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Hydrogen adsorption in the nanoporous metal-benzenedicarboxylate $M(OH)(O_2C–C_6H_4–CO_2)$ ($M = Al^{3+}, Cr^{3+}$), MIL-53

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Received (in Cambridge, UK) 29th July 2003, Accepted 23rd October 2003
First published as an Advance Article on the web 4th November 2003

Hydrogen adsorption has been studied in the nanoporous metal-benzenedicarboxylate $M(OH)(O_2C\text{-}C_6H_4\text{-}CO_2)$ ($M = Al^{3+}, Cr^{3+}$); these solids show a hydrogen storage capacity of 3.8 and 3.1 wt.% respectively when loaded at 77 K under 1.6 MPa.

The search of new materials for hydrogen storage is an exciting challenge since hydrogen could be used as an alternative fuel for vehicles or involved in the energy supply of various mobile electric devices.[1] Current works are focused on different classes of solids[2] such as metallic hydrides (AB_n : A = Rare earth, 3d metals or Mg; B = 3d metals; $n = 1, 2$ or 5) or carbonaceous material. Despite good reversibility and fast kinetics under ambient pressure at room temperature, metallic hydrides suffer from poor weight capacity due to the heavy molar mass of metal atoms. New materials with lighter elements like magnesium are sought but still hindered by poor kinetic behavior at room temperature. Concerning carbonaceous materials, the reports of promising hydrogen sorption capacities (> 8 wt.% for nanotubes) are the subject of controversy since the high values claimed in a few works[3,4] have not been reproducible. Moreover, thorough studies[5,6] seemed to indicate that the hydrogen storage capacity is limited to less than 1wt.% at room temperature. Recently, the use of zeolites as potential hydrogen storage materials was investigated.[7,8] Depending on the pore geometries and compositions, various zeolites[8] (A, X, Y and RHO) have shown the capability to store up to 1.8 wt.% at 77 K under 15 bar of hydrogen pressure.

Other extra-large microporous crystalline compounds have also been considered for their hydrogen sorption properties. The nickel phosphate VSB-5,[9] which possesses a 1D 24-ring channels system (diameter ≈ 10.2 Å), exhibits a hydrogen adsorption capacity (60 $cm^3\ g^{-1}$ at 600 Torr). Yaghi *et al.*[10] reported very encouraging results with the metal-organic framework series (MOFs). The properties of the compound MOF-5, with large cubic cavities (diameter ≈ 18.5 Å), were investigated and it adsorbs up to 4.5 wt.% at 78 K and 1 wt.% at ambient temperature under 20 bar. This outcome opened up a new direction for research into potential materials for hydrogen storage.

In this context, we describe here the hydrogen sorption properties of the nanoporous metal-benzenedicarboxylate $M(OH)(O_2C\text{-}C_6H_4\text{-}CO_2)$ containing trivalent chromium[11,12] or aluminium[13] (M), denoted MIL-53. The latter is synthesized from an aqueous mixture of soluble metal precursor (aluminium nitrate or chromium nitrate/HF) and 1,4-benzenedicarboxylic acid (BDC) to give a three-dimensional metal–organic framework encapsulating non-reacted BDC within the pores. The structure is built up from infinite *trans* corner sharing octahedra $MO_4(OH)_2$ chains linked to each other through the BDC molecules. It results in the formation of 1D lozenge-shape tunnels, which are occluded by the BDC species; they are evacuated upon heating at (300–320 °C) and a porous solid with pores of 8.5 Å is obtained (BET surface area ≈ 1100 $m^2\ g^{-1}$). At room temperature, the solid absorbs one water molecule (Fig. 1), which can be rapidly removed upon heating (> 100 °C), leaving the pores empty for potential molecular sorption.

First attempts† to load the sample at room temperature does not lead to significant adsorption up to 2.5 MPa of hydrogen pressure. At this stage, the sample holder was plunged into liquid nitrogen in order to cool it down to 77 K. At this temperature, significant adsorption was observed and the corresponding PCI curves for the MIL-53 samples are reported in Fig. 2 for $M = Al^{3+}$ and Cr^{3+}.

The chromium compound shows a maximal capacity of 3.1 wt.% under 1.6 MPa whereas the aluminium one exhibits 3.8% at the same pressure. Reversibility was then evaluated by measuring the desorption branch down to 0.01 MPa. Capacities of 1.8 wt.% and 2.2 wt.% were recovered for Cr^{3+} and Al^{3+} respectively. Adsorption and desorption branches do not follow exactly the same path. However, a behaviour of type I is expected from the shape of the isotherms. It is also worth noting that after desorbing the sample at 125 °C under primary vacuum for one night, adsorption process could be repeated with remarkable reproducibility. Moreover, attempts to fully load the sample in one-step in order to evaluate the kinetic behavior showed that 90% of the capacity is adsorbed in less than one

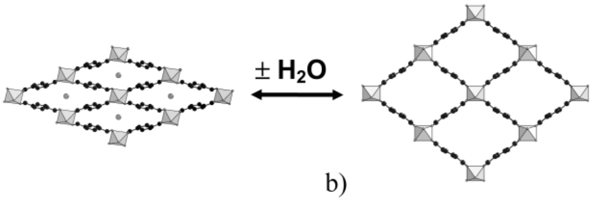

Fig. 1 Representation of the structure of MIL-53 showing the expansion effect due to the removal of a water molecule, (a) hydrated (left), (b) dehydrated (right); octahedra: $MO_4(OH)_2$, $M = Al^{3+}, Cr^{3+}$. The dehydrated form of MIL-53 was tested for the hydrogen adsorption experiment.

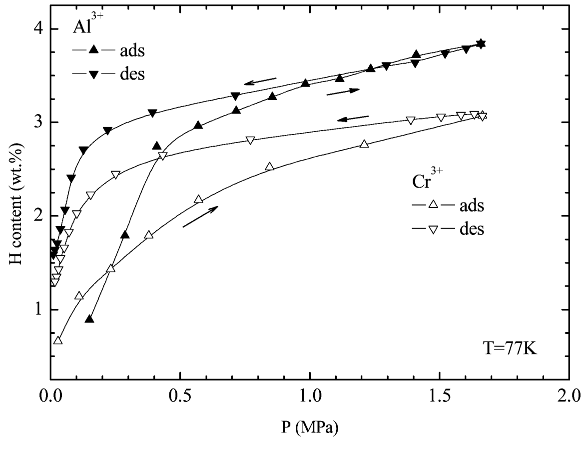

Fig. 2 PCI curves (▲: adsorption; ▼: desorption) measured at 77 K up to 1.6 MPa of hydrogen pressure for the MIL-53 samples with $M = Cr^{3+}$ (open symbol) and $M = Al^{3+}$ (full symbol).

DOI: 10.1039/b308903g

minute (Fig. 3). Finally, after loading in liquid nitrogen, each sample was allowed to warm up until it reached room temperature. From the observed pressure variations, it can be concluded that desorption occurs between 100 and 200 K, confirming the low capacity for these materials at 25 °C. X-ray analyses performed on the samples after hydrogenation do not show any evidence for structural changes within the host compounds. The BET surface areas of the solids after hydrogen sorption are not modified (measured values : 1020 and 1026 m^2 g^{-1} for MIL-53 (Al) and MIL-53 (Cr), respectively).

According to the data reported here, the nanoporous metal-benzenedicarboxylate $M(OH)(O_2C\text{-}C_6H_4\text{-}CO_2)$ shows significant hydrogen storage properties at 77 K. By comparison with other systems, capacities are larger than that reported for carbonaceous materials, silica and alumina. Most of these materials have been evaluated for hydrogen adsorption capacities by Nijkamp *et al.*[14] Maximum hydrogen uptake (2.15 wt.%) is observed for activated carbon Norit 990293. Our values can be also compared to the 1.8 wt.% reported by Langmi *et al.*[8] for the NaY zeolite. However, the maximum value (3.8 wt.%) observed here for $Al(OH)(O_2C\text{-}C_6H_4\text{-}CO_2)$ is slightly lower than that claimed by Yaghi *et al.*[10] for the compound MOF-5 (4.5 wt.% at 78 K). Moreover, no significant hydrogen uptake is observed in metal-benzenedicarboxylate at room temperature.

For the materials reported here, BET surface areas of 1100 m^2 g^{-1} are larger than that measured for zeolite materials but comparable to what is commonly observed for activated carbon. Most of the work carried out on hydrogen adsorption in meso- or micro-porous materials at low temperature has attempted to relate hydrogen capacities to specific areas. Studying such correlations, Nijkamp *et al.*[14] concluded that the relationship is not very straightforward. They suggest that a better correlation can be found with the micropore volumes by deconvoluting the hydrogen adsorbed in the micropores from that on the surface of the mesopores. They concluded that large storage capacity could be achieved with adsorbents containing a large volume of micropores with suitable diameter. Diameter of cages in zeolites varies between 6 to 12 Å depending of the zeolite type. These values are comparable to the tunnel size ($\approx$ 8.5 Å) reported for the present materials. However, one should keep in mind that some zeolites exhibit 3D system of channels with reduced diameter apertures whereas metal-benzenedicarboxylate can be considered as 1D-channel materials without bottlenecks. Further investigation using neutron scattering and diffraction will be necessary to determine the exact mechanism of hydrogen adsorption in these compounds, but they already show promising properties as regards hydrogen storage applications.

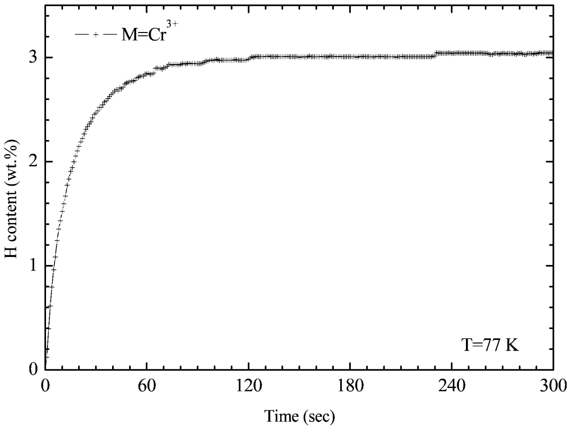

Fig. 3 Hydrogen uptake *versus* time obtained in one step for the compound MIL-53 (M = Cr^{3+}). 90% of the full capacity is attained in less than one minute. Total capacity reaches 3.04 wt.% at T = 77 K under 1.5 MPa of H_2 pressure.

The authors thank C. Thouvenot (Institut Lavoisier) for her technical assistance in this contribution.

Notes and references

† For the hydrogenation measurements, about 500 mg of powder were transferred in a tight stainless steel sample holder connected to a volumetric device equipped with pressure gauges to measure the hydrogen amount loaded (or unloaded) from the sample. Before measuring the sorption properties, outgassing of the samples was performed overnight at 125 °C under primary vacuum for dehydration. Thus, all data given here refer to mass capacity for dehydrated materials. Adsorption and desorption pressure–composition–isotherm (PCI) curves were measured step by step from pressure variation measurements in calibrated and thermalised gauged volumes (Sievert's method). All measurements were calculated assuming the ideal gas law.

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