.1 wt% of hydrogen in the Cu<sub>3</sub>(BTC)<sub>2</sub> framework corresponds to three hydrogen atoms per BTC linker molecule. To analyze the changes in the MOF structure directly after the sorption measurement powder X-ray diffraction was performed.

4.3.3 Analysis of the hydrogenated Cu<sub>3</sub>(BTC)<sub>2</sub>



**Figure 4.5** PXRD of activated (blue) and hydrogenated (black) Cu<sub>3</sub>(BTC)<sub>2</sub>. The asterisks indicate reflections that correspond to Cu<sup>0</sup> nano-particles.

The powder X-ray diffraction pattern (Figure 4.5) of hydrogenated copper-based MOF shows an overall decrease in peaks intensity in comparison to as synthesized and activated  $Cu_3(BTC)_2$  sample, and complete alteration of the pattern. This result indicates the loss of crystallinity and the framework collapse. Next to the decomposed structure, broad reflections are visible at  $2\theta = 43$ , 51 and 74°, which are indicative of the presence of large amounts of nanoscaled copper(0) particles with cubic structure (a = 3.61 Å). Because the high temperature heat treatment is performed in a reducing hydrogen atmosphere, copper metal particles rather than  $Cu_2O$  are produced. In contrast,  $Cu_2O$  is formed when  $Cu_3(BTC)_2$  is decomposed in air.<sup>22</sup> Clearly, upon hydrogenation the porous  $Cu_3(BTC)_2$  structure is destroyed and as a consequence is no longer able to physisorb hydrogen molecules.

To explain the observed reaction with  $H_2$  and collapse of the structure, three reaction schemes could be considered. Hydrogen may bind to the benzene ring to form a cyclohexane body as a linker. Another possibility is a reaction of hydrogen

with the oxygen from the CuO clusters to form water vapor. This reaction will cause the linker to detach from the copper base and collapse the structure to form amorphous material, i.e. the linkers with copper particles. The third possibility is the reaction of hydrogen with the carboxylate functionality (-COO) on the benzene rings, forming the carboxylic acid group functionalities (-COOH). In all cases the presence of active centers in the structure is required, which promote the hemolytic bond cleavage of the hydrogen molecules. To gain insight into which kind of organic species the 1.1 wt% of the hydrogen becomes fixated FT-IR and NMR were performed.



Figure 4.6 FT-IR spectra of activated (blue) and hydrogenated (black) Cu<sub>3</sub>(BTC)<sub>2</sub>.

The changes in the hydrogenated  $Cu_3(BTC)_2$  FT-IR spectra (transmission mode) are shown in Figure 4.6. In the spectrum of the hydrogenated sample four new band frequencies characteristic for the presence of carboxylic acid groups were found. The v(O-H) bending and stretching frequencies are located at 904 cm<sup>-1</sup> and in the region 3000-2500 cm<sup>-1</sup> respectively. A relatively narrow and sharp band, centered around 1694 cm<sup>-1</sup>, is indicative of the carboxylic acid v(C=O) stretching mode. The band at 1270 cm<sup>-1</sup> is associated with the v(C-O) stretching mode. The existence of those four extra modes in the infrared spectrum of hydrogenated sample in comparison with the spectrum of Cu<sub>3</sub>(BTC)<sub>2</sub> before hydrogenation provides clear evidence for the presence of the carboxylic acid groups at the benzene ring. Water molecules, if present, should vibrate at 1643 cm<sup>-1</sup>, 2127 cm<sup>-1</sup> and 3404 cm<sup>-1</sup>. However, for both measured samples, bands at mentioned frequencies do not appear. This indicates that for the hydrogenated sample the hypothesis of significant water molecule formation from absorbed hydrogen and the CuO clusters can be excluded, and that the activated sample indeed has lost its water.



Figure 4.7 1H NMR spectra of activated (a) and hydrogenated (b) Cu<sub>3</sub>(BTC)<sub>2</sub>.



**Figure 4.8** <sup>1</sup>H NMR spectra of ordinary  $Cu_3(BTC)_2$  with a  $T_1$  filter time of 10 ms (a) and 500µs (b).

As a further characterization <sup>1</sup>H MAS NMR was used as an analyzing tool for the identification of the absorbed hydrogen in the hydrogenated  $Cu_3(BTC)_2$  sample. Measurements were performed for both activated and a hydrogenated sample (Figure 4.7 and Figure 4.8). The spectrum measured for ordinary  $Cu_3(BTC)_2$  is characterized by two peaks, with relatively low intensity in comparison with hydrogenated sample. The low intensity results from the strong paramagnetic relaxation induced at the framework atoms by the presence of  $Cu^{2+,23}$  The signals at  $\sim$  9 ppm and 2 ppm can be associated respectively with the hydrogen on the benzene ring and some traces of DMF used during synthesis that is still present in the pores of the framework. The hydrogenated  $Cu_3(BTC)_2$  has a strongly altered spectrum. The central peak of the <sup>1</sup>H MAS NMR spectrum at 8.1 ppm is still assigned to the benzene ring protons of the BTC linker. The low peak at ca. 5 ppm present in the proton NMR spectrum is usually assigned to traces of water molecules, indicating that here not all water was removed. Finally, the peak positioned at around 14 ppm in the spectrum of the hydrogen-chemisorbed sample can be assigned to protons from carboxylic acid groups. This confirms the FT-IR observation of such moieties. Additionally the acid proton signals have roughly the same peak area as the aromatic protons, indicating that approximately all carboxylate (-COO<sup>-</sup>) groups are converted to carboxylic acid (-COOH) groups. The measurement for the non-hydrogenated Cu<sub>3</sub>(BTC)<sub>2</sub> sample with two T<sub>1</sub> filter times (Figure 4.8) illustrates the short relaxation time induced by the presence of paramagnetic Cu(II) in the structure. In the intact structure the paramagnetic Cu<sup>2+</sup> suppresses the NMR signals of the organic component, which is not the case in the hydrogenated material, which is in agreement with the formation of non magnetic Cu particles. Some H<sub>2</sub>O was still present in this sample, adsorbing near the Cu<sup>0</sup> ions, yielding a signal at ~ 12 ppm.

The combined results of XRD, NMR and FT-NMR indicate that the MOF structure has disintegrated, and that there are only free or dangling linkers next to the copper metal particles present.

It is known from literature that a hydrogen molecule when adsorbed on some metal surfaces can show chemical activity leading to splitting of H<sub>2</sub> and subsequent hydrogenation reactions. According to Vol'pina and Kolomnikova<sup>24</sup> the activation of the hydrogen may take place on a single metallic center or on two such centers. The dissociative H<sub>2</sub> chemisorption by the metal center is an activated process and the activation energy must be delivered to the molecule for the dissociation to occur, as is evidenced here from the increased hydrogenation at higher temperatures. Transition metals such as copper have in general partially filled dorbitals and they can accept an *s*-electron from a hydrogen atom. In this case local *s*  $\rightarrow$  d transfer occurs where the difference in the energies between the d-orbitals and the next vacant s-orbitals is comparatively small. At the same time the repulsive Pauli forces are much weaker on the transition metals than on simple metals. Depending on the transition metal the physisorption state can disappear and the hydrogen molecule can directly enter into a chemisorption regime. Next to the presence of suitable vacant orbitals with sufficiently low energy another important factor is the nature of the ligands attached to the metal ions. The probability of dissociative splitting of the hydrogen molecule is higher if the metal ion is attached to basic ligands which can play a role of proton acceptors<sup>25</sup>, such as is the case here.

In the current work the presence of the open metal sites  $Cu^{2+}$  in the  $Cu_3(BTC)_2$  compound gives stronger interactions with the hydrogen molecules at low temperature during physisorption. When the temperature is increased above room temperature, the dissociation probability rises, since the vibrational and rotational energy of the hydrogen molecule will rise and the electron transfer between dissociated H<sub>2</sub> and Cu<sup>2+</sup> is possible in the process. The overall reaction for this hydrogenation process can be summarized as follows:

$$Cu_3(BTC)_2 + 3H_2 \xrightarrow{T > 295K} 2H_3BTC + 3Cu$$
(4.1)

The ability of Cu<sup>2+</sup> to break the bonds of the hydrogen molecule and absorption of the dissociated parts of the hydrogen molecule is possible because of the conducive electron configuration of copper. The observation of such effect in Cu<sub>3</sub>(BTC)<sub>2</sub> indicates that care should be taken with designing MOF-based hydrogen storage materials with open transition metal sites, since too strong interactions open up the possibility to destructive reactivity. Also the use of such MOF's as template for light metal hydrides is limited due to such reactivity at elevated temperature under hydrogen.

# 4.4 Conclusions

The  $Cu_3(BTC)_2$  metal-organic framework has been investigated during the remarkable irreversible hydrogenation process at temperatures above room temperature. Instead of physisorption, which is the common process in a MOF system at low temperature, the hydrogen dissociates on the Cu(II) sites and reacts chemically, resulting in three hydrogen atoms per organic BTC linker and metallic Cu<sup>0</sup> nanoparticles. FT-IR and NMR results confirm the presence of 1,3,5-benzenetricarboxylic acid, resulting from the hydrogenation of the BTC linkers. The obtained results indicate that the design of MOF's with exposed metal-ion sites for increased hydrogen interaction can actually show interactions strong enough to cleave the hydrogen molecule. Furthermore the application of the investigated compound as space confinement porous host for reversible light metals hydrogen

storage materials may be excluded. The presented results might also be helpful to understand the irreproducible data of dissociated hydrogen absorption in porous materials via the spillover technique.<sup>26</sup>

# 4.5 References

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## Chapter 5

# Long range van der Waals interactions as probed by hydrogen adsorption in large pore silica's

The chapter is based on the submitted article:

**Grzech A.**, Yang J., Glazer P.J., Dingemans T.J., Mulder F.M., submitted to *Microporous and Mesoporous Materials* 



The low temperature hydrogen adsorption capacity of mesopores silica aerogel was investigated and compared with that of other large pore silica based materials (MCM-41, HMS) within a range of surface area and pore sizes. The hydrogen uptake of the aerogel measured at pressure of 1 bar and a temperature of 77 K is around 2.5 times lower than that of MCM-41, although it has a comparable specific surface area (just 25% smaller). The explanation found is the relation between lower hydrogen heat of adsorption and larger pore size for the investigated materials, which leads to higher surface coverage in the smaller pores.

#### 5.1 Introduction

Climate changes arising from global warming give the strong signal that gradual shift to environmental friendly renewable energy sources is required. Hydrogen is a promising replacement for fossil fuels as a clean, low emission energy carrier, which is renewable and abundant in nature. The systems presently considered for hydrogen storage are: liquefied hydrogen at low temperature, high pressure tanks, chemisorption in metal hydrides or physisorption on high surface area adsorbents. In the case of physisorption processes, hydrogen molecules adsorb on the surface of adsorbent due to the van der Waals interactions.<sup>1</sup> As the interactions between adsorbate and adsorbent are weak, typically less than 10 kJ mol<sup>-1</sup>, the process takes place at low temperatures, preferably at 77 K. Wide varieties of porous materials have already been developed and investigated. The most well-known examples are carbon-based materials like carbon nanostructures, graphitic nanofibers<sup>23</sup>, amorphous activated carbon<sup>4</sup> and zeolites<sup>5,6</sup>, while recent intensive research focuses on metal organic frameworks<sup>7.9</sup> and silica-based materials.<sup>10</sup> All those materials exhibit large surface area with varying pore sizes ranging from 0.2 to about 3.5 nm. It has been reported that for carbon-based porous materials hydrogen storage capacity shows good correlation with the specific surface area and with the pore volume both at room temperature and at 77 K.<sup>11,12</sup> Similar correlations were also found for zeolites and Prussian blue analogues.513,14 Moreover this correlation seems to be independent from the type of investigated nanostructures, as it was also found for hydrogen uptake in metal organic frameworks at medium

pressure.<sup>15</sup> The correlation found between maximum storage capacity and effective surface areas indicates that a large surface area is a necessary condition to obtain high hydrogen storage capacity for those materials.<sup>16</sup> However, it is important to stress that towards the lower applied pressure limits the adsorption energies play the most important role, while at high pressures the pore volume of adsorbent is crucial.

The aim of this work is to investigate whether the relation between surface area and pore volume can be extended to hydrogen uptake in very large pores of in this case silica based materials. More specifically we are interested in observing the adsorption characteristics in the limit of extending to significantly larger pore sizes than conventionally considered, i.e. extending the range towards 20 nm.

#### 5.2 Methods and materials characterization

The experimental work was performed on silica's MCM-41 (Mobil Crystalline Material no. 41), HMS (Hexagonal Mesoporous Silica) and an aerogel. The MCM-41 and HMS, with specific surface area of ~ 1000 m<sup>2</sup> g<sup>-1</sup> and 910 m<sup>2</sup> g<sup>-1</sup> respectively, were purchased from Sigma-Aldrich. Porous silica aerogel, with particle size of around 1 mm, was purchased from CABOT Corporation. This investigated aerogel possesses large effective surface area of ~ 600-800 m<sup>2</sup> g<sup>-1</sup>, which is thus similar to the surface area of the other two materials. The pore size of the chosen materials as given by the manufacturers is ~2.3 nm for MCM-41, ~3.9 nm for HMS, and ~20 nm for the aerogel respectively. Silica is chosen because it provides largely varying pore sizes with only Si and O as building blocks, i.e. a chemically similar pore surface. MCM-41 and HMS are mesoporous materials that belong to a molecular sieves family that forms hexagonal, cubic or wormhole like arrays of pores respectively. The pore walls of aerogel, MCM-41 and HMS are amorphous, but the high regularity of the pore distribution in the material generates a diffraction peak at low scattering angles ~ 3°20 (Figure 5.1).



Figure 5.1 XRD patterns of aerogel (black) HMS (blue) and MCM-41 (red).

Silica aerogel was chosen as a representative of the silica family, with a high surface area just as the other microporous materials, but in contrast to the other materials, possesses an extremely large pore sizes. According to our knowledge its hydrogen storage characteristics have not been reported yet, although the aerogel is well known as an efficient adsorbent of e.g. oils and some organic liquids.<sup>17</sup> In any case the low volumetric density limits its practical applicability.

Macroscopic properties of silica aerogel, like bulk density or pore volume, can differ within a wide range which is caused by the different synthesis mechanisms. Therefore structural data give limited information. The porous structure of this silica gel is obtained by sol-gel reaction. In the first phase of this process (sol), colloidal particles are dispersed in a liquid whereas in the second phase (gel) solid network filled with a liquid exist. In the next step the liquid from the pores is removed by solvent exchange with CO<sub>2</sub> followed by supercritical drying, which results in branched silica networks. By varying the drying procedure of "wet" gels different types of silica gel may be formed. For example xerogel is created by increasing temperature or decreasing pressure during drying and cryogels are formed during freeze drying method as described in literature.<sup>18</sup>

The investigated aerogel is a very light (bulk density 90-100 kg m<sup>-3</sup>), amorphous (Figure 5.1) and porous material (90% porosity). The structure of aerogel is very irregular, as illustrated on the electron micrographs presented in Figure 5.2. The material is mesoporous with well-accessible, cylindrical, branched, relatively large pores. It may be remarked here that besides adsorption studies, the large pore size and extremely low density could make it a promising candidate as a supporting material, similar to mesoporous materials like HMS and MCM-41 which were already used as a space confinement for metal nanoparticles.<sup>19</sup>



Figure 5.2 SEM images of silica aerogel.

Volumetric hydrogen uptake measurements for aerogel, HMS and MCM-41 were performed on a home built Sievert apparatus. The sample was loaded into the sample container made of stainless steel with a copper O-ring, and degassed at temperature of 150 °C for prolonged periods of time (days) under high vacuum (10-6 mbar).

The system was then immersed in a liquid nitrogen Dewar to reach the temperature of 77 K. The amount of hydrogen loaded was determined volumetrically from the pressure drop in a calibrated volume at room temperature. Additional hydrogen uptake experiments at 55 K and 64 K were performed for heat of adsorption determination. A correction was made for the free volume of the capillary and the empty sample chamber by performing a blank experiment for all the temperatures with a non-adsorbing material.

#### 5.3 Results and discussion

#### 5.3.1 Hydrogen adsorption properties at 77 K

Hydrogen adsorption isotherms measured for the aerogel, HMS and MCM-41 at 77 K and pressure of 1 bar (Figure 5.3) show hydrogen uptake of 0.21 wt%, 0.40 wt% and 0.52 wt% respectively.



**Figure 5.3** Low pressure total hydrogen uptake of aerogel (black), HMS (red) and MCM-41 (blue) at 77 K after correction for the empty volume in the sample container.

Despite the fact that MCM-41, HMS and aerogel have similar surface area they show significant difference in hydrogen storage capacity. Figure 5.3 illustrates that the aerogel, with only slightly lower surface area than that of HMS, shows around two times lower hydrogen storage capacity. In addition the aerogel has only around 25% smaller specific surface area than that of MCM-41, but its hydrogen uptake is around 2.5 times smaller.

The hydrogen uptake capacity against surface area and pore size was plotted for the materials (Figure 5.4). The correlation between hydrogen uptake and surface area of silica based materials is clearly linear but with a line that does not extend through the origin. As can be seen in Figure 5.4b the hydrogen uptake and the materials pores size can be placed on an asymptotic line at 77 K and 1 bar. To exclude the contribution of hydrogen uptake from extra surface area, hydrogen uptake per specific surface area was plotted against pore size in Figure 5.5. This also shows an asymptotic correlation.



**Figure 5.4** Hydrogen uptake capacity at 77 K and 1 bar plotted against surface area (left) and pore size (right) for silica materials. The lines are a guide to the eye.



**Figure 5.5** Hydrogen uptake capacity at 77 K per specific surface area (SSA) plotted against pore size for silica materials. The line is a guide to the eye.

The local Si-O structural chemical features are expected to be similar for the materials investigated since the synthesis follows similar chemical routes with only differences in resulting pore size. Thus these figures (Figure 5.4 and Figure 5.5) illustrate that it is conceivable that this phenomenon is related to the different van der Waals potential acting on hydrogen molecule inside the pores.

#### 5.3.2 Determination of the heat of adsorption

In order to determine the heat of adsorption experimentally, hydrogen uptake measurements at three temperatures 55 K, 64 K and 77 K (Figure 5.6) were performed. Using methods earlier described in<sup>20</sup> the isosteric heat of adsorption due to the weak van der Waals interactions is obtained. The absolute values of the isosteric heat of adsorption are:  $2.07 \pm 0.21$  kJ mol<sup>-1</sup> for MCM-41,  $1.75 \pm 0.4$  kJ mol<sup>-1</sup> for HMS and  $1.68 \pm 0.15$  kJ mol<sup>-1</sup> for aerogel respectively, estimated at a hydrogen concentration of 0.3 wt%. There are thus differences between the different samples

with different pore sizes where the largest pore size aerogel shows a significantly lower value than the smallest pore size MCM-41. Previously the values of the heat of adsorption were studied for compounds like MOFs with smaller pore size than discussed here.<sup>21</sup> In these MOF-s there is, apart from the smaller and varying pore sizes, also large chemical variety present, which is unlike the situation for the silica studied here.



Figure 5.6 Hydrogen uptake capacity of all silica's measured at different temperatures.

#### 5.3.2 Heat of adsorption and surface coverage relation

To determine the influence of such adsorption interaction difference one can estimate the following. In the Langmuir description of surface adsorption a dynamic equilibrium of molecules in the gas phase and molecules adsorbed on the surface is assumed. The time spent by hydrogen molecules in the adsorbed phase (residence time  $\tau$ ) is related to heat of adsorption *Q*:

$$\tau = \tau_0 e^{Q/kT} \tag{5.1}$$

In addition in the Langmuir description a basic assumption is that  $\sigma = n(1-\sigma/\sigma_0) \tau$ where  $\sigma$  is the surface coverage,  $\sigma_0$  the available amount of surface adsorption sites for a monolayer adsorption, and n is the flux of molecules flying towards the surface. For low coverage this reduces to  $\sigma = n\tau$ . For the same pressure and temperature *n* is fixed and the residence times  $\tau$  determine the coverage. Now we can estimate a ratio of residence times of MCM-41 ( $\tau_{MCM-41}$ ) and aerogel ( $\tau_{aerogel}$ ) at temperatures of 55, 64 and 77 K using the different observed Q values, and assuming that  $\tau_0$  is the same. From the calculations at each temperature we obtain  $\tau_{MCM-41}$ :  $\tau_{aerogel} = 2.35$ , 2.07 and 1.85, respectively which means that the residence time for hydrogen molecules adsorbed in MCM-41 is about two times longer than that for the aerogel. If the size of pores is relatively big the molecules may collide with the wall of the capillary, evaporate immediately and collide again. If the size of the pores of adsorbent is smaller the collision of the molecules with the walls and adsorption happens with higher frequency than in the previous case. Since the size of the pores is smaller the time spent in adsorption phase is longer. In the case of very small capillaries the chance of adsorption is significantly bigger and the amount of the adsorbed gas is greater due to the overlapping of van der Waals potentials.22

For larger coverage the number of accessible sites becomes important. However, since the same fundamental building block (silica) is used for the materials the number of accessible sites  $\sigma_0$  is the same. The adsorption isotherms at pressures up to 1 bar are far from saturated, i.e. the system is still far from saturating the available sites. It can thus be deduced that the more negative heat of adsorption of MCM-41, and the associated two times longer residence time than for the aerogel, are responsible for the two times larger adsorption in MCM-41 per SSA at 77 K and 1bar. If the values of heat of adsorption (Q) would be the same for aerogel and MCM-41 only the ratio of adsorbed molecules to free molecules would change

according to surface/volume ratio. Since here the Q is not the same the ratio of adsorbed/free molecules changes more than surface/volume ratio.

Recently Afanasiev and Minogin showed that for a concave cylindrical surface the van der Waals energy potential (Equation 5.2) of an atom placed inside infinite submicrometer-size cylinder can be up to four times larger ( $\mu = 4$ ) than that for an atom placed in the vicinity of a flat surface, and two times ( $\mu = 2$ ) larger than for an atom placed in between two parallel flat surfaces.<sup>23</sup> The submicrometer-size cylinder regime is satisfied for cylinders with radius around twice as big as the distance between atomic dipole and concave surface of the cylinder.

$$U = -\frac{C_3}{x_0^3} \ \mu \tag{5.2}$$

where:  $C_3$  – van der Waals coefficient,  $x_0$  – distance between gravity center of molecule and adsorption surface,  $\mu$  - internal cylindrical surface factor

If the radius of the cylinder is much bigger than the distance from the molecule to the center of the cylinder, the interactions between molecule and the walls of the cylinder can be simplified to the interactions of the molecule with a flat surface. However when the cylinder size reduces additional interactions between the molecule and surrounding cylinder have to be taken into account and in that case the van der Waals potential energy increases up to a factor of four.

When the hydrogen molecules adsorb on the surface of the adsorbent, for a homogeneous body with no special adsorption sites, all molecules are in the same close distance ( $x_o$ ) from the surface. Therefore, the force that acts on the hydrogen molecule at the surface should have the same value for all investigated materials. However, the molecules are also interacting with the surrounding and opposite walls of the pore and those latter interactions will depend on the size of the pore. The van der Waals energy potential acting on an adsorbed molecule, as a function

of distance from the concave cylindrical surface, is proportional to  $1/x_0^3$ , where  $x_0$  is

the distance between center of gravity of the molecule and adsorption surface.<sup>23</sup> If we assume that the adsorption distance is equal to around 0.3 nm,<sup>24</sup> we can subtract

this value from the radius (*R*) of the pore  $-g_0$  as illustrated in Figure 5.7. The  $g_0/R$  ratio for an aerogel is close to unity. In that case, according to Afanasiew and Minogin,<sup>23</sup> the internal cylindrical surface factor is close to 1 which means that the adsorption process in aerogel can be simplified and treated as hydrogen adsorption on a flat surface. For this pore size and larger the adsorption process is then totally driven by the effective surface area. However, for the smaller pore size of MCM-41, the hydrogen molecule does still interact with the concave cylinder as a whole (Figure 5.8). The surrounding concave shaped and opposite wall contributes to the total adsorption interactions and double the hydrogen uptake capacity per SSA.



Figure 5.7 Hydrogen molecule adsorbed on the surface of the concave cylinder.



**Figure 5.8** Difference in surface coverage for big and small pores as a result of the difference in van der Waals interaction.

#### 5.4 Conclusions

Hydrogen uptake of representatives of porous silica's with meso pores (2.3 – 20 nm) were measured at cryogenic temperatures and at the low pressure range 0-2 bar. The results are compared in the context of the surface area and pore size. Under the same conditions the hydrogen uptake decreases with increasing pore size and is around twice as high for MCM-41 and HMS as that for the largest pore aerogel. There appears an asymptotic correlation between pore size and hydrogen adsorption capacity for these silica-based materials. In addition, the reduced isosteric heat of adsorption caused by reduced van der Waals interactions in the larger pore aerogel can explain the halved hydrogen uptake for aerogel compared to the smaller pore MCM-41.

For these mesopore silica materials the effect of reduced long range van der Waals interactions can be observed directly. This has not been observed as such in microporous materials like MOFs that also have larger chemical composition variability.

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### Chapter 6

# Microscopic study of $\mathrm{Ti}F_3$ as hydrogen storage catalyst for $\mathrm{MgH}_2$

The chapter is based on the published article:

Grzech A., Lafont U., Magusin P.C.M.M., Mulder F.M., J. Phys. Chem. C, 2012, 116, 26027.



To understand the influence of TiF<sub>3</sub> addition on the de- and re-hydrogenation process of ball milled MgH<sub>2</sub>-TiF<sub>3</sub> a detailed study has been performed of the different crystallographic phases of the de- and re-hydrogenated materials. Rietveld refined XRD analysis of the dehydrogenated material indicates the presence of a rutile, non-stoichiometric MgF<sub>2x</sub> phase, and a hexagonal Mg<sub>1y</sub>Ti<sub>y</sub>F<sub>z</sub> phase. After re-hydrogenation three different fluorine environments were found by <sup>19</sup>F NMR, which can be attributed to MgF<sub>2x</sub>, MgF<sub>2x</sub>H<sub>x</sub> and MgF<sub>2x</sub> dispersed with MgO nanodomains. The remarkable MgF<sub>2x</sub>H<sub>x</sub> phase, which is apparently formed from the non-stoichiometric MgF<sub>2x</sub> phase in the dehydrogenated material, may indicate a diffusion pathway of hydrogen within Mg / MgH<sub>2x</sub>. Furthermore the previously found non-stoichiometric MgH<sub>2x</sub> phase appears to be metastable as is observed by XRD analysis after long-term storage.

TEM with EDX measurements performed for both dehydrogenated and rehydrogenated samples provide information that the nanoparticles are highly crystalline and that the catalyst is homogenously distributed over the sample when viewed on a 100 nm scale. More locally the fluorine containing phase is observed mainly at the surface of the Mg and MgH<sub>2</sub> particles and the Ti containing species are present throughout the particles, likely as TiH<sub>2</sub> inclusions in the Mg structure and/or as Mg-Ti-F compound. Additionally an about 2-5.5 nm MgO layer covers the Mg aggregates. A model of the hydrogen uptake and sample morphology is proposed.

#### 6.1 Introduction

Hydrogen as a future energy carrier requires storage of hydrogen in a compact and safe way. An important candidate for lightweight hydrogen storage is MgH<sub>2</sub> since it has a high hydrogen capacity and, because of the abundance of Mg, a relatively low anticipated cost. However, practical application of this system is largely hampered by poor kinetics of hydrogen release and uptake and a relatively high thermodynamic stability ( $\Delta H = -74$  kJ mol<sup>-1</sup>).<sup>1</sup> Several methods to improve hydrogen sorption in MgH<sub>2</sub> have been proposed<sup>2</sup>, such as transforming rutile MgH<sub>2</sub> into a fluorite structure by alloying with a transition metal<sup>34</sup> or forming

MgH<sub>2</sub> nano-domains by Mg melt-infiltration into porous carbon.<sup>5</sup> An alternative method is to decrease particle size, by means of high-energy ball milling, which provides more surface area, more hydride nucleation sites, and shortened diffusion paths.<sup>67</sup> However, for pure nanostructured MgH<sub>2</sub> it has been observed that during heat treatment in e.g. the desorption process the Mg particles grow spontaneously to large sizes.<sup>8</sup> With catalysts like Nb or V, however, consistently small sizes occurred feeding the notion that adding catalyst could play a major role in grain refining light metal hydride materials.<sup>9,10</sup> Various types of additives for magnesium hydride have been tested for accelerating the hydrogenation and dehydrogenation process also including mixed transition metal catalysts.<sup>11,12</sup> Besides of some of the transition metals<sup>13</sup> transition metal oxides<sup>14,15</sup> or hydrides, transition metal halides (NbF<sub>5</sub>, TiF<sub>3</sub>, FeF<sub>3</sub>)<sup>16-18</sup> are widely investigated as additives. These are believed to act as a catalyst for the chemisorption of hydrogen and transport into the magnesium phase.<sup>2</sup> Among of these  $TiF_3$  additive appears to be a particularly effective catalyst.<sup>10,19,20</sup> It has been reported<sup>21</sup> that MgH<sub>2</sub> ball milled with TiF<sub>3</sub> lowers the desorption temperature compared to ball milled MgH<sub>2</sub> alone. Moreover, the hydrogen sorption kinetics is clearly faster and large numbers of cycles can be performed without significant changes in storage capacity.<sup>22</sup> Ball milled MgH<sub>2</sub>-TiF<sub>3</sub> can, after dehydrogenation, re-absorb a large fraction of its hydrogen-storage capacity rapidly near room temperature.<sup>10</sup> Adding Ti or TiH<sub>2</sub> itself along with ball milling already improves the sorption kinetics, but the effect is not that strong as for TiF<sub>3</sub>.<sup>23,24</sup> Mulder et al. have proposed that a MgF<sub>2</sub> phase with a rutile structure closely similar to MgH<sub>2</sub>, plays a role as nano-seed crystals leading to grain refinement for the MgH<sub>2</sub> phase.<sup>10</sup> The MgH<sub>2</sub> phase can grow on the abundant small MgF<sub>2</sub> particles and therefore each individual crystallite grows to small size.<sup>10</sup> Liu and Suda concluded from their research that formation of a fluorinated surface layer enhances hydrogen reactivity and protects the material from passivation.<sup>25</sup>

Several results on the titanium and fluorine containing MgH<sub>2</sub> are available.<sup>19-21,26</sup> However, a detailed microscopic understanding of the different phases and their possible roles is still missing. Therefore we have investigated the MgH<sub>2</sub>–0.05TiF<sub>3</sub> system at various hydrogen sorption stages by means of X-ray diffraction

spectroscopy, transmission electron microscopy (TEM) and magic-angle spinning (MAS) <sup>1</sup>H and <sup>19</sup>F nuclear magnetic resonance (NMR).

#### 6.2 Materials and methods

#### Material preparation

MgH<sub>2</sub> powder with purity > 98 % and TiF<sub>3</sub> powder of purity > 99.9 % were purchased from Alfa Aesar. The dry powders were heated in an Ar glovebox (oxygen and water level < 1 ppm) at 150 and 250 °C, respectively, to remove any remaining volatile impurities. The MgH<sub>2</sub> powder was ball-milled with 5 mol% of TiF<sub>3</sub> under Ar in a Fritsch Pulverisette 6 planetary monomill for a period of 60 min. (4 × 15 min. milling with 15 min. time intervals in between) with a rotational speed of 400 rpm. The ball to powder ratio was around 50:1, where the weight of the powder was around 3 g. In the next step the sample was made to gradually release hydrogen in a heated open container inside the glovebox at temperatures between room temperature (RT) and 300 °C within 3 hours.

#### Powder X-ray diffraction (PXRD)

Powder XRD characterization was performed by use of a PANalytical X'Pert Pro PW3040/60 diffractometer with Cu K<sub>a</sub> radiation operating at 45 kV and 40 mA. An air-tight sample holder with a Kapton<sup>®</sup> window was employed. Rietveld refinements were performed with the least squares method as implemented in GSAS.<sup>27</sup> Particle sizes were calculated from the fitted line broadening. Peak broadening from strain effects were also considered but were not necessary to improve the fitted lineshapes.

#### Hydrogen absorption

A volumetric Sievert's apparatus was used to determine the amount of hydrogen absorbed into previously dehydrogenated samples. First the sample was loaded into a stainless steel container with a copper O-ring in the glovebox, and connected via a thin capillary to the setup. After removal of the argon gas from the capillary the sample was re-hydrogenated at 150 °C within pressures ranging from 1-20 bars.

#### Transmission electron microscopy (TEM)

For transmission electron microscopy (TEM) a FEI Monochromated Tecnai 200STEM-FEG was employed, operated in the bright field mode with an accelerating voltage of 200 kV, to obtain information about the local structure of the sample, such as the location of the catalyst elements and the thickness of the MgO layer. During the TEM characterization, the elemental composition of the samples was obtained by energy dispersive X-ray spectroscopy (EDX) using the microprobe mode for bulk average values or nanoprobe for more local investigation.

#### Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR)

<sup>1</sup>H and <sup>19</sup>F MAS NMR experiments of dehydrogenated and re-hydrogenated samples were performed on a Bruker DMX500 spectrometer operating at <sup>1</sup>H and <sup>19</sup>F NMR frequencies of 500 and 471 MHz, respectively. The samples were all packed in a MAS sample holder and closed inside an Ar glove box with oxygen level below 1 ppm. The 2.5-mm MAS sample holders were rotated inside the probehead using a dry nitrogen flow at a sample spinning rotation rate of 20 or 25 kHz. For chemical-shift calibration the <sup>1</sup>H NMR signal of tetramethylsilane (TMS) was set to 0 ppm, and the <sup>19</sup>F NMR signal of polytetrafluoroethylene (PTFE) was set to -124 ppm. To suppress the <sup>1</sup>H and <sup>19</sup>F NMR background signal (relatively strong for the small 2.5-mm MAS sample holders), we have employed the pulse sequence  $90^{\circ}$ +x- $90^{\circ}$ #x- $\tau$ - $90^{\circ}$ #- $\tau$ - $90^{\circ}$ - $\tau$ = time  $\tau$  of 10 ms and  $90^{\circ}$  pulses of 2 µs. Two-dimensional <sup>19</sup>F exchange spectroscopy (2D Exsy) was carried out by use of the standard pulse sequence  $90^{\circ}$  –  $t_1$  –  $90^{\circ}$  –  $t_{mix}$  –  $90^{\circ}$  –  $t_2$ , whereby the mixing times  $t_{mix}$  were fixed to 0.001, 0.01, 0.1 or 1 s.

#### 6.3 Results and discussion

#### 6.3.1 XRD analysis of the dehydrogenated and re-hydrogenated MgH<sub>2</sub>-0.05TiF<sub>3</sub>

The freshly prepared ball-milled sample contains a large fraction of a high pressure  $\gamma$ -MgH<sub>2</sub> phase and strain that are not representative for the sample when cycled once. For this reason the samples are always first dehydrogenated.

Apart from the main reaction MgH<sub>2</sub>  $\rightarrow$  Mg + H<sub>2</sub>, hydrogen desorption of ballmilled MgH<sub>2</sub> with TiF<sub>3</sub> catalyst at elevated temperature induces a side-reaction in which the TiF<sub>3</sub> is consumed, 3MgH<sub>2</sub>+ 2TiF<sub>3</sub>  $\rightarrow$  3MgF<sub>2</sub> + 2TiH<sub>2</sub> + H<sub>2</sub>. In subsequent cycles the resulting MgF<sub>2</sub> and TiH<sub>2</sub> phases have to be considered to be the active catalysts. TiH<sub>2</sub> is has a more negative formation enthalpy (-136 kJ mol<sup>-1</sup>), than MgH<sub>2</sub> (-74 kJ mol<sup>-1</sup>) and it stable under the conditions at which desorption of the MgH<sub>2</sub> phase takes place.<sup>10</sup> Several nano-crystalline samples were produced by highenergy ball-milling and subsequently after de- and re-hydrogenation have been investigated by means of X-ray diffraction. From Rietveld refinement of the XRD patterns of dehydrogenated systems (Figure 6.1) the presence of a major  $\alpha$ -Mg phase, and minor  $\beta$ -MgF<sub>2x</sub> MgO and TiH<sub>2</sub> has been determined. The presence of the non-stoichiometric  $\beta$ -MgF<sub>2x</sub> phase has been denoted due to the lower (< 2) fluorine occupancy and changes in lattice parameters in comparison to the stoichiometric MgF<sub>2</sub>.  $\gamma$ -MgH<sub>2</sub> does not occur after de- and re-hydrogenation.

Additional reflections from an unknown hexagonal minor phase show up, with small but distinct peaks positioned at  $2\theta = 31^{\circ}$ ,  $33^{\circ}$ ,  $35^{\circ}$ , thus having a similar diffraction pattern as  $\alpha$ -Mg, but with significantly larger lattice parameters. This small amount of phase was detected here by X-ray diffraction for the first time. A different hexagonal Mg-Ti structure was described before in the literature by the group of Asano et al. The authors reported that a  $Mg_{x}Ti_{100x}$  (x = 80) alloy with hexagonal structure can be formed during high-energy ball-milling.<sup>28</sup> However, the lattice parameters derived here for the unknown phase (a = b = 3.35 Å, c = 5.44 Å) differ from the parameters reported by Asano et al. (a = b = 3.18 Å, c = 5.14 Å) and surprisingly are larger than the lattice constants of both hexagonal Mg (a = b = 3.20Å, c = 5.21 Å) and Ti (a = b = 2.95 Å, c = 4.68 Å). Therefore it is concluded that the new peaks are related to a hexagonal Mg - rich Mg-Ti phase with some F dissolved into the lattice which apparently causes the lattice to expand. It is difficult to provide exact experimental conditions needed to form this phase, but it is clear that the phase forms as a result of hydrogen desorption at gradually increased temperatures up to 300 °C.

As a measure for the long-terms stability of the material, the hydrogen sorption of a dehydrogenated sample after different aging times was analyzed. Samples stored

during a few months in the glovebox tend to absorb hydrogen more difficultly under the same conditions at which freshly desorbed samples absorb hydrogen rapidly. Detailed Rietveld analysis on longer stored material showed a slight decrease in the fluorine occupancy accompanied by an increase in the  $\beta$ -MgF<sub>2x</sub> phase fraction.



Figure 6.1 XRD pattern of the dehydrogenated  $MgH_2$ -0.05TiF<sub>3</sub> sample (a) and a small section enlarged (b).

Samples reloaded with various amounts of hydrogen were also characterized by means of X-ray diffraction. For instance, a sample, denoted as "MgH<sub>1.5</sub>-0.05TiF<sub>3</sub>", was prepared from dehydrogenated MgH<sub>2</sub>-TiF<sub>3</sub> by re-hydrogenation up to an overall hydrogen to magnesium (H/Mg) ratio ~1.5 (determined using the Sieverts setup) at the temperature of 150 °C and hydrogen pressure up to 20 bar. Rietveld refinement indicates a major  $\beta$ -MgH<sub>2-x</sub> phase and minor MgO,  $\beta$ -MgF<sub>2-x</sub> TiH<sub>2</sub> phases and remarkably small remains of  $\alpha$ -Mg (Figure 6.2). In earlier work we observed that  $\beta$ -MgH<sub>2-x</sub> is formed<sup>10</sup> under these conditions instead of stoichiometric  $\beta$ -MgH<sub>2</sub>, which is consistent with the presence here of a less than expected amount  $\alpha$ -Mg. It is therefore concluded that in this freshly re-hydrogenated sample non-stoichometric  $\beta$ -MgH<sub>2-x</sub> also exists.

In addition to the reflections of the mentioned phases reflections of an unknown rutile phase appear at the angles  $2\theta \sim 26.73^\circ$ ,  $34.44^\circ$ ,  $38.08^\circ$ ,  $39.51^\circ$ . This may be compared to the XRD pattern of the  $\beta$ -MgF<sub>2x</sub> with reflections at  $2\theta \sim 27.63^\circ$ ,  $35.46^\circ$  and  $39.44^\circ$ . In view of these similarities we propose that the unknown phase is  $\beta$ -MgF<sub>2x</sub>H<sub>x</sub> with increased lattice parameters a = 4.71 Å, c = 3.13 Å caused by the uptake of hydrogen. After all the only difference between the samples is the rehydrogenation. These are larger lattice parameters than those of both MgH<sub>2</sub>(a = b = 4.52 Å, c = 3.02 Å) and stoichiometric MgF<sub>2</sub> (a = b = 4.69 Å, c = 3.09 Å). To study the presence of such new phase, again <sup>19</sup>F MAS NMR was employed (see below).

In previous work<sup>10</sup> a new cubic MgTi<sub>2</sub>H<sub>6</sub> phase (a = 4.49 Å) was reported having clear diffraction peaks at  $2\theta = 24.2^{\circ}$ ,  $28.1^{\circ}$ ,  $40.1^{\circ}$  and  $72.9^{\circ}$ . Their absence in the current XRD pattern can be explained with different desorption conditions since in our previous study<sup>10</sup> this phase was only observed after much more prolonged sample heating and sorption experiments below  $285 \,^{\circ}$ C.



**Figure 6.2** XRD pattern of dehydrogenated MgH<sub>2</sub>-0.05TiF<sub>3</sub>re-hydrogenated up to overall hydrogen to magnesium ratio of 1.5.

The XRD pattern of MgH<sub>1.5</sub>-0.05TiF<sub>3</sub> stored during five months in the glovebox shows (Figure 6.3) a remarkable change: the peak intensities of the  $\beta$ -MgH<sub>2x</sub> phase slightly decrease while the reflections of the  $\alpha$ -Mg phase significantly increase in intensity with prolonged storage time. Rietveld analysis shows that the phase fraction of  $\beta$ -MgH<sub>2x</sub> is about 9 % lower for the aged sample whereas the fraction of the Mg phase raised by a similar amount. This result indicates that the  $\beta$ -MgH<sub>2x</sub> phase separation changes over the course of storage time. Also the size of the  $MgH_{2x}$  and Mg nanodomains increases over time, probably as a result of hydrogen diffusion. The  $\beta$ -MgH<sub>2-x</sub> non-stoichiometric phase, which has already been observed in nano-sized material<sup>6</sup>, is thus metastable: since no H will spontaneously escape from the material in prolonged times, the material strives to convert into more stable MgH<sub>2</sub> with less vacancies. During the long waiting time there must be migration of hydrogen into the  $\beta\text{-MgH}_{2\text{-x}}$  phase towards MgH\_2 domains and simultaneous hydrogen depletion of other fractions of the material (other  $\beta$ -MgH<sub>2-x</sub> that disappears). As a result, the amount of  $\alpha$ -Mg phase increases over time next to a smaller amount of more fully hydrogenated  $\beta$ -MgH<sub>2</sub> phase (Figure 6.4). This observation is very important from the thermodynamical point of view. It indicates that the state in which the  $\beta$ -MgH<sub>2x</sub> and the  $\alpha$ -Mg are in close contact is in fact less stable, i.e. metastable, than the reorganized system in which the H phase separates out further. The observation of reduced stability corroborates with the previously<sup>10</sup> obtained lower enthalpies of hydride formation for low concentration hydrogen loaded into the MgH<sub>2x</sub>-0.05TiF<sub>3</sub> sample. In fact this observation indicates that the nanostructuring and grain refinement mechanism proposed in<sup>10</sup> indeed leads to a destabilized system, which, in the long term, is apparently not fully maintained. The ultimately stable configuration at infinite times may thus be the fully phase separated – bulk like Mg, MgH<sub>2</sub>, TiH<sub>2</sub> and MgF<sub>2</sub>, but for moderate waiting times such situation is not reached and the phases are arrested in nanostructured destabilized form.

At the same time there are some changes visible in the  $\alpha$ -Mg average particle size, determined from the line width of the XRD reflections of  $\alpha$ -Mg phase, which is ~97 nm for freshly prepared sample and ~123 nm for the sample stored five months in the glove box. The refined XRD particle size of the MgH<sub>2-x</sub> phase does not change significantly and is 39 nm and 41 nm for a fresh and aged sample, respectively. As can be noticed the typical size of the  $\beta$ -MgH<sub>2-x</sub> domains is smaller than that of the  $\alpha$ -Mg domains. This is in agreement with the previous hypothesis that  $\beta$ -MgF<sub>2-x</sub> effectively works as a MgH<sub>2</sub> grain refiner.



**Figure 6.3** XRD spectra of freshly re-hydrogenated MgH<sub>1.5</sub>-0.05TiF<sub>3</sub> sample and the same sample measured after five-months storage in the glove box, normalized to the largest  $\beta$ -MgH<sub>2-x</sub> peak. Note that for the aged sample relatively more  $\alpha$ -Mg phase is present while, judging from the background that is lifted after normalization at the highest peak  $\beta$ -MgH<sub>2-x</sub> this  $\beta$ -MgH<sub>2-x</sub> phase is lower.



**Figure 6.4** Metastability of  $\beta$ -MgH<sub>2-x</sub> phase: with time it converts to a smaller amount of MgH<sub>2</sub> next to an increased Mg amount.

#### 6.3.2 TEM analysis of nanostructured MgH $_2$ with TiF $_3$ additive.

Elemental analysis performed by energy dispersive X-ray (EDX) spectroscopy during the TEM investigation confirms that the titanium and fluorine are homogeneously distributed over the dehydrogenated sample. The average atomic composition is 9.8 % F, 3.2 % Ti, 16% O and 71% Mg. The Ti:F ratio is in agreement with the composition at the start of the material preparation. In addition, oxygen is present in the dehydrogenated sample indicating the presence of an oxide phase. The larger amount of O in TEM than in other measurements will be related to small traces of oxygen that could not be avoided during the preparation of the TEM measurements. The TEM micrographs presented in Figure 6.5 show the typical morphology of the dehydrogenated sample. The material is made of particles that are present within a thin shell. It is difficult to distinguish particle boundaries from the TEM image due to particle aggregation and overlap. The high-resolution picture presented in Figure 6.5b clearly shows the Mg crystalline phase crystallites surrounded by an about 2-5.5 nm MgO layer. The typical distances of 2.78, 2.45 and 2.11 Å measured from the lattice spacing can be assigned to the Mg (100), Mg (101) and MgO (200) plane, respectively. The lattice parameters of the grains were determined by measuring the distance between discernible grain boundaries and dividing by the number of the planes within the grain. The EDX analysis performed using the nanoprobe centered on a Mg crystallite (Figure 6.5b) mostly shows the presence of Mg, O and Ti atoms, but does not exhibit the presence of F atoms. When the EDX analysis is performed on a wider area (Figure 6.5a), the F to Ti ratio is around 3:1. From this elemental difference it is concluded that the Ti containing species are also present in the middle part of the particles as inclusions in the Mg structure (Figure 6.5), whereas the F is located on the surface of the particles only. The F partially present as Mg-Ti-F alloy should then be near the surface of the particles.



Figure 6.5 TEM of the dehydrogenated sample (a) and (b).



**Figure 6.6** TEM of the re-hydrogenated sample (a) and (b) with indicated EDX and electron diffraction area.

The re-hydrogenated sample exhibits some instability under the electron beam and undergoes partial desorption via interaction with the high energy electrons and associated sample heating. The average elemental composition of the rehydrogenated TEM sample is: 66 % Mg, 2.8 % Ti, 20 % O, 11 % F. This elemental composition is practically the same as the one made on the dehydrogenated sample. The catalyst dispersion is homogeneous and as seen in Figure 6.6a, the particles present a 3-5 nm shell that can be related to the MgO phase (Figure 6.6b). The diffraction patterns present as middle inset in Figure 6.6b show the presence of a hexagonal phase that could be attributed to  $\alpha$ -Mg. However, reflection at *d*-spacing 2.26 and 2.02 Å that fit the (200) and (210) reflections of a rutile MgH<sub>2</sub> phase are also still visible. According to the EDX analysis using the nanoprobe on the well-crystalline area presented in Figure 6.6b exhibits 95.8 % Mg and 4.2 % Ti. This composition is inconsistent with a pure Mg phase, which is expected, at first sight, from the presence of the hexagonal lattice clearly shown by electron diffraction.

Figure 6.7 presents a high-resolution micrograph of the area discussed above. The diffraction pattern is well in line with a hexagonal crystal structure. A pure Mg phase will imply a parameter c = 5.21 Å and a d-spacing related to the (002) planes of 2.60Å. The distances deduced from the HR-TEM pictures (Figure 6.7) show a non-regular lattice parameter along the [0001] direction (*c* axis) of 4.8 and 5.2 Å, alternatingly. In the [11-20] direction the distance between 2 adjacent atoms alternate between 2.7 and 3.1 Å whereas they should be around 3.19 Å in a pure Mg crystal. This distortion along the *c* - axis as well as the presence of Ti is well in line with the inclusion of TiH<sub>2</sub> into the Mg phase. Recently Hao and Sholl showed with DFT calculations that the presence of strains in epitaxial MgH<sub>2</sub> / TiH<sub>2</sub> interfaces can reduce enthalpy of hydrogen release and that the formation of these two immiscible phases is expected to exist experimentally.<sup>29</sup> However, it is difficult to conclude from TEM results obtained here whether Ti is present as TiH<sub>2</sub> nanodomains, well aligned with Mg / MgH<sub>2</sub> structures, or as part of an Mg<sub>x</sub>Ti<sub>y</sub>H<sub>z</sub> alloy.



**Figure 6.7** HR-TEM micrograph of the re-hydrogenated sample (on the area shown in the middle of Figure 6.6b).

#### 6.3.31H and 19F Magic Angle Spinning (MAS) NMR analysis of the samples.

NMR is a powerful technique to investigate the chemical environment of hydrogen-storage materials and therein chemisorbed hydrogen atoms.<sup>30-33</sup> In this study dehydrogenated and re-hydrogenated MgH<sub>2</sub>-0.05TiF<sub>3</sub> have been investigated by use of <sup>1</sup>H (Figure 6.8) and <sup>19</sup>F MAS NMR (Figure 6.9). The dehydrogenated sample was first measured as prepared, then stored in the glove box in sealed containers and measured again three months later. Part of the dehydrogenated material from the same batch was loaded with hydrogen up to a hydrogen-to-metal ratio of ~ 1.5 at pressures up to 20 bar. Three months later the NMR measurements were repeated to observe whether changes would occur in both de- and re-hydrogenated samples over time that could be related to the changes in XRD patterns.

As shown in Figure 6.8, there is no significant change in the <sup>1</sup>H NMR signals of the fresh and aged dehydrogenated samples. According to the XRD pattern and our

previous publication<sup>10</sup> the hydrogen remaining after desorption should be in a TiH<sub>-2</sub> phase. However, there is no bulk-TiH<sub>2</sub> signal with the typical Knight shift -149 ppm in the <sup>1</sup>H NMR spectra of both the re-hydrogenated and dehydrogenated  $MgH_2-0.05TiF_3$  samples. Rather, there are only signals visible at 3 ppm, close to e.g.  $MgH_2$  (diamagnetic at 3 ppm) with an intensity corresponding to about 0.02 H per Mg atom. A much less negative Knight shifted and broadened signal at around -43 ppm was observed earlier in TiD-2 for Mg-Ti nanostructured materials in hydrided state.<sup>34</sup> However, since these signals were strongly broadened this may be hardly visible in the present case, having much less TiH<sub>2</sub> in the material. The reason why the <sup>1</sup>H NMR signals from TiH<sub>2</sub> lose their characteristic bulk Knight shift in nanosystems is that the local density of states in the conducting nanoparticles or nanodomains is disturbed; essentially metallic character is lost.<sup>35</sup> The materials in <sup>34</sup> were produced by co-sputtering of Mg and Ti metal, and subsequent deuteration leading to partial phase separation between Mg and Ti containing material. The samples considered here are produced from ball-milled MgH<sub>2</sub> and TiF<sub>3</sub> where only after the dehydriding the  $TiF_3$  reacts to form very small  $TiH_2$  in the vicinity of Mg. The X-ray diffraction line shape analysis of both hydrogen-depleted and rehydrogenated sample shows that the  $TiH_2$  domains are very small (~3 nm) compared to Mg ( $\sim$ 120 nm) or MgH<sub>2</sub> ( $\sim$ 40 nm). There are thus reasons why a signal of TiH<sub>2</sub> protons can show much reduced Knight shifts. However, the signal observed has essentially lost its Knight shift which may indicate that this is H in a TiH<sub>2</sub> environment which is further perturbed by the presence of inclusion of Mg, or it is H at the interface between TiH<sub>2</sub> and Mg respectively MgH<sub>2</sub>.

Although the chemical shift of  $Mg(OH)_2$  is at a different position of ~0 ppm<sup>36</sup> we have also considered that  $Mg(OH)_2$  or Mg-OH moieties due to (unintended) exposure to air could give a signal at the position of the observed spectrum in Figure 6.8a (3 ppm). However, this would not explain the absence of Knight shifted TiH<sub>2</sub> related signals. No  $Mg(OH)_2$  is visible in XRD.

The re-hydrogenated material shows a single <sup>1</sup>H NMR signal at the same shift position as  $\beta$ -MgH<sub>2</sub>, 3.0 ppm. After three months storage the <sup>1</sup>H NMR spectrum shows an additional small signal at chemical shift ~4.5 ppm (Figure 6.8b). According to the literature this peak is assigned to H in the  $\alpha$ -Mg metal phase.<sup>37,38</sup>

Deconvolution of the two overlapping <sup>1</sup>H MAS NMR signals at 3.0 and 4.5 ppm indicates that the latter signal corresponds to around 1% of total hydrogen signal. Such amount of H in the  $\alpha$  phase thus corresponds to MgH-0.015 since the rehydrogenated material was loaded up to H/Mg ratio 1.5. Such finding confirms previous *in situ* neutron diffraction results indicating strongly altered H solubility in the  $\alpha$ -Mg where H concentrations up to ~0.4 could be observed. In literature a signal at 4.5 ppm is assigned to molecular H<sub>2</sub> which is trapped at high pressure in voids in large AlH<sub>3</sub> crystals<sup>39</sup>. However, AlH<sub>3</sub> is thermodynamically unstable while the sample considered here is thermodynamically stable and absorbs hydrogen at RT. This excludes such assignment for this sample since any high pressure H<sub>2</sub> is absorbed.

Except the MgH<sub>2-x</sub> and TiH<sub>2</sub> phases, hydrogen in the re-hydrogenated sample can possibly exist in the ternary phases Mg<sub>x</sub>Ti<sub>y</sub>H<sub>z</sub> and  $\beta$ -MgF<sub>2-x</sub>H<sub>x</sub>. However, despite the fast magic-angle spinning, the broad <sup>1</sup>H MAS NMR centerband signal does not provide information on the presence of those phases.

<sup>19</sup>F MAS NMR spectra of the dehydrogenated and re-hydrogenated, freshly prepared and aged materials show a range of overlapping resonances between -165 and -205 ppm (Figure 6.9). The line shapes observed for the fresh and aged dehydrogenated samples are different. These <sup>19</sup>F NMR spectra have a low signal-tonoise level, which is caused by the metallic character of the dehydrogenated sample, and consequently, required mixing with a diamagnetic powder (KBr) for stable sample rotation. For both samples the spectra are clearly broadened and shifted with respect to the reference sample MgF<sub>2</sub>, which has a single <sup>19</sup>F resonance at -196 ppm. In the <sup>19</sup>F NMR work of Scholz et al.<sup>40</sup> a study is made of various MgF<sub>2</sub> materials that are modified by H and O insertion either as O substitution or OH substitution. MgF<sub>2</sub> crystallizes in the rutile-type structure in which each Mg<sup>2+</sup> is surrounded by six F-ions. Three Mg<sup>2+</sup> ions are the nearest neighbors of F-ions in the first coordination sphere where two different bond distances exist indicated by [FMg<sub>3</sub>] environment. The second coordination sphere consists of 11 F- ions  $[FMg_3F_{11}]$  and only if all positions in the second coordination sphere are occupied by fluorine the signal at -196 ppm appears.

For the other O and OH substituted materials low-field shifts are observed. Therefore such substitution and reduced F content may also explain the spectra obtained in our case. Such observation is in agreement with the XRD data as a  $\beta$ -MgF<sub>2x</sub> phase was refined with lower F content. The combined NMR and XRD results can be explained by inclusion of O as is present in ref. 40 where a single O substitutes 2 F ions. In view of the similar XRD cross section of F and O and the apparent decrease of the cross section on the F site this can be consistent only when the F is replaced by less O ions as in e.g. MgF<sub>2x</sub>O<sub>x</sub>.

The chemical shift of the strongest signal measured for freshly dehydrogenated sample is around -194 ppm around 2 ppm shifted in comparison with stoichiometric MgF<sub>2</sub>. This thus may correspond to non-stoichiometric  $\beta$ -MgF<sub>2×</sub> but with content of F close to 2. Remarkably for the aged sample the <sup>19</sup>F signal is shifted from -196 ppm (for ordinary MgF<sub>2</sub>) further to -188 ppm. Detailed Rietveld analysis of XRD patterns of fresh and aged dehydrogenated samples showed that the occupancy of F in the  $\beta$ -MgF<sub>2×</sub> phase decreases with time, accompanied with a slight change in lattice parameters. Such decrease may not only be explained by disappearance of F from the structure, increasing the phase amount, but it can also indicate a gradual change in composition where possibly nearby O replaces more of the F. Such alteration can influence the grain refinement capabilities of the fluorine containing phase.



**Figure 6.8** <sup>1</sup>H MAS NMR of a) dehydrogenated MgH<sub>2</sub>-0.05TiF<sub>3</sub> fresh (black), old (red), (because of the conductive properties mixed with KBr for stable sample rotation) and b) MgH<sub>1.5</sub>-0.05TiF<sub>3</sub> fresh (black), aged (red). For comparison spectrum of MgH<sub>2</sub> (blue) is also shown in both panels. The sample rotation rate was 20 kHz.


**Figure 6.9** <sup>19</sup>F MAS NMR of a) dehydrogenated MgH<sub>2</sub>-0.05TiF<sub>3</sub> fresh (black), old (red), and b) MgH<sub>1.5</sub>-0.05TiF<sub>3</sub> fresh (black), old (red), 20 kHz. The spectrum of MgF<sub>2</sub> (blue) is also shown for comparison. The sample rotation rate was 25 kHz and 50 wt% KBr was added to the (conductive) dehydrogenated material.

The <sup>19</sup>F NMR centerband of the re-hydrogenated sample consist of a number of partly resolved signals (Figure 6.9b). Apparently, fluorine is present in the hydrogen loaded sample in few forms: the most upfield signal at -196 ppm comes

from F atoms in a MgF<sub>2</sub>-like environment. A second signal around -190 ppm may be assigned to F in the  $\beta$ -MgF<sub>2x</sub>H<sub>x</sub> environment, which was already suggested in the diffraction pattern. Such signal cannot be detected clearly in the dehydrogenated sample which therefore indicates that hydrogen plays a role in this <sup>19</sup>F environment. A third signal at -185 ppm can be assigned to an even less fluorine rich  $\beta$ -MgF<sub>2-x</sub>H<sub>x</sub>, environment with MgO nanodomains embedded in MgF<sub>2</sub> structure since Prescott et al.<sup>41</sup> have reported a <sup>19</sup>F NMR shift of -185 ppm for MgF<sub>2-x</sub>-(OH)<sub>x</sub> compounds. The authors claim that such a chemical shift can be a result of MgO nano domain formation in the  $MgF_2$  lattice.  $MgO_6$  octahedra in MgO can be incorporated into the fluoride network of MgF<sub>6</sub> units. Furthermore, in one of the reported Mg(OH) $_{0.4}$ F<sub>1.6</sub> samples with high content of fluorine mostly MgF<sub>2</sub> with O<sup>2-</sup> species were found. According to XPS results obtained by the authors the ratio of O:Mg on the surface of that sample is below 2 (1.9). This means that the sample consist of MgF<sub>2</sub> and some O<sup>2</sup>- species in the phase and also that -OH groups are present only at the surface. The mentioned sample possesses the most similar NMR spectrum from all presented samples in the cited article to the spectrum presented here.

Additional information on the spatial connectivity between the different fluorine environments in the MgH<sub>2x</sub>-0.05TiF<sub>3</sub> system was obtained from 2D <sup>19</sup>F – <sup>19</sup>F, spin diffusion driven, correlation experiments with a spin diffusion mixing time (Figure 6.10). Since there is no rapid F atomic diffusion at room temperature nuclear spin diffusion is measured. Spin diffusion is the temperature independent exchange of magnetization between adjacent nuclear spins. The 2D spectra provide insight into the different F environments in the compound and their locations relative to each other. During the mixing time of selected duration (0.001-1 s) <sup>19</sup>F – <sup>19</sup>F spin diffusion between different fluorine nuclei takes place. As a consequence of the short range of the nuclear magnetic dipolar interaction this only occurs for <sup>19</sup>F nuclei in close proximity. Spin exchange between NMR distinct F sites is reflected by off-diagonal cross peaks between the signals of the magnetization exchanging sites and such exchange necessarily reflects close proximity of these different F environments. Fluorine that does not participate in the magnetization exchange process (separated

in space from the other sites) shows only autocorrelation peaks on the diagonal of the 2D spectrum.

The 2D spectrum recorded with a short mixing time of 0.001 s shows only diagonal intensity (Figure 6.10a). As expected, no substantial spin diffusion occurs between the NMR distinct F sites at this short timescale. In contrast, for a mixing time of 1 s significant cross-peaks are observed between the signals at -196, -190 and -185 ppm (Figure 6.10b). This indicates that the F environments involved, respectively  $MgF_{2-x}$  $\beta$ -MgF<sub>2x</sub>H<sub>x</sub> and those with embedded MgO nanodomains, are close together in space. In addition to these three connected F environments the 2D spectra reveal a signal present at approximately -160 ppm which does not give rise to cross-peaks and therefore reflects F in a more separate phase. The F amount associated with this phase is very small as can be noticed from the intensity of the peak, and its apparent invisibility in the 1D NMR spectra. In view of the XRD results this separate phase may be Mg-Ti-F. Ma et al.<sup>19</sup> based on XPS measurements also detected a new bonding state of fluorine in the dehydrogenated sample and proposed that this bonding state might come from Mg-Ti-F species. However the obtained XPS signal is relatively strong and therefore more likely related to one of the other the <sup>19</sup>F NMR signals obtained in this research for the  $\beta$ -MgF<sub>2-x</sub>H<sub>x</sub> phase.



**Figure 6.10** 2D Exsy MAS <sup>19</sup>F NMR of MgH<sub>2-x</sub>-0.05TiF<sub>3</sub>, mixing time 0.001 s (a) and 1 s (b), 25 kHz.

A second possibility for the weak signal at -160 ppm could also be F dissolved in the  $\alpha$ -Mg phase. In our previous research<sup>10</sup> we indicated that a small amount (~2 %) of F can be found in the  $\alpha$ -Mg phase. Then it could be concluded that Mg-F and the

Mg-H are prone to similar alterations of the solubility limits: when nanostructured the solubility limits change to higher possible uptake of H / F in the  $\alpha$ -phase before the  $\beta$ -phase is formed, as well as a larger amount of vacancies x that can be accommodated in the  $\beta$ -phase MgH/F<sub>2-x</sub>.

The rapid low temperature uptake of H in fresh catalyzed samples reduces in speed under similar conditions for aged samples. Here a redistribution of F and/or H over the phases is found that may be related to this altering catalytic activity at low temperature. Indications are that for the  $\beta$ -MgF<sub>2-x</sub> it is important to keep higher fluorine concentrations.

Another factor in the fluorine activity is the effect that was seen in calculations on the decomposition enthalpy for  $Na_{12}Al_4H_{24}$  system which were performed with a few hydrogen anions substituted by F anions.<sup>42</sup> For progressive substitution of F for H the decomposition enthalpy is reduced from 59.1 to 45 kJ mol<sup>-1</sup> when 4 F anions substitute 4 H anions. For MgH<sub>2</sub> catalyzed by TiF<sub>3</sub> the absorption kinetics is much faster as a result of the reduced size of the particles, the mutual influence through matching lattices that induce altered solubility limits<sup>10</sup>, and also fluorine dissolution in the MgH<sub>2-x</sub>.

Taking all information gained from the experiments described above, we propose the following model of the (de-) re-hydrogenated catalyzed sample as illustrated in Figure 6.11. Initially after ball-milling (left) of MgH<sub>2</sub> and TiF<sub>3</sub> nano-sized MgH<sub>2</sub> and TiF<sub>3</sub> phases exist with small amounts of MgO which cannot be completely avoided. During desorption (middle) TiF<sub>3</sub> is consumed and new phases mainly  $\beta$ -MgF<sub>2-x</sub>, TiH<sub>2</sub> and Mg appear. A TiH<sub>2</sub> phase in a form of very small particles or layers occurs as inclusions in the Mg and also in the MgH<sub>2</sub> matrix in the case of the rehydrogenated sample. The influence of O in the  $\beta$ -MgF<sub>2-x</sub> phase spectra indicates that this phase is located at the grain surface as is the MgO. After absorption (right) part of the non-stoichiometric  $\beta$ -MgF<sub>2-x</sub> phase is loaded with hydrogen and exists as a modified stable  $\beta$ -MgF<sub>2-x</sub>H<sub>x</sub> phase.



**Figure 6.11** Cross-section models of the ball milled (left), desorbed (middle) and partly rehydrogenated (right)  $TiF_3$  catalyzed MgH<sub>2</sub> sample. The top part shows the morphology at the grain scale, while the bottom shows smaller area's near surfaces.

#### 6.4 Conclusions

MgH<sub>2</sub> with 5 mol% of TiF<sub>3</sub> additive was investigated in order to understand the role of the catalyst and gain more information about the local chemical changes that occur during de- / re-hydrogenation processes. Combined X-ray diffraction and MAS NMR experiments indicate a small amount of a Mg-Ti-F in the dehydrogenated sample and of  $\beta$ -MgF<sub>2x</sub>H<sub>x</sub> in the re-hydrogenated material. In the partially hydrogen loaded sample it appears that non-stoichometric  $\beta$ -MgH<sub>2x</sub> transforms over time into less but more stable stoichiometric MgH<sub>2</sub> next to increased amount of  $\alpha$ -Mg. This indicates that the material is in fact metastable, which corroborates with the less negative enthalpy of formation observed in earlier

work. On large scale average the catalytic additive is homogenously distributed over the sample. On a more local scale EDX indicates that the fluorine is present rather on the surface of the Mg / MgH<sub>2</sub> particles and Ti, present as very small TiH<sub>2</sub> particles is embedded in the Mg / MgH<sub>2</sub> phase. MgO is normally present in these samples as a 3-5 nm shell which surrounds Mg / MgH<sub>2</sub> grains. We have observed four different fluorine environments in the re-hydrogenated sample via <sup>19</sup>F NMR experiments. The influence of MgO domains included in the MgF2 can explain part of the signals, where the proximity of the different sites is shown using 2D NMR. Sub-stoichiometric  $\beta$ -MgF<sub>2-x</sub> occurs with in addition time dependent decreasing F occupancy in the dehydrogenated sample. Such time dependence may change the catalytic activity. During the hydrogen sorption process insertion of H in the  $\beta$ - $MgF_{2x}$  phase takes place. This indicates that besides acting as a grain refiner and nucleation site for the MgH<sub>2</sub> phase the  $\beta$ -MgF<sub>2-x</sub>H<sub>y</sub> can transport H. It is suggested that in the nanoscale Mg-F phase diagram behaves similarly to the Mg-H phase diagram, possessing altered solubility limits. Morphologies of de- and rehydrogenated samples and its different phases were proposed.

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### Summary

In this thesis representatives of two different types of materials for potential hydrogen storage application are presented. Usage of either nanoporous materials or metal hydrides has both operational advantages and disadvantages. A main objective of this thesis is to characterize the hydrogen storage mechanism of selected Metal-Organic Framework (MOF) materials. Such knowledge may provide information in which direction improvements of the materials may be possible. Detailed analysis of the hydrogen storage mechanism was performed using experimental techniques like powder X-ray diffraction, FT-IR, TEM, hydrogen sorption experiments and solid state NMR. Apart from the hydrogen sorption characteristics also knowledge about the stability of the frameworks themselves was obtained. Additional insight on the MOFs structure and on hydrogen sorption kinetics and thermodynamic factors was gained from modeling methods which includes Density Functional Theory and force field calculations.

One of the issues of the low hydrogen storage capacity in MOFs, under close to ambient conditions, is the weak adsorption interaction between hydrogen and adsorbent. Therefore, to find a way to increase the effective strength of van der Waals interactions experienced by hydrogen in the MOFs has become an important topic. To study this in detail one of the most famous representatives of the MOFs family, MOF-5, with modified linkers was employed and the results are presented in *Chapter 3*. The results show that modification of the organic linker by substitution of one hydrogen atom on the benzene ring with electron donating –CH<sub>3</sub> and electron withdrawing –Br, -Cl groups have an influence on the structural stability, and as a consequence also on the hydrogen storage capacity of the modified MOFs. On the other hand the CH<sub>3</sub>-MOF-5 possesses higher hydrogen uptake than MOF-5 at the temperature of 77 K and the pressure below 1 bar. Additionally, when two of the four hydrogen atoms on a benzene ring are substituted with –CH<sub>3</sub> groups the modified material interestingly possesses improved stability against moisture i.e. water. Because moisture sensitivity is very often an issue for MOFs this discovery is

particularly important. Although computational and experimental results show that the heat of adsorption values for investigated MOF-5 derivatives are very similar, the large difference in specific surface area and pore volume, which result from the altered framework stability, has significant impact on hydrogen adsorption capabilities. The hydrogen diffusion in modified MOF structures is influenced by both spatial hindrance of bigger functional groups and by the hydrogen increasing loading itself which cause hydrogen diffusion coefficients to decrease.

Small metal hydride nanoparticles appear to have considerable promise for hydrogen sorption under close to ambient conditions. Inclusion of metal hydrides within MOFs was considered in order to host these small metal particles and at the same time allow free hydrogen diffusion access. However, it occurred to be an impracticable approach for some types of MOFs. One of the copper based MOFs - Cu<sub>3</sub>(BTC)<sub>2</sub> - has been tested for this purpose and the obtained results are described in *Chapter 4*. Since the metal hydride requires elevated operating temperatures, high temperature tests in a hydrogen environment were performed. The Cu<sub>3</sub>(BTC)<sub>2</sub>, which normally has good thermal stability in vacuum, loses this irrevocably in the presence of hydrogen and is reduced into copper particles and carboxylic acid groups. Therefore this candidate is definitively excluded for such application. This result shows that care should be taken when choosing a porous material as a template for metal particles reacting with hydrogen at given pressure and temperature conditions.

In *Chapter 5* mesoporous silica's materials with bigger pore size than most of the metal-organic frameworks are described. In particular the hydrogen adsorption capacity of the silica's was investigated and their relation with pore size and specific surface area, with the basic goal to understand the pore size dependence of effective van der Waals interactions. Silica's were chosen because they can have very large pore size with essentially the same internal chemical surface. Despite the fact that the correlation between hydrogen storage capacity and specific surface area for the studied materials is clearly linear, like in the case of porous carbons or zeolites, it

does not extend through the origin due to the in this case reducing interaction strength for larger pores. The asymptotic correlation between pore size and hydrogen uptake is associated with van der Waals potential energy of the internal pore surface which decreases for larger pores. MCM-41 which has around ten times smaller pore size than that of the aerogel can store two times more hydrogen by weight and per specific surface area. The difference in values of isosteric heats of adsorption estimated for all the compounds is distinctly measurable. Although not large the obtained difference in isosteric heat of adsorption can explain the doubling of hydrogen surface coverage of MCM-41 in comparison with aerogel. From the obtained results it can be concluded that the pore size of the material remains a factor of high importance when considering efficient hydrogen storage, even up to relatively large distance scales.

*Chapter 6* contains the microscopic study of a nanostructured metal hydride system.  $MgH_2$  was investigated which is well known from its hydrogen storage potential due to its high gravimetric hydrogen capacity. Because the hydrogen loading process to the Mg metal suffers from slow kinetics 5 mol% of TiF<sub>3</sub> was added to catalyze the hydrogen sorption reaction. Previously this system was shown to have improved hydrogen absorption/desorption kinetics and a lower dehydrogenation temperature in comparison to the pure MgH<sub>2</sub>. However, the mechanism of the reaction and the reason of the improvement were not fully understood until now. New insight on the microstructure of the complex is gained and subsequently the models of the dehydrogenated and re-hydrogenated structures are proposed. According to detailed Rietveld refinement analysis in the dehydrogenated sample the following phases are present:  $\alpha$ -Mg, MgF<sub>2-x</sub>, cubic TiH<sub>2</sub>, MgO and a new Mg-Ti-F phase. During re-hydrogenation next to the MgH<sub>2-x</sub>, MgF<sub>2-x</sub>, TiH<sub>2</sub>, MgO, and Mg some hydrogenated MgF<sub>2-x</sub> $H_x$  phase appeared. Such MgF<sub>2-x</sub> $H_x$  phase may play a role in improving hydrogen absorption/desorption kinetics by allowing H transport through the vacant fluorine sites. Furthermore long term storage of a partially hydrided material shows that the morphology, containing  $\alpha$ -Mg and  $\beta$ - $MgH_{2x}$  in different ratio's, evolves. Such evolution is consistent with the initial

lower enthalpy of formation of the material, i.e. the system evolves to a slightly more stable state.

The catalyst is homogenously distributed on the large scale over the de- and rehydrogenated sample according to TEM EDX results. On the more local scale the fluorine containing phases are present more on the surface of the Mg/MgH<sub>2</sub> particles whereas the TiH<sub>2</sub> phase can be found in the form of small particles embedded in the Mg/MgH<sub>2</sub> phase. Different fluorine environments corresponding with modified MgF<sub>2</sub> phases were found using solid state <sup>19</sup>F NMR experiments in the re-hydrogenated sample. Comparison with literature shows that the fluorine has close proximity to MgO. A model for the morphology of the material is deduced in which the different phases are placed that can either transport hydrogen or that play a role in stabilizing the Mg or magnesium hydride surfaces.

## Samenvatting

In dit proefschrift worden vertegenwoordigers van twee verschillende types van materialen voor potentiële toepassing in waterstofopslag gepresenteerd. Gebruik van ofwel nanoporeuze materialen ofwel metaalhydriden heeft zowel operationele voordelen als nadelen. Een belangrijk doel van dit proefschrift is het karakteriseren van het mechanisme van waterstofopslag in geselecteerde Metal-Organic Framework (MOF) materialen. Deze kennis kan informatie verschaffen in welke richting verbeteringen van de materialen mogelijk zijn. Gedetailleerde analyse van het mechanisme van waterstofopslag werd uitgevoerd met experimentele technieken FT-IR, zoals poeder Röntgendiffractie, transmissieelektronenmicroscopie, waterstofsorptie experimenten en vastestof-NMR. Naast de waterstofsorptie-eigenschappen werd ook kennis over de stabiliteit van de frameworks zelf verkregen. Extra inzicht in de structuur van de MOFs en in de waterstofsorptie-kinetiek en thermodynamische factoren werd verworven door modelleren onder andere met Density Functional Theory en force field berekeningen.

Een van de problemen van de lage capaciteit voor waterstofopslag in MOF's, onder omstandigheden nabij die van de omgeving, is de zwakke adsorptiewisselwerking tussen waterstof en adsorbens. Een belangrijk onderwerp is het vinden van manieren om de effectieve sterkte van de van der Waals interacties tussen waterstof en de MOFs te verhogen. Om dit in detail te onderzoeken werd een van de beroemdste vertegenwoordigers van de MOF familie, MOF-5, met gemodificeerde linkers gebruikt en de resultaten worden in *Hoofdstuk 3* gepresenteerd. De resultaten tonen dat modificatie van de organische linker door substitutie van een waterstofatoom op de benzeenring door electronendonerende -CH<sub>3</sub> en elektronenaccepterende -Br, -Cl groepen invloed heeft op de stabiliteit van de structuur, en daardoor dus ook op het vermogen tot opslag van waterstof door de gewijzigde MOFs. Anderzijds neemt CH<sub>3</sub>-MOF-5 meer waterstof op dan MOF-5 bij een temperatuur van 77 K en druk beneden 1 bar. Bovendien, als twee van de vier

waterstofatomen op een benzeenring zijn gesubstitueerd door -CH<sub>3</sub> groepen, bezit het gemodificeerde materiaal interessant verbeterde stabiliteit tegen water in bijvoorbeeld de lucht. Omdat vochtgevoeligheid vaak een probleem voor MOFs is, is deze ontdekking bijzonder belangrijk. Hoewel rekenkundige en experimentele resultaten tonen dat de waarden voor de adsorptiewarmte voor de onderzochte MOF-5 derivaten sterk op elkaar lijken, heeft het grote verschil in specifiek oppervlak en porievolume, die het gevolg zijn van de gewijzigde stabiliteit, grote invloed op het vermogen tot adsorptie van waterstof. De waterstofdiffusie in gemodificeerde MOF structuren wordt beïnvloed door zowel ruimtelijke belemmering door grotere functionele groepen als de verhoging van de hoeveelheid waterstof zelf. Beide veroorzaken een afnamen van de diffusiecoëfficiënten van waterstof.

Kleine metaalhydride-nanodeeltjes beloven veel voor waterstofsorptie onder omstandigheden nabij die van de omgeving. Opneming van metaalhydriden in MOFs werd overwogen om deze kleine metaaldeeltjes vast te leggen en tegelijkertijd vrije diffusie van waterstof toe te laten. Het bleek echter een onpraktische benadering voor bepaalde typen MOFs. Een op koper gebaseerde MOF - Cu<sub>3</sub>(BTC)<sub>2</sub> - is voor dit doel getest en de verkregen resultaten worden in 4 beschreven. Aangezien het metaalhydride Hoofdstuk verhoogde werktemperaturen vereist, werden tests bij hoge temperatuur in een waterstofomgeving uitgevoerd. Cu<sub>3</sub>(BTC)<sub>2</sub> heeft goede thermische stabiliteit in vacuum maar verliest dit onherroepelijk in aanwezigheid van waterstof en wordt chemisch gereduceerd tot koperdeeltjes en carbonzuurgroepen. Daarom wordt deze kandidaat definitief voor een dergelijke toepassing uitgesloten. Dit resultaat toont, dat zorg moet worden betracht bij het kiezen van een poreus materiaal als basis voor metaaldeeltjes, wanneer deze mogelijk met waterstof reageren bij gegeven druk en temperatuur.

In *Hoofdstuk 5* zijn mesoporeuze silicamaterialen met veel grotere poriën dan de meeste metal-organic frameworks beschreven. In het bijzonder werd de waterstofadsorptie-capaciteit van de silica's onderzocht en hun relatie met poriegrootte en specifiek oppervlak. Het fundamentele doel was om te begrijpen hoe de effectieve van der Waals interacties afhangen van de poriegrootte in zeer grote poriën. Silica's werden gekozen omdat zij zeer grote poriegrootte hebben met wezenlijk identieke inwendige chemische oppervlakken. Ondanks het feit dat de correlatie tussen waterstofopslag-capaciteit en specifiek oppervlak van de onderzochte materialen duidelijk lineair is, zoals in het geval van poreuze koolstof of zeolieten, gaat de grafiek niet door de oorsprong, omdat in dit geval de interactiesterkte voor grotere poriën afneemt. De asymptotische correlatie tussen poriegrootte en waterstofopname is geassocieerd met de van der Waals potentiële energie van het interne porieoppervlak, die afneemt voor grotere poriën. MCM-41 dat een ongeveer tien keer kleinere poriegrootte dan de aerogel heeft, kan twee keer zoveel waterstof in gewicht en per specifiek oppervlak opslaan. Het verschil in waarden van isosterische reeksen van adsorptiewarmte geschat voor alle verbindingen is duidelijk meetbaar. Hoewel niet groot, kan het verkregen verschil in isosterische adsorptiewarmte de verdubbeling van de oppervlaktebedekking door waterstof van MCM-41 in vergelijking met aerogel verklaren. Uit de verkregen resultaten kan worden geconcludeerd dat de poriegrootte van het materiaal een factor van groot belang blijft bij de efficiënte opslag van waterstof, zelfs tot op relatief grote afstandsschalen.

*Hoofdstuk* 6 bevat de microscopische studie van een nanogestructureerd metaalhydride-systeem. Onderzocht werd MgH<sub>2</sub>, dat goed bekend is om zijn potentieel voor de opslag van waterstof vanwege de hoge gravimetrische waterstofcapaciteit. Omdat het laadproces van waterstof in het Mg metaal lijdt onder een langzame kinetiek, werd nanostructurering toegepast en 5 mol% TiF<sub>3</sub> toegevoegd om de waterstofsorptie te katalyseren. Eerder was aangetoond, dat dit systeem een verbeterde waterstofabsorptie- / desorptie-kinetiek en een lagere dehydrogenatietemperatuur heeft in vergelijking met zuiver MgH<sub>2</sub>. Het mechanisme van de reactie en de reden van de verbetering waren tot nu toe echter niet volledig begrepen. Nieuw inzicht in de microstructuur van het complex wordt verkregen en vervolgens worden modellen voor de gedehydrogeneerde Rietveld

verfijningsanalyse zijn in het gedehydrogeneerde sample de volgende fasen aanwezig:  $\alpha$ -Mg, MgF<sub>2-x</sub> kubisch TiH<sub>2</sub>, MgO en een nieuwe Mg-Ti-F fase. Bij opnieuw hydrogeneren is naast de MgH<sub>2-x</sub>, MgF<sub>2-x</sub>, TiH<sub>2</sub>, MgO en Mg een gehydrogeneerde MgF<sub>2-x</sub>H<sub>x</sub> fase verschenen. Een dergelijke MgF<sub>2-x</sub>H<sub>x</sub> fase kan een rol spelen bij het verbeteren van de waterstofabsorptie- / desorptie-kinetiek door H transport via de fluor vacatures. Verder blijkt uit opslag gedurende een lange termijn van een gedeeltelijk gehydreerd materiaal dat de morfologie, met α-Mg en  $\beta$ -MgH<sub>2-x</sub> in verschillende verhoudingen, langzaam evolueert. Deze evolutie is consistent met de initiële lagere vormingsenthalpie van het materiaal, dat wil zeggen dat het systeem zich in de tijd ontwikkelt naar een enigszins stabielere toestand. De katalysator is op grote schaal homogeen over het gede- en gerehydrogeneerde sample verdeeld volgens TEM EDX resultaten. Op meer lokale schaal zijn de fluor bevattende fasen aanwezig op het oppervlak van de Mg/MgH<sub>2</sub> deeltjes terwijl de TiH<sub>2</sub> fase in de vorm van kleine insluitingen in de Mg/MgH<sub>2</sub> fase wordt gevonden. Verschillende fluoromgevingen, die overeen komen met gemodificeerde MgF<sub>2</sub> fasen werden met behulp van vastestof-<sup>19</sup>F-NMR experimenten in het gerehydrogeneerde sample gevonden. Uit vergelijking met literatuur blijkt dat fluor in de nabijheid van MgO wordt gevonden. Een model voor de morfologie van het materiaal wordt afgeleid waarin de verschillende fasen zijn geplaatst die hetzij waterstof transporteren hetzij een rol spelen bij het stabiliseren van de Mg- of magnesiumhydride-oppervlakken.

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### About the author

Anna was born on August 25, 1984 in Czarnkow, Poland. In 2003, she graduated with honors the secondary school in Czarnkow. In the same year she moved to Poznan to study Applied Physics at Poznan University of Technology. In July 2006 she did traineeship at Delft University of Technology during which she investigated biomass char particles and bed material originating from Circulating Fluidized Bed gasification of Miscantus Gigantus and quality A wood by means of scanning electron microscope (SEM). In September 2007 Anna attended summer school about microand nanotechnology at University of Applied Sciences in Brandenburg. She joined Molecular Physics Division at Poznan University of Technology for her Master project entitled "Photothermal processes in chlorins modified with metal ion". In June 2008 she received her Master of Science and Engineering (MSc. Ir) Degree. In November 2008 she joined the group of Fundamental Aspects of Materials and Energy (FAME) at Delft University of Technology and started her Doctoral studies under supervision of Prof. Dr. F.M. Mulder. The results obtained during four years of her research are described in this thesis.