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Hydrogen physisorption in high SSA microporous materials – A comparison between AX-21_33 and MOF-177 at cryogenic conditions

Maurice Schlichtenmayer, Barbara Streppel, Michael Hirscher*

Max Planck Institute for Metals Research, Stuttgart, Germany

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ABSTRACT

The two most promising materials for a hydrogen cryo-adsorption tank, activated carbon AX-21_33 and metal-organic framework MOF-177, have been investigated in the pressure range up to 2 MPa and at temperatures from 77 K to 125 K and at room temperature. The total hydrogen storage, including adsorbed hydrogen and gaseous hydrogen, has been determined for both samples. The results were evaluated with respect to the operating conditions of a tank system at cryogenic conditions, assuming a maximum tank pressure of 2 MPa and a minimum back pressure for the hydrogen consumer of 0.2 MPa. AX-21_33 shows a usable capacity of 3.5 wt.% in the case of isothermal operation at 77 K and 5.6 wt.%, if the tank is loaded at 77 K and the temperature is increased by 40 K during unloading. Under the same conditions, MOF-177 has a usable capacity of 6.1 wt.% and 7.4 wt.%, respectively. The results show that the heat of adsorption has a high impact on the amount of hydrogen remaining in a tank after unloading and that the heat management plays a crucial role for the design of a cryogenic tank system.

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1. Introduction

Hydrogen storage is a bottleneck for the widespread usage of hydrogen as an energy carrier. Among other technical approaches, hydrogen cryo-adsorption in microporous materials is a promising way due to its high gravimetric storage density, fast kinetics and complete reversibility [1]. In the last decade a large number of adsorption materials have been developed with the best adsorption capacities up to now reached by highly porous carbons [2–4] and a new class of materials, the so called metal-organic frameworks (MOF) [5,6]. It has been shown, that the hydrogen excess uptake is roughly proportional to the specific surface area (SSA) of a material, giving 1 wt.% hydrogen uptake at 77 K per 500 m²/g of surface area [7,8]. Therefore the development of materials with high

specific surface areas has been one aim of research on adsorbents. However, since a significant hydrogen uptake can only be achieved at cryogenic temperatures, another goal is to develop materials, that show a stronger interaction with hydrogen molecules, thus lowering the cooling requirements for efficient hydrogen storage [9–12]. Up to now, adsorption materials have been mainly compared using their hydrogen excess uptake, however, this is not sufficient for predicting the capacity of a real storage system, since it neglects hydrogen gas, which can also be present in the free volume of adsorption materials [3,13] (see section 2). In this work, the total hydrogen capacities of two commercially available materials have been measured and discussed regarding the pressure and temperature requirements of a real tank system [1,6,11]. These two materials, activated carbon AX-21_33 and metal-organic

* Corresponding author.

E-mail addresses: schlichtenmayer@mf.mpg.de (M. Schlichtenmayer), streppel@mf.mpg.de (B. Streppel), hirscher@mf.mpg.de (M. Hirscher).

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framework MOF-177 [13,14] show the highest hydrogen uptake among all carbons and MOFs, respectively, that are available in large amounts, and therefore are the most promising candidates for commercial cryo-adsorption tanks [15].

2. Background

Microporous materials typically have pore sizes in the range of 1–10 nm. Hydrogen molecules can enter these pores and interact with the material via Van der Waals forces. Even though this interaction is rather weak, it leads to a formation of an additional phase of the hydrogen, the so called adsorbate. The strength of the interaction between hydrogen and the material (adsorbent) is expressed by the heat of adsorption, that is released when hydrogen molecules change from the gas phase to the adsorbed phase, which is typically in a range of 1 kJ/mol to 10 kJ/mol [16]. Due to this low interaction strength, only hydrogen molecules close to the inner surface of the pores can be efficiently bound by Van der Waals forces, so in the temperature range from 77 K to room temperature adsorption only occurs in a monolayer of hydrogen molecules. Therefore the adsorption capacity of a microporous material is proportional to its inner pore surface area, which typically lies in the order of 1000 m²/g. Most adsorbents have pores larger than 0.6 nm (double kinetic diameter of a hydrogen molecule) and the remaining pore space can be filled with hydrogen gas (see Fig. 1). Furthermore, adsorption materials are mostly available in powder form. A vessel filled with such a powder will have additional interparticle void space, which can also contain hydrogen gas. Therefore the total capacity of an adsorbent is the sum of the adsorbed hydrogen and the hydrogen gas in the pores and the interparticle voids. However, for an easy comparison of the adsorption properties of microporous materials it is common practice to measure the excess adsorption, where the amount of hydrogen in the sample cell with an adsorbent is compared to the amount of hydrogen in the sample cell filled with a non adsorbing reference sample (see Section 3.2). At low pressures it is a good parameter to describe the ability of a material to adsorb hydrogen. However, the excess uptake usually has a maximum at a certain pressure and monotonously decreases at higher pressures. This is

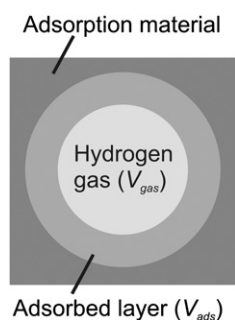


Fig. 1 – Picture of a large micropore with adsorbed layer and hydrogen gas inside the pore. The amount of hydrogen in the adsorbed layer, occupying the volume V_{ads} , is called absolute uptake. The remaining pore volume V_{gas} is filled with hydrogen gas. Adsorbed layer plus hydrogen gas together are called total uptake.

because as hydrogen is adsorbed, the adsorbed layer displaces some of the gaseous hydrogen from the pores. As the adsorbed layer saturates, the amount of hydrogen in the sample cell can only be increased by the compression of hydrogen gas. Since in the saturated adsorbent there is less space available than in the reference sample, this compressed gas contribution has a smaller inclination than the gas in the reference sample. Theoretically, the excess uptake would become zero, if the hydrogen gas is compressed to the same density as the adsorbed layer. With an assumption for the density of the adsorbed layer its volume can be calculated and the hydrogen uptake can be corrected (see Section 3.2). This gives the so called absolute uptake [17].

3. Experimental section

3.1. Samples

AX-21_33 is an activated carbon from Kansai Coke and Chemical Co., derived from the well studied AX-21 also known as Maxsorb MSC 30 [18–20]. The other sample investigated is MOF-177 [13,14,21,22], a metal-organic framework synthesized by BASF. Prior to all measurements the samples were activated in high vacuum at 470 K for 24 h.

3.2. Technique

The hydrogen uptake was measured utilizing a commercial sieverts type apparatus (PCT Pro 2000 with microdoser, HyEnergy), which fully automatically measures adsorption and desorption isotherms in a sample volume of ≈ 1.3 ml up to pressures p of 3 MPa using ultra high purity hydrogen gas (99.999%) [23]. It also automatically measures the free gas volume in the sample cell V_{He} with helium gas at room temperature in the pressure range between 0.1 MPa and 0.5 MPa.

The original setup is upgraded by a heating and cooling device to regulate the sample temperature T in a range from 77 K to 500 K. When the sample cell is kept at a different temperature than the gas reservoir, a temperature gradient appears, so the PCT Pro 2000 does not measure the adsorption isotherm itself, but an apparent uptake $n_{app}(p, T)$. For the correction of this temperature gradient the apparent uptake $n_{sand}(p, T)$ of a non adsorbing reference sample (sea sand) with the same free gas volume was measured at the same temperature. Thus the excess amount of hydrogen $n_{exc}(p, T)$ adsorbed can be calculated by:

$$n_{exc}(p, T) = n_{app}(p, T) - n_{sand}(p, T) \quad (1)$$

To make excess adsorptions of samples with different masses m comparable, the relative excess uptake in wt.% is calculated by:

$$\text{exc.uptake} = 100 \frac{n_{exc} \cdot M}{n_{exc} \cdot M + m} [\text{wt.}\%] \quad (2)$$

M denotes the molar mass of hydrogen ($M = 2,01588$ g/mol).

The absolute hydrogen adsorption is calculated by the multiplication of a correction factor:

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