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Ordered micro-porous carbon molecular sieves containing well-dispersed platinum nanoparticles for hydrogen storage

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ABSTRACT

Ordered micro-porous carbon molecular sieves containing highly dispersed platinum nanoparticles with tunable sizes from 1 to 6 nm are synthesized in this work. The synthesis is simply realized by nanocasting of furfuryl alcohol precursor on Pt-impregnated NaY zeolite hard templates and complemented by chemical vapor deposition by propylene gas. During the carbonization, Pt ions can be reduced to form highly dispersed Pt nanoparticles on the carbon matrixes. This method allows a very high Pt-loading up to 40 wt % while maintaining a high metal dispersion. X-ray diffraction and transmission electron microscopy measurements reveal the existence of uniformly dispersed Pt nanoparticles and microstructural regularity. Nitrogen adsorption isotherms show that the ordered micro-porous carbon molecular sieves possess a high surface area around 2750 m^2/g, large micro-pore volume 1.38 cm^3/g, and narrow pore size distribution (~1 nm) in the micropore-range. A high hydrogen uptake up to 2.8 wt% at 77 K and 1 bar is observed. A high and relatively homogeneous value of hydrogen adsorption heat 11 kJ/mol in 1% Pt contained carbon was obtained, which exceeds the literature reported values for other carbon based adsorbents or metal organic framework compounds and is very close to the optimal value, 15 kJ/mol, recommended in the literature, suggesting a great potential for hydrogen storage or fuel cell applications.

1. Introduction

Because of shortage of fossil fuels and global warming caused by carbon dioxide emission from these fuels, hydrogen as a clean and high capacity chemical energy has been claimed as an ideal alternative future energy source. Production of hydrogen does not present pronounced problems, as there are several efficient methods to obtain this element. Currently, one of the main obstacles for using hydrogen as a fuel is the lack of efficient and recyclable methods of storage, removal and recharging of the containers because of its low volumetric and gravimetric density at ambient pressure and temperature [1,2]. Conventionally available methods to store hydrogen are: liquid hydrogen [3], compressed gas, metal hydrides [4,5] and sorption on different porous materials [6–16]. However, none of the above mentioned methods have met the DOE's goals.

It is well known in the literature that micro-porous materials such as carbon and metal organic frameworks (MOFs) have very promising hydrogen storage capacities at 77 K [17–19], however, the capacity will be significantly reduced at ambient temperatures which are preferred by the DOE for practical and economic reasons. Researchers [20] have established that the main reason for this phenomena is because the heat of hydrogen adsorption derived from these carbons is normally in the range from 4 to 8 kJ/mol which is not strong enough to adsorb enough hydrogen. In order to obtain hydrogen storage at moderate temperatures, efforts must be made to increase the adsorption potential or the adsorption heat, ΔH, to enhance the binding energy between hydrogen and adsorbent. Bhatia and Myers have recommended an optimum enthalpy of adsorption of about 15 kJ/mol with respect to the affinity of hydrogen: strong enough to store a large amount of gas at the charging pressure but weak enough to release most of that hydrogen at the discharge pressure [21,22]. Many novel approaches to control the carbon pore structures have been proposed in the literature [23–27]. Among them, the templating carbonization method has gained more attraction as a feasible method for the preparation of well-structured micro-porous/meso-porous carbons, wherein

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carbon precursors were infiltrated into the template nano-channels, employing a large number of silica and zeolites viz. USY, NaY, Hβ, KL, mordenite (H-form) and ZSM-5 (H-form) as templates and furfuryl alcohol, propylene gas, acetylene gas or acrylonitrile as carbon precursors [28–35]. Chemical vapor deposition (CVD) is also utilized for preparing carbon molecular sieves because of its high degree of pore-filling in the templates and avoiding the formation of additional microporosity. Highly ordered micro-porous carbons with three-dimensional (3-D) regularity and very high surface areas (4100 m^2/g) as well as controlled pore-structures can be readily synthesized [36]. Considering the small pore size, large micro-pore volume and surface area of these templated carbon molecular sieves, they are expected to be good hydrogen adsorbents. Recently, our group [37] synthesized micro-porous carbons from cation exchanged zeolite Y template using butylene and propylene as carbon precursors and studied hydrogen uptake of these samples and achieved promising results at 77 K and 1 bar. Yang et al., have also templated high surface area carbons with β zeolite as a template and acetonitrile as a carbon precursor and achieved around 6.9% hydrogen adsorption at 77 K and 20 bar [38].

In our current work, we are aiming to synthesize a carbon adsorbent which is not only highly micro-porous but also contain well-dispersed Pt nanoparticles in the carbon matrix because both the micro-porosity and the presence of Pt will enhance the hydrogen adsorption potential due to the overlapping of the potential fields generated at the pore walls and the increased polarizability of the adsorbent surface with the presence of well-dispersed Pt nanoparticles [39,40]. Pt contained ordered porous carbons [41–47] have been reported in literature to be used as a catalyst or fuel cell electrode. No literature on their hydrogen storage have been reported so far. In our work, we synthesized ordered micro-porous carbon molecular sieves containing well-dispersed Pt nanoparticles by a templating approach using Pt impregnated NaY as template. Hydrogen adsorption isotherms on the synthesized carbon samples were measured afterwards. The carbon products not only display an essentially high hydrogen storage capacity of 2.8 wt% at 77 K and 1 bar but most importantly an enhanced homogeneous adsorption heat of 11 kJ/mol was indeed observed for our sample. According to our observation, the heat of adsorption obtained in our work is not declining with hydrogen loading as those pure carbon samples. An enhanced heat of hydrogen adsorption was indeed developed in our materials.

2. Experimental

2.1. Material synthesis

In general, the well-dispersed Pt-containing micro-porous carbon molecular sieves were prepared according to the following procedure: (i) powder zeolite NaY (CBV 100, ZEOLYST international with a Si/Al $\approx$ 2.55) was added into $[Pt(NH_3)_4](NO_3)_2$ (99.9+%, Sigma Aldrich) solution with stirring for the incipient wetness impregnation. Noted as parent template, *m*%-PtY, *m*% referring to the platinum loading weight percentage on the final HF leached carbon samples and was measured by the thermal gravimetric analysis by burning off the carbon component. The three parent templates produced in our experiments were 1%-PtY, 6%-PtY, and 40%-PtY. (ii) The *m*%-PtY templates were dehydrated by heating to 400 °C with a slow ramping rate under inert nitrogen purge, and then cooled down to room temperature and impregnated with an organic precursor, 99% furfuryl alcohol (FA, 99%, Sigma Aldrich), in a vacuum Rota-vapor for 24 h. The samples were centrifuged and polymerized at 150 °C and then carbonized at 700 °C for 4 h. (iii) After the carbonization, a CVD process was immediately conducted by using propylene gas (5.18 ± 0.1% in nitrogen) for 4 h with a flow rate of approximately 400 ml/min at 700 °C. Then heat treatment at 900 °C was carried out for another 3 h to further strengthen the carbon structure. The samples produced from this step are the composite carbon samples, noted as *m*%-PtYcom. (iv) The silicate template was leached by immersing the composite sample in 48% hydrofluoric acid for 3 h, followed by washing and drying in a vacuum oven at 30 °C for 24 h. The final produced carbons were denoted as *m*%Pt-C.

2.2. Characterization

Powder X-ray diffraction (XRD) patterns were acquired using an X-ray diffractometer (Philips PW1130) with Cu Kα radiation (λ = 1.5405 Å) at 40 kV and 25 mA. Scanning electron microscopy (SEM) images were obtained with a JEOL FESEM 6300 at an accelerating voltage of 5 kV. The samples were mounted on a copper stub with conductive carbon sticky tape. A thin (*ca.* 5 nm) coating of gold was deposited on the sample prior to analysis. Transmission electron microscope (TEM) images were recorded on a JEOL model JEM 2011 and a Philips CM 20 electron microscope operated at 200 kV. The samples for TEM measurements were drop-dried from ethanol solution onto a holey carbon film supported on a copper grid. Thermal gravimetric analyses (TGA) were carried out on a Mettler Toledo TGA/SDTA851. The samples were heated in an alumina crucible under 20 ml/min oxygen flow from room temperature to 700 °C in a stepwise mode at a ramping rate of 10 °C min^{-1}. Nitrogen sorption measurements were performed on a Micromeritics ASAP 2020 volumetric adsorption analyzer. The samples were out-gassed under vacuum at 350 °C for 6 h prior to use. Specific surface areas were calculated by the Brunauer–Emmett–Teller (BET) method at $P/P_0 = 0.1$. Total pore volumes were taken at $P/P_0 = 0.97$. Micro-pore volumes were calculated from the Dubinin–Radushkevich (DR) equation using the data of adsorption isotherms. Mesopore volume was determined by subtracting the micro-pore volume from the total pore volume. Pore size distributions (PSDs) were obtained using non-local density functional theory (DFT) for slit pore geometry.

2.3. Hydrogen uptake measurement

Hydrogen adsorption isotherms at 77 and 87 K over the pressure range 0–1 bar were measured using an ASAP 2010 Gas Adsorption Analyzer (Micromeritics, USA). Heat of adsorption was analyzed using the Clausius–Clapeyron equation [39,49]:

$$Q_{st} = \frac{R \cdot \ln(P_{87.4}/P_{77.3})}{(1/77.3 - 1/87.4)},$$

where Q_{st} is the heat of adsorption, R is the real gas constant, $P_{87.4}$ and $P_{77.3}$ are H_2 pressures obtained from the H_2 isotherms at liquid argon and liquid nitrogen temperatures, respectively.

The samples were outgassed (10^{-6} torr) under heating at 350 ºC for overnight before measurement. The purity of the hydrogen was 99.999%.

3. Results and discussion

3.1. XRD patterns

The parent templates 1%-PtY, 6%-PtY, 40%-PtY (here the percentages refer to the Pt percentages on the final carbons) prepared by incipient wetness impregnation show well-resolved XRD peaks (Fig. 1a), which can be indexed to a face-centred cubic structure (space group of *Fd3m*), indicating that the FAU structure of Y zeolites is retained after the Pt impregnation. Compared to that of the original template NaY, the intensities of the diffraction peaks are