Nanoporous carbon - metal composites for hydrogen storage

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Received 30 March 2011; Accepted 21 June 2011

Abstract: Metal-carbon composites have shown considerable hydrogen storage potential at room temperature. In the present work the behaviour of two different Pd amalgam doped carbon substrates, namely a carbogenic foam and a mildly oxidised ordered mesoporous carbon, are compared on the basis of their hydrogen sorption properties at 77 and 298 K and low pressures, aiming to investigate the effect of surface on the storage capacity. In both cases, the introduction of alloy nanoparticles leads to an improvement of the hydrogen uptake with respect to pure carbons. This effect is significant for the carbogenic foam however small for the ordered carbon.

Keywords: Hydrogen storage • Nanostructured materials • Composite materials • Hydrogen sorbents

1. Introduction

As a result of pressing environmental and energy demands, scientific and technical interest in hydrogen as an energy carrier has grown dramatically in the last decade. One of the major problems hampering its practical use pertains to storage, especially for mobile applications. Conventional technologies (compressed gas or cryogenic liquid) have inherent limitations and thus a potential solution entails storage in solid materials that chemically bind or physically adsorb hydrogen.

Several types of nanoporous solids ranging from Metal Organic Frameworks (MOFs) to various carbon forms (activated carbon, fullerenes, nanotubes, nanofibers, etc.) have received great attention as potential H2 stores, however all of these materials are efficient only at cryogenic temperatures due to weak solid-hydrogen interactions. At present, one of the few promising solid storage concepts is the use of metal-carbon composite materials, where nanosized metal particles (e.g. Pd and Pt) seem to catalytically enhance hydrogen sorption on carbon surfaces at room temperature [1-5]. H2 sorption on metal doped porous solids, is supposed to involve dissociative hydrogen chemisorption followed by surface diffusion and sorption to various support sites. This mechanism, referred to as storage by spillover, has been considered by a part of the hydrogen scientific community as a potential route for enhancing the absolute hydrogen capacity of carbon materials, as supported by both experimental and theoretical studies. Indeed, relatively high capacities have been measured after metal decoration of a wide range of porous materials including graphite nanofibers [6], activated carbons [7], graphite oxides [8], carbon nanotubes [4], but also carbon–MOFs/COFs composites [9,10]. In all these cases, hydrogen storage capacities between 1-4 wt% (room temperature, up to 10 MPa) have been reported; nevertheless, the storage process details remain poorly understood. In addition, the very existence of the spillover mechanism has been strongly debated since there are also experimental results revealing very low storage capacities after doping [11,12,13]. In all cases, the relevant studies have been based on systems combining the smallest attainable catalytic nanoparticle size (usually either Pt or Pd) with high specific surface area receptors, while lately particular emphasis has been placed on the manipulation of the substrate’s surface chemistry as well.

Quite recently, our group developed a novel Pd amalgam (Pd4Hg)/carbon foam composite (12 wt% metal loading), which revealed enhanced H2 sorption capacities (2-5 wt%) at room temperature and 20 bar.

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The carbogenic foam [14] (denoted hereafter as CF) derived from simple calcination of sodium chloranilate dihydrate, has the average formula C₁₂₄H₂₄O₁₆ and a very active oxygen-rich surface (mainly –C=O and –OH groups) with a high spin concentration. The increased hydrogen storage capacity of the material has been attributed to this surface activity, which may offer a high concentration of binding sites [15].

On the other hand, ordered mesoporous carbons (OMCs) are considered quite advantageous sorbents due to their high specific surface area (~1500 m² g⁻¹), large pore volume (>1 cm³ g⁻¹), uniform and tailored pore sizes (in the range 3-10 nm), high degree of structural ordering, facile synthesis, high thermal, chemical and mechanical stability, etc. These materials are also capable of hosting high dispersions of metal nanoparticles and their nanopore walls can be functionalized with various chemical groups. Thus, they comprise an excellent “basis” to investigate the alleged hydrogen spillover phenomena. In this context, in the present work we have prepared a Pd₄Hg doped, mildly oxidised OMC (CMK-3 type [16]) and compared its hydrogen sorption properties at low pressures with our original CF-Pd₄Hg composite in an attempt to elucidate the effect of surface area and surface activity on hydrogen storage via spillover.

2. Experimental procedure

2.1 Material synthesis

CF was synthesised through the calcination of the molecular precursor sodium chloranilate dihydrate at 300°C in air as described elsewhere [14]. The ordered mesoporous carbon sample of CMK-3 type was produced through a standard nanocasting route [17]. In brief, an ordered mesoporous silica substrate (2-D hexagonal SBA-15 silica purchased from Claytec Inc., USA) was loaded twice with a carbon source (sucrose solution containing sulfuric acid as catalyst), carbonized at 900°C, and then treated with HF in order to remove the siliceous template and thus enable the formation of a porous carbon with a “negative” replica structure. The sample was subsequently mildly oxidised by H₂O₂ reflux (6 h). Both CF and the oxidised OMC samples were subsequently doped with Pd/Hg nanoparticles by suspension in de-ionized water, followed by dissolution of anhydrous PdCl₂ and HgCl₂ (Panreac), using NaBH₄ as reducing agent. The suspensions were centrifuged, washed (with both water and acetone), and dried (65°C) affording black solids with a metal content of ~12 wt% and a molar ratio (Pd:Hg) of 4. The same procedure was followed without the presence of dispersed carbon in order to produce pure Pd₄Hg particles.

2.2 Characterisation

X-ray powder diffraction (XRPD) spectra were collected using a Bruker D8 diffractometer with Cu Kα radiation, operated at 40 kV and 40 mA. FT-IR spectra were collected on a Thermo Scientific Nicolet 6700 FTIR equipped with an N₂ purging system and a LN₂-cooled wide range Mercuric Cadmium Telluride detector.

N₂ isotherms were measured at 77 K on samples of 40-50 g, using a volumetric gas adsorption analyser (Autosorb-1-MP, Quantachrome). The same apparatus was also used for the measurement of H₂ adsorption/desorption isotherms at 77 K and 298 K in the pressure range 0-1 bar. It should be noted that for the case of H₂ measurements at 298 K the isothermal points recorded are far from equilibrium, nevertheless, 1 h equilibration time was used for all of them for both practical and comparative reasons. In all cases the samples were appropriately outgassed (48 h at 120°C and 12 h at 250°C for CF and OMC, respectively) under high vacuum (10⁻⁶ mbar), while ultra-pure N₂ (99.9999%) and H₂ (99.9999%) were used.

3. Results and discussion

The two pristine CF and OMC carbon substrates (as well as their doped analogues) are distinctively different both in terms of structural and surface properties. According to the low angle XRPD patterns (Fig. 1a), CF is quite amorphous with no sign of long range order. In contrast the OMC pattern depicts well-resolved peaks that can be assigned to (10), (11), and (20) reflections of the 2-D hexagonal space group (p6mm) and point to an ordered arrangement of the carbon nanorods. Upon doping, both XRD patterns (inset of Fig. 1a) reveal the potarite mineral phase (PdHg, Space Group: P4/mmm) [18]. In all cases, the metal nanoparticles have a mean size of 10 nm (based on Scherrer XRD peak analysis and TEM images). However, the OMC pattern depicts signs of pure Pd phase as well implying that the nanoparticles are partly de-alloyed.

Additionally, the two carbons exhibit clearly different porous systems. The N₂ adsorption isotherm of CF (Fig. 1b) is of type IV with an H3 hysteresis indicating a slit-like multiscale pore system spanning the whole range from the micro- to macro- pore region. The calculated Brunauer-Emmet-Teller (BET) surface area is ca. 700 m² g⁻¹. On the other hand, CMK-3 (Fig. 1b) is characterised by larger uptake at low pressures, revealing a much larger surface area (~1500 m² g⁻¹) and enhanced microporosity. There is also an abrupt capillary condensation regime with an H₂ hysteresis loop; Barrett-Joyner-Halenda (BJH) pore
analysis points to a mean pore size of appr. 3.5 nm. As shown in Fig. 1b the Pd\textsubscript{4}Hg analogues of the two parent materials have almost identical N\textsubscript{2} sorption isotherms (slightly reduced – by 10% for the OMC and 7% for the CF at p/p\textsubscript{0}=0.995 - due to the extra weight of the non-sorbing nanoparticles) proving that the pore structure of both materials is preserved after the incorporation of the metal nanoparticles.

The two samples (CF and OMC) also have completely different chemical properties, as illustrated in Fig. 2 presenting the IR spectra of the parent materials (it should be noted that the spectra are identical after doping). Unlike the practically featureless OMC pattern, that of CF exhibits the characteristic carbonyl absorption at 1710 cm\textsuperscript{-1} along with broad absorptions in the range 1500-1100 cm\textsuperscript{-1} and 600 cm\textsuperscript{-1} that signal the presence of abundant -OH functional groups.

The H\textsubscript{2} adsorption isotherms of the metal doped carbons at 77 K over the pressure range 0-1 bar (Fig. 3) depict the same trend as the N\textsubscript{2} isotherms of their carbon precursors at low pressures (p/p\textsubscript{0}<0.1). The results also point to a reduction in the surface area of the doped carbon analogues of 4-6%. This observation might be explained either by partial hydride formation even at 77 K and/or small intercalation of nanoparticles in the carbon matrix in a way that previously inaccessible parts of the matrix become accessible after doping (however, only to hydrogen).

The picture is completely overturned at 298 K, where the effect of the metal dopants is evident. Both CF and OMC pure carbons appear to retain negligible amounts of hydrogen (Fig. 4), whereas the introduction of the alloy particles leads to a significant increase of the hydrogen uptake. Taking into account the sorption behaviour of the alloy particles at 298 K this enhancement cannot be attributed solely to them and a certain cooperative mechanism should hold. In fact if the phenomenon was simply additive, OMC-Pd/Hg would give rise to a curve resembling that labelled as 88%OMC+12%Pd/Hg. The enhancement in the OMC case seems to be limited. On the contrary incorporation of alloy particles on the CF surface dramatically changes its uptake, pointing to a 4-fold enhancement at 1 bar (compared to the calculated 88%CF+12%Pd/Hg case). It should nevertheless be mentioned that for the CF-Pd/Hg composite the process seems irreversible (in the frame of the experimental conditions adapted in this work, *i.e.*, short equilibration times). However, this is not the case since, after outgassing, exactly the same behaviour has been recorded and identical hydrogen uptakes were measured for 4 subsequent cycles.
A direct conclusion of the above results is that the amount of accessible surface area is not relevant with the hydrogen “spillover” enhancement, since OMC (1500 m$^2$ g$^{-1}$) behaves much worse than CF (700 m$^2$ g$^{-1}$). In fact, unlike the 77 K case, the results at 298 K point to “anti-Chahine” [19] behaviour. In contrast, surface chemistry, or else the availability of functional surface groups, seems to play a dominant role. As shown by the IR data, although CF is characterised by an oxygen rich surface (C=O and OH groups), the conditions chosen for the surface modification of OMC are rather mild and cannot accomplish the desired degree of oxidation and, thus, the critical surface oxygen content required. This is in accordance with recent theoretical work [20] that highlights the positive effect of oxygen surface functionalities (epoxy groups) on the spillover mechanism. The inferior behaviour of the OMC composite might also be explained on the basis of the partial de-alloying suggested by the XRD data. The presence of free Pd is however considered of minor importance as Pd nanoparticles can sorb hydrogen or even enhance hydrogen storage through spillover, given that such a mechanism is active.

4. Conclusions

The hydrogen sorption isotherms of both CF- and OMC-based composites at 77 K resemble those of the respective metal-free carbon substrates. In contrast, an enhancement of the hydrogen storage capacity upon metal-doping is observed at room temperature in both cases, pointing to a synergistic effect between the alloy nanoparticles and the different carbon matrices. The surface oxygen content may further promote the catalytic effect of the metal as shown by the substantially higher efficiency of the more oxygen-rich CF-based composite.

Acknowledgments

Partial funding by the EU project NESSHY (FP6 Contract No. SES6-518271) is gratefully acknowledged.

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