Hydrogen storage in Co-and Zn-based metal-organic frameworks at ambient temperature

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ABSTRACT

Hydrogen adsorption properties of some Co-and Zn-based Metal-Organic Framework (MOF) materials were studied at near ambient temperatures. Maximal hydrogen storage capacity of 0.75 wt% was found for a Zn-based material at 175 Bar hydrogen pressure and T = 4 °C. Hydrogen adsorption correlated linearly with BET surface area and strongly depends on temperature. Relatively low structural stability of some MOF's results in framework collapse during degassing and hydrogen adsorption measurements.

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1. Introduction

Hydrogen is widely recognized as a fuel of future since it is environmentally clean, abundant in nature and shows high gravimetric energy capacity [1]. However, problem of safe and reversible storage of the sufficient amount of hydrogen is the main obstacle to application of hydrogen as a conventional fuel. There are four main possibilities to store hydrogen: as a liquid, as a compressed gas, to split hydrogen molecules into atoms which form strong chemical bond with solids (chemisorption) or to bound molecular hydrogen to a sorbent with high specific surface area through the weak Van der Waals force (physisorption). The most frequently studied sorbents which store hydrogen through the physisorption are activated carbons [2,3], carbon nanostructures (e.g. carbon nanotubes, graphite nanofibres, carbon nanohorns) [4,5], zeolites [6,7], clathrate hydrates [8] and metal-organic frameworks (MOFs) [9,10]. MOFs are crystalline coordination polymers which contain metal ions or clusters connected by organic linkers. They show some advantages for hydrogen storage compared to other porous solids. Some of these materials have a very high specific surface area with a record values registered for MIL-101 (a Langmuir surface area equals to 5900 m²/g) [11] and for MOF-177 (Langmuir: 5994 m²/g) [12]. Through the combination of different organic ligands and ion clusters it is possible to get almost an infinite number of geometrical and chemical variations for structures of these materials. Moreover, the post-synthetic modification of MOFs could be done in order to introduce additional active sites for stronger hydrogen binding [13,14]. All of above listed characteristics make MOFs one of the most promising sorbent materials for hydrogen storage. A lot of research activities were focused...
during last few years on hydrogen storage in MOFs with most exciting results reported at cryogenic temperatures (77 K). For instance, well-known and one of the most studied MOF-177 was reported to adsorb gravimetrically 7, 6 wt% of H$_2$ (or 32 g L$^{-1}$ in terms of volumetric adsorption) at 77 K and 66 bar hydrogen pressure [15] or 11,0 wt% of H$_2$ (or 46 g L$^{-1}$) at 77 K and 100 bar hydrogen pressure [12]. At the room temperature, the binding energy between hydrogen and MOFs is relatively weak and hydrogen uptake usually does not exceed 1 wt% [16]. However, even with values of gravimetric storage capacity on the level of 1 wt% the MOF’s are some of the best materials for physisorption of hydrogen. It’s gravimetric capacity is on the same level as for best activated carbons [2] and carbon nanotubes [4], but volumetric properties are far more superior. Unlike to e.g. activated carbons, which require extremely high dispersion (and therefore extremely low bulk density, tens times below the real density of graphite), high surface area is combined in MOF’s with bulk densities comparable to real density. Therefore, the real tank filled by crystalline MOF powder will be able to store far greater amounts of hydrogen compared to highly dispersed activated carbons.

New MOF’s are currently synthesized in large numbers and crystal structures solved by X-ray or neutron diffraction are regularly reported; see e.g. refs [17,18]. Therefore, it is important to investigate new kinds of MOF’s for hydrogen adsorption properties, to reveal most important parameters which control hydrogen storage in these materials and, possibly, to use accumulated knowledge for more target oriented design of new MOF’s aimed for hydrogen storage applications.

Recently H. Chun et al. synthesized a set of new Zn- and Co-based MOFs with different pore structure. Using unusual flexibility of 1,4-benzeneedicarboxylate (bdc) ligands they obtained two topological isomers of [Zn$_2$(bdc)$_2$(dabco)] (dabco is 1,4-diazabicyclo[2.2.2]octane, chemical formula: C$_{22}$H$_{20}$N$_2$O$_8$Zn$_2$). One of them (ZBDt) was found to have a square-grid net topology (square channels) [19], while another one (ZBDh) consisted of triangle and hexagonal channels (pillared Kagome net) [20]. Changing connection ligands H. Chun and coworkers reported later synthesis of [Zn$_4$(ipp)$_3$(dabco)[OH$_2$]$_2$] which is a new MOF with a unique 5-connected topology (ZID and ZID$_n$, chemical formula: C$_{58}$H$_{32}$N$_8$O$_{18}$Zn$_4$) [21], and [Zn$_n$(O)(mip)$_3$] which is based on a non-uniform six-connected net (chemical formula: C$_{42}$H$_{55}$N$_5$O$_{19}$Zn$_4$) [22]. All of mentioned above MOFs have a different pore geometry and as a consequence show different hydrogen adsorption characteristics. Low temperature hydrogen sorption studies revealed that all reported MOF have a hydrogen storage capacity in the range 1.5-2.1 wt% at 1 bar of hydrogen pressure. The Co-based MOF, where 2,6-naphthalenedicarboxylate and 1,4-diazabicyclo[2.2.2]octane (CND, chemical formula: C$_{22}$H$_{20}$N$_2$O$_8$Co$_2$) is used as a connection ligands forming a variation of primitive cubic net, was reported to adsorb 2,45 wt.% of hydrogen at 77 K and 1 bar of hydrogen pressure and 77K [23]. It is worth to mention that known MOFs with the best adsorption properties could adsorb hydrogen in the range of 2, 59-3, 42 wt% at the same conditions as it was recently reported by J.R. Long et al [17].

Hydrogen adsorption studies at cryogenic temperatures are interesting for fundamental research. However, the technical requirements for hydrogen storage materials are that they could be operated at near ambient temperatures and pressures below 200 Bar. In this study we report hydrogen storage properties of recently synthesized MOF’s at temperatures near ambient and broader pressure interval up to 150 Bar. Hydrogen adsorption on well-known MOF-5 material [24] was also measured for comparison. Structural stability of these materials in process of hydrogen adsorption experiments is verified.

2. Experimental section

Zn- and Co-based MOFs were synthesized by H. Chun and coworkers, details for synthesis and structure of these materials can be found elsewhere [19–23]. MOF-5 was synthesized by the solvothermal (convective heating) method [25,26]. 1,34 g of zinc nitrate hexahydrate (Zn(NO$_3$)$_2$6H$_2$O, 98%, Sigma-Aldrich) and 0,25 g of terephthalic acid (H$_2$BDC, 98%, Sigma-Aldrich) were dissolved in 40 ml of N, N-dimethylformamide (DMF, 99.8%, A.C.S. reagent, Sigma-Aldrich) under mild stirring. Then the transparent solution was transferred into a 50 ml vial and put in the oven maintained at 105 ºC. After 72 h the solution was filtered off and MOF-5 crystals were washed three times by DMF. Finally, prior BET and hydrogen sorption measurements, MOF-5 were activated in vacuum at 120 ºC for 12 h. Structural stability of samples was verified prior and after measurements of hydrogen adsorption using powder X-ray diffraction (Siemens D5000 diffractometer with CuK$_\alpha$ radiation). Hydrogen adsorption was measured by gravimetric method using magnetic suspension balance from Rubotherm. Details of Rubotherm system employed for our measurements of hydrogen adsorption can be found in previously published study [27]. The measurements were performed using samples of about 0.2–0.4 g, hydrogen pressures up to 180 bars and temperature interval of −5 ºC–100 ºC. The temperature was controlled using thermostat with circulated liquid which goes through a shell around measurement cell. Precision of the temperature control was ±0.02 ºC. The accuracy of the balance was 0.01 mg allowing a reproducibility of ±0.02 mg. The magnetic suspension system allows disconnection the crucible from the rest of the balance allowing regular calibration of the balance during the experiment. It also minimizes the volume of the weighed system for the buoyancy effect correction [27,28]. Regular measurements included several steps:

- Degassing of the sample at high vacuum conditions (10$^{-5}$ Torr) and at temperatures selected based on previously published thermo gravimetical studies (CND [23], ZID [21] – at 20 ºC, ZBD [19,20], ZBDh [20] – 100 ºC, Zn$_4$(O)(mip)$_3$ [22] – 110 ºC). The time of degassing was controlled by direct observation of mass loss in process of treatment and stopped when gravimetric curve become flat. Typical duration of degassing was about 12 h.
- Hydrogen adsorption at 20 ºC or −4 ºC (later only for ZBDh as for the MOF, which had a highest hydrogen uptake within all measured samples at 20 ºC) and up to 150 bar hydrogen pressure and desorption at high vacuum conditions.
- Total volume V$_{he}$ (volume of the sample together with cell and holder) was determined using step-like increase of...
helium pressure, amount of adsorbed hydrogen calculated after correction to buoyancy effect.

The nitrogen sorption isotherms were recorded using Quantachrome NOVA 1200 gas sorption analyzer at the liquid nitrogen temperature. Prior to the measurement all samples were degassed in order to remove guest solvent molecules using the same degassing condition as for the hydrogen adsorption measurement. The BET surface area and the total pore volume calculation were performed using the standard NOVAWin-P version 10.0 + software.

3. Results and discussion

Hydrogen sorption isotherms for all investigated MOFs, which were recorded in hydrogen pressure range 0–120 bar at \( T = 20 \, ^\circ\text{C} \), are shown on Fig. 1. The highest hydrogen uptake equal to 0.51 wt% was observed for ZBDh. After decreasing the temperature down to \(-4 \, ^\circ\text{C} \), the hydrogen uptake was slightly higher: 0.63 wt% at 120 bar. However, the saturation for both temperatures was not achieved at 120 Bar. Therefore, pressure was farther increased and at 175 bar the hydrogen uptake achieved 0.75 wt%, see Fig. 2. Even at that pressure the adsorption curve do not seem to reach saturation.

The hydrogen adsorption was found to be completely reversible and the equilibrium value of hydrogen uptake was established every time within few minutes after the hydrogen pressure was stabilized. That is in agreement with previous results which claimed that the hydrogen adsorption in MOFs is caused by physisorption \[16\].

The hydrogen uptake for ZBDt was found to be slightly smaller (0.42 wt% at 120 bar of hydrogen pressure and \( T = 20 \, ^\circ\text{C} \)) then for ZBDh. This result is opposite to the data obtained by H. Chun et al (at the liquid nitrogen temperature and 1 bar of hydrogen pressure) which showed higher hydrogen adsorption for ZBDt compared to ZBDh, see Table 1 \[20\].

However, as it could be seen on Fig. 1, the saturation for both ZBDh and ZBDt samples was not achieved. When isotherms were extrapolated to a higher-pressure region using a Langmuir fit, the hydrogen adsorption saturation value was found to be 1.85 wt% for ZBDt (1.63 wt% for ZBDh). The saturation according to this fit would be achieved at the rather high pressure (4000–5000 bar).

Lower hydrogen adsorption seems to be in contradiction with higher BET surface area of the ZBDt sample. Typically, MOFs with higher specific surface area (SSA) are known to have larger hydrogen uptake values at high pressures \[16\]. The difference in hydrogen adsorption capacity could possibly originate from partial collapse of structure in process of measurements: e.g. due to the temperature induced decomposition in process of degassing or due to relatively high pressures of hydrogen. It should be noted that data on pressure stability of MOF’s are not present in previously published studies. Some MOF’s could be rather sensitive to pressure since the framework structure with very large pores is more likely to collapse under elevated conditions. Therefore, it was important to verify stability of both ZBDt and ZBDh using powder diffraction data recorded from samples subjected to degassing and hydrogen adsorption experiment, see Fig. 3.

Powder diffraction patterns were indexed for both ZBDh and ZBDt using structures previously identified by Chun et al. \[20\] and appeared to be in a good agreement. However, the XRD pattern of ZBDh exhibited some unidentified reflections which indicate that the phase was not completely pure. It might be that some additional product was formed in process of prolonged degassing conducted prior to adsorption measurements or due to exposure of sample to relatively high hydrogen pressures (120 Bar). XRD pattern of ZBDt shows reflections from only one phase. This result confirms that difference in hydrogen adsorption results should be related to structural difference in ZBDt and ZBDh but not to partial collapse of structure. It should be noted that the difference is not large and might also depend on degassing procedures used in our experiments. The problems of structural stability become even more obvious in experiments with some other MOF’s (see below).

Another kind of MOF’s studied here for hydrogen adsorption are ZID and ZIDs \[29\] which are, in principle, the same...
materials, but prepared using different methods resulting in somewhat different properties [29]. Material synthesized by solvothermal reaction (ZIDs) was also obtained as fine powder while ZID consisted of relatively large crystals. Nitrogen sorption studies showed that ZID had higher BET surface area and total pore volume comparing to the less pure ZIDs sample (for more details see Table 1). The difference is possibly explained by short exposure of sample to air. The material is rather sensitive to humidity and, possibly, ZIDs was affected stronger due to its microcrystalline powder state. The hydrogen adsorption value measured for ZID was relatively small, on the level of 0, 2 wt%, what was almost two times higher then the ZIDs hydrogen uptake value measured at the same conditions. Low hydrogen adsorption measured for these sample is in agreement with relatively small BET surface area. According to XRD data both materials survived degassing of material was not achieved in our experiments. Therefore, it might be that complete degassing of material was not achieved in our experiments. Relatively low structural stability the CND should be considered as critical problem for its application as hydrogen storage material since even slight heating results in structure collapse.

Attempts to measure hydrogen adsorption were also made for Zn₄(O)(mip)₃. However, measured adsorption appeared to be rather low, see Table 1. These results could be explained using structural characterization by powder X-ray diffraction recorded before and after adsorption experiments. Analysis of diffraction patterns showed that Zn₄(O)(mip)₃ collapsed during hydrogen sorption measurements. It should be noted that these materials were reported as less stable [22]. Typically it is stored immersed into some liquid which fills large pores and stabilizes the structure.

The Zn₄(O)(mip)₃ sample should be relatively stable according to previously published data and was degassed at temperature T = 110 °C. This temperature was selected based on results the thermogravimetric analysis, previously published by H. Chun et al [22]. However, analysis of XRD patterns recorded in this study after degassing and hydrogen adsorption measurements proved that the sample framework structure collapsed. It should be noted that heat treatment in our experiments was relatively long (12 h) compared to TGA experiments which typically take much shorter time. Possibly Zn₄(O)(mip)₃ could be kept stable using lower degassing temperature but in this case it could be rather difficult to remove all traces of solvent from it’s structure. Therefore, relatively weak structural stability of this material is the major obstacle for possible applications.

<table>
<thead>
<tr>
<th>Name</th>
<th>Surface area (exp.), m²/g</th>
<th>Surface area (literature), m²/g</th>
<th>Pore volume (exp.), g/cm³</th>
<th>Pore volume (literature), g/cm³</th>
<th>Hydrogen uptake (exp.), wt.%a</th>
<th>Hydrogen uptake (literature), wt.%b</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZBDt</td>
<td>1961</td>
<td>1450 [12,13]</td>
<td>0,69</td>
<td>0,75 [12,13]</td>
<td>0,42</td>
<td>2,0 [12,13]</td>
</tr>
<tr>
<td>ZBDh</td>
<td>1674</td>
<td>1603 [13]</td>
<td>0,59</td>
<td>0,86 [13]</td>
<td>0,51</td>
<td>1,8 [13]</td>
</tr>
<tr>
<td>ZID</td>
<td>403</td>
<td>1609 [14]</td>
<td>0,56</td>
<td>0,86 [14]</td>
<td>0,2</td>
<td>1,5 [14]</td>
</tr>
<tr>
<td>ZIDs</td>
<td>198</td>
<td>–</td>
<td>0,11</td>
<td>–</td>
<td>0,09</td>
<td>–</td>
</tr>
<tr>
<td>Zn₄(O)(mip)₃</td>
<td>34,4</td>
<td>1062 [15]</td>
<td>0,017</td>
<td>0,56 [15]</td>
<td>0,1</td>
<td>2,1 [15]</td>
</tr>
<tr>
<td>CND</td>
<td>1375</td>
<td>1502 [10]</td>
<td>0,47</td>
<td>0,822 [10]</td>
<td>0,33</td>
<td>2,45 [10]</td>
</tr>
<tr>
<td>MOF-5</td>
<td>1203</td>
<td>839,6 [18]</td>
<td>0,66</td>
<td>0,34 [18]</td>
<td>0,3</td>
<td>3,6 [18]b</td>
</tr>
</tbody>
</table>

a Data were recorded at: 1) 77 K and 1 bar of hydrogen pressure (literature), 2) at RT and 120 bar of hydrogen pressure (our experiment).

b Data were recorded at 77 K and 17, 4 bar of hydrogen pressure.

![Fig. 3 – Powder diffraction patterns recorded from samples of ZBDt and ZBDh after adsorption experiments. For ZBDh reflections were indexed as P-3m1 a = 21.57 Å c = 9.56 Å, for ZBDt as P4/mmm a = 10.945 Å, c = 9.567 Å. Unidentified reflections are marked by stars.](image-url)
The research field of hydrogen storage materials was plagued by set of erroneous reports of high hydrogen adsorption over past decades. Therefore, we paid special attention to verification of our measurement procedures to ensure high precision of results. For this purpose we performed set of measurements on samples of MOF-5 which has well-known structural properties and is so far most studied for hydrogen adsorption. The structure of MOF-5 samples synthesized for this study was in a good agreement with previously published [30]. Powder XRD patterns recorded from our samples were indexed as Fm-3m with a refined cell-parameter a = 25,9 Å. The BET (Langmuir) surface area was measured to be 1203 m²/g (1838 m²/g) with a total pore volume of 0,6 cm³/g. These values are lower compared to results obtained by W-J. Son and coworkers [26] (3200 m²/g as Langmuir surface area and 1, 21 g/cm³ as a total pore volume). However, it is known that a BET (Langmuir) surface area and a total pore volume of MOF’s strongly depend both on a synthesis method and an activation procedure [24,25,30]. Surface area values measured for MOF-5 samples prepared and activated previously by the similar procedure (BET (Langmuir) surface area: 839,6 (1029,1) m²/g, pore volume: 0,34 cm³/g) are in reasonable agreement with our results [25].

The hydrogen adsorption in our MOF-5 samples was found to be reversible with the maximum value of 0,3 wt% at 120 bar of hydrogen pressure which is in good agreement with literature data [16].

Summary of all adsorption data collected in this study can be found in the Table 1. It is interesting to verify possible trends in hydrogen adsorption and dependence of hydrogen storage capacity on various parameters, first of all BET specific surface area.

As it could be seen on Fig. 4 there is a linear relationship between the hydrogen adsorption uptake and the BET specific surface area in MOFs. The linear relationship on BET specific surface area was observed for both hydrogen adsorption data measured at 120 bar and for a Langmuir fit of this data. The slope of the red line (Langmuir fit) was found to be equal to 0,86 × 10⁻³ wt%/(m² × g⁻¹) and was significantly bigger then the slope of the black line (1,97 × 10⁻⁴ wt%/(m² × g⁻¹)), which represents data measured at 120 bar of hydrogen pressure.

For comparison, the slope of a maximum hydrogen adsorption value against SSA at the liquid nitrogen temperature was published in the literature [16] and was found to be equal to 1, 92 × 10⁻⁵ wt%/(m² × g⁻¹). As follows from these results, in order to achieve 6,0 wt% at room temperature (the DOE target for on-board hydrogen storage system by the year 2010), a MOF with a BET specific surface area equal to 7000 m²/g have to be synthesized. It does not look impossible since MOFs with a Langmuir surface area up to 5994 m²/g were already reported [12]. However, at the same time a hydrogen isosteric heat of adsorption should be increased in order to shift down the saturation pressure which is too high for any practical applications according to our experimental results.

Another important parameter of a material typically considered for hydrogen adsorption is pore volume [31]. The values of pore volume measured for our samples are shown in Table 1. Correlation of this parameter to hydrogen adsorption is less profound since the measurements were performed at ambient temperatures, while the pore volume in the studied range of pressures is more important parameter for hydrogen adsorption at cryogenic temperatures.

Another problem in application of novel MOFs for hydrogen storage is their relatively low structural instability compared to e.g. nanostructured carbon materials. So far, this problem received relatively little attention in literature. Structural characterization of samples is typically performed before hydrogen adsorption tests and rarely was reported for samples after adsorption experiments. This could be one of possible reasons for strong difference in hydrogen adsorption capacity of some MOF’s reported by various groups, see for example [24,25,30]. Certainly the structural stability of MOF materials needs to be verified after each adsorption experiment and degassing temperature must be adjusted to each material individually.

As it is demonstrated in this study, some of the MOF structures collapse already upon drying, while for others degradation occurs after relatively mild heat treatment required for complete degassing of samples. Therefore, structural stability is an important factor which should be taken into account in future attempts to design new MOF’s for hydrogen storage applications.

**Fig. 4 – The relationship between hydrogen adsorption value and BET specific surface area measured on different MOFs:** – hydrogen adsorption at 120 bar and room temperature with linear fit shown by black line, ▲ – the saturation value of hydrogen adsorption obtained using Langmuir fit with linear fit shown by red line, blue line-experimental results plotted according to hydrogen adsorption measured on MOFs at 77 K [9].

**4. Conclusion**

Hydrogen storage capacity was measured for several MOF materials at temperatures near ambient and H₂ pressures up to 175 Bar. The highest hydrogen adsorption value was recorded for ZBDh (0,51 wt% at 120 bar of hydrogen pressure and room temperature or 0,75 wt% at 175 bar and – 4 °C). The hydrogen uptake is found to depend linearly on the BET specific surface area and to depend strongly on temperature. It is shown that some MOF’s collapse even after relatively mild
treatments required for removal of solvent traces and complete degassing. Relatively low structural stability of framework structures is one of the key factors which need to be taken into account in a search for new MOF materials suitable for hydrogen storage applications.

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[29] ZID is synthesized by diffusion methods, while ZIDs is obtained by solvothermal reactions. Unpublished.