

A COMPARISON OF GAS STORAGE CAPACITIES IN MOF-5 AND ACTIVATED CARBONS

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Introduction

In the last decades, there has been an increasing interest to develop gas storage systems for different applications such as H₂ storage for automotive applications or carbon dioxide due to concerns over greenhouse gas emissions. One of the technologies that have been proposed is the application of porous materials having high adsorption capacity [1-4]. Several types of adsorbents are continuously being developed and tested. Among them, activated carbons (AC) and, more recently, metal organic frameworks (MOF) [2-4], are subject of research. In most of the gas storage studies, the results are reported in gravimetric basis [3,4]. However, from an applied point of view, where the adsorbent has to be confined in a given volume, it would be more interesting to report the adsorption capacity in a volumetric basis, instead of an a gravimetric ones by using a appropriate adsorbent density value [2]. The main goal of this work is to highlight the importance of this issue, analyzing the suitability of different densities (i.e. tap density, packing density) for gas storage applications.

Experimental

In this work, we have selected two kinds of well known commercially available highly porous adsorbents; an AC (Maxsorb3000 from Kansai Coke & Chemicals) and a MOF (MOF-5, supplied by BASF, also know as IRMOF-1). For comparison purposes, we have also selected an AC (named AC-1) prepared in our laboratory by KOH activation of an anthracite, as described elsewhere [5]. These three materials have been selected because they all have very similar adsorption capacities per unit of gram. The porous texture of the samples were analysed by physical adsorption of N₂ at 77 K and CO₂ at 273 K (using an automatic adsorption system, Autosorb-6, Quantachrome) and their densities were determined by three methods: (i) filling and vibrating a container with a known weight of sample, obtaining the occupied volume (i.e., tap density also called bulk or apparent density); (ii) pressing a given amount of sample in a mould at a pressure of 415 kg/cm² (packing density) [1,2] and (iii) the real or true density (helium density) which was determined using a Micromeritics Accupyc 1330 pycnometer. H₂ adsorption measurements were carried out at both, room temperature (up to 20 MPa) and 77 K (up to 4 MPa). CO₂ storage was studied at 273 and 298 K up to 4 MPa in a DMT high-pressure microbalance after degassing at 423 K during 4 h under vacuum. In both cases, the experimental results were

corrected for buoyancy effects related to the displacement of gas by the sample, sample holder and pan [6].

Results and Discussion

Table 1 collects the porous texture characterization including: the apparent BET surface area, the total micropore volume, V_{DR}(N₂), and the narrow micropore volume, < 0.7nm, V_{DR}(CO₂), by applying Dubinin-Raduskevich equation. From these values it can be seen that the three samples have a similar range of apparent BET surface area and have quite similar micropore volumes, being their main differences the narrow micropore volume (0.44 cm³/g of the MOF compared to 0.70 cm³/g of the AC).

Table 1. Porous texture characterization results of the samples analysed per unit of weight

Sample	S _{BET} (m ² /g)	V _{DR} (N ₂) (cm ³ /g)	V _{DR} (CO ₂) (cm ³ /g)
Maxsorb3000	3180	1.31	0.70
AC-1	3120	1.25	0.70
MOF-5	2800	1.13	0.44

Fig. 1 shows the H₂ excess adsorption isotherms at 77 K up to 4 MPa for these three samples, including the isotherm of MOF-5 (IRMOF-1) reported by Wong-Foy et al. [4]. Two points should be remarked from this Figure; i) the H₂ uptakes expressed as wt.% (gravimetric basis) for the two AC and MOF-5 are quite similar, confirming that, independently of the type of adsorbent used, the BET and the micropore volume control the H₂ uptake at 77 K and ii) it is concluded that both MOF (IRMOF-1 from reference [4] and MOF-5 used in this work) are the same because their H₂ adsorption isotherms are very similar.

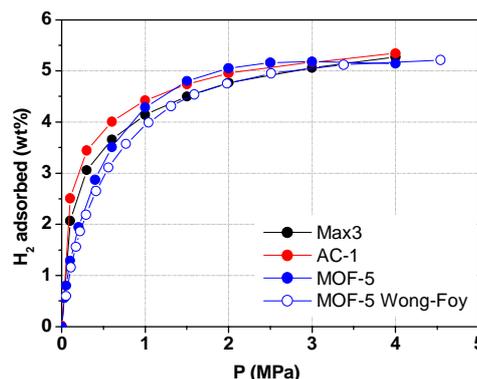


Fig. 1. Excess adsorption isotherms for hydrogen at 77 K on the different materials (gravimetric basis). IRMOF-1 isotherm from data reported by Wong-Foy et al. [4].

In order to know the amount of H₂ adsorbed per volume unit of adsorbent, the density of the material has to be measured. Table 2 summarizes the different samples densities

(packing, tap and He) assessed as well as the calculated crystal density of these adsorbents.

Table 2. Values for the different densities of the samples.

Sample	True density (g/cm ³)	Tap density (g/cm ³)	Packing density (g/cm ³)	Crystal density (g/cm ³)
Maxsorb3000	2.1	0.36	0.41	0.48
AC-1	2.1	0.38	0.50	0.52
MOF-5	2.0	0.30	0.57	0.58

As expected, the density differs according to the experimental procedure used to assess it, increasing in the following sequence: tap density < packing density < crystal density < true density. As a result, the H₂ adsorption capacity per volume unit will unrealistically be different depending on the density used to convert the gravimetric H₂ adsorption data. These results highlight the importance of report the density of the material and how this density is measured. As an example, Fig. 2 presents the H₂ excess adsorption at 77 K up to 4 MPa on volumetric basis calculated using the tap density. Contrarily to Fig. 1, Fig. 2 shows two different aspects; i) the results of the three samples are now quite different being clearly better for the AC in relation to MOF-5 and ii) the isotherm corresponding to MOF-5 presents a H₂ uptake (about 15g of H₂/L) which is almost half of the reported value on Ref [4] which was calculated using its crystal density (about 30 g of H₂/L).

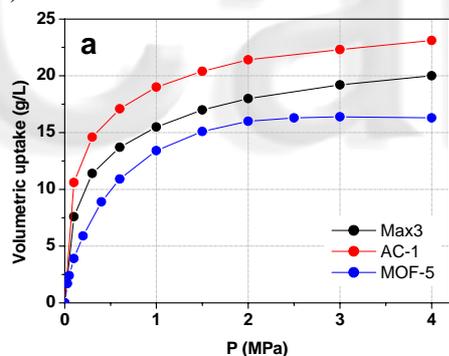


Fig. 2. Excess adsorption isotherms for hydrogen at 77 K on the different materials in volumetric basis obtained using the tap density of the materials.

Besides H₂ storage, the study has been extended to other gas such as CO₂. Fig.3 plots the CO₂ adsorption isotherms at 273 K in gravimetric basis for the three selected samples. Unlike H₂ storage, important differences can be observed between ACs and MOF: i) the CO₂ uptake is higher in the case of ACs and ii) MOF exhibits an unusual S-shaped isotherm. Analyzing the CO₂ storage in volumetric basis by using the tap densities, differences between ACs and MOF become higher since tap densities of ACs are higher (Table 2). Therefore, ACs have shown a substantially higher volumetric adsorption capacity for CO₂ than for MOF-5.

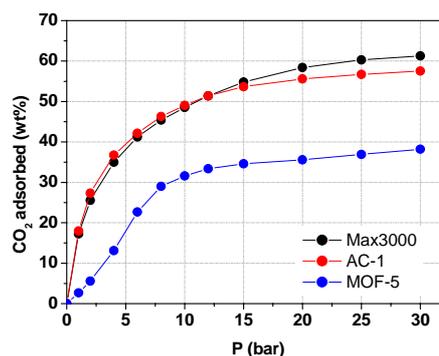


Fig. 3. CO₂ adsorption isotherms at 273 K on the different materials (gravimetric basis).

Conclusions

This comparative storage study, carried out in three selected adsorbents having similar adsorption capacity per unit of gram, shows that gas storage depends strongly on the sample porosity, when the results are expressed in gravimetric basis. Consequently the three selected samples have the same uptakes. Contrarily, gas storage in a volumetric basis is very much depending on the value of density used. Our results show that higher amounts of AC can be put in a given tank than MOF-5 because of their higher tap density (see Table 2). Consequently, the gas storage of the two AC studied are higher than for MOF-5, in a volumetric basis. Finally, the crystal density, usually used in MOF for gas storage studies gives over estimated values because the inter-particle space is not considered. Hence, the use of the tap density of the adsorbent or its packing density is strongly recommended.

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