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Graphitic N-free/N-doped Nanostructured carbon molecular sieves via CVD method and their hydrogen storage

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Abstract. Graphitic N-free and N-doped carbon molecular sieves were prepared using zeolite NaY as a template via one-step chemical vapor deposition method (CVD) with propylene and acetonitrile as N-free and N-doped carbon precursors, respectively. The morphology, structure and properties of the carbons prepared were characterized via XRD, SEM, TEM and adsorption measurements. A large proportion of pore volume is associated with micropores in the carbons prepared. A high hydrogen uptake capacity is observed.

Introduction

Fabrication of porous carbons with high surface area is of great importance, especially for applications as catalysts, gas storage materials, and fuel cells [1-4]. Much work has been carried out to prepare carbon materials with ordered porous structures, and the template carbonization process has attracted considerable attention [3,5-6]. Templated carbon structures from zeolites are one of the efficient approaches in the preparation of structured microporous carbon materials [2,5,7-8], which are potentially useful as hydrogen storage materials due to a combination of adsorption ability, high specific surface, pore microstructure and low mass density [1]. It is proposed that there is a link between surface area, particularly, surface area associated with microporosity, and hydrogen uptake [9-10]. Mokaya and co-workers have reported on the synthesis of N-doped zeolite β-templated carbons via chemical vapor deposition (CVD) with acetonitrile as carbon source. However, these hollow shell carbons have very low proportion of micropore volume (<25.8%) [11]. In this work, we attempted a one-step CVD process that produces nanostructured graphitic carbons with large micropore volume. N-free and N-doped carbon molecular sieves are prepared using platinum-contained zeolite NaY as a solid template. We compare the properties of carbon materials derived from two carbon sources and discuss the hydrogen sorption properties.

Experimental

Materials Synthesis. Well-dispersed Pt-containing carbon molecular sieves were prepared according to the following procedure: (i) powder zeolite NaY (CBV 100) 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. For example, 1-PtY stands for 1 wt% Pt loading. (ii) After degassing the m-PtY templates at 400 ^oC under nitrogen flow, the samples were packed in a quartz reactor under an inert environment. Chemical vapor deposition (CVD) with propylene/acetonitrile as the carbon source was conducted at a specified temperature for 4 h. CVD with propylene (5.18± 0.1% in nitrogen) was performed at 700 ^oC with a flow rate of approximately 400 cm^3/min then further heat-treatment was conducted at 850 ^oC for 3 h. CVD with. acetonitrile (acetonitrile saturated in N_2 of 400 cm^3 (STP)/min at room temperature) was conducted at

800 °C then further heat treatment was conducted at 850 °C for 3 h. The resultant carbon/zeolite composites were subjected to hydrofluoric acid treatment to extract carbon from the zeolite frameworks. The final produced carbons templated with propylene were denoted as m-PtY-P carbons, while those from acetonitrile were denoted as m-PtY-AN carbons.

Materials Characterization. Powder XRD analysis was performed using a Philips PW1130 powder diffractometer with CuKα radiation (λ=1.5405 Å) at 40 kV and 25 mA. Nitrogen sorption measurements were conducted on a Micromeritics ASAP 2020 volumetric adsorption analyzer. SEM images were recorded using a JEOL FESEM 6300 system. Hydrogen sorption measurements on the samples at both cryogenic temperatures (77 K and 87 K, respectively) over the pressure range 0-1 bar were analyzed using an ASAP 2010 gas adsorption analyzer (Micromeritics, USA).

Results and Discussion

Graphitization and Porosity. Fig. 1 shows the representative powder X-ray diffraction (XRD) patterns of the carbon samples. For propylene-derived carbons, the XRD patterns show a peak, similar to that present in the zeolite NaY, at ca. 2θ = 6.2º, indicating that when the CVD is performed under the conditions employed, the resulting carbon materials exhibit some structural ordering with a periodicity of about 1.4 nm that corresponds to the spacing of the (111) plane of zeolite templates [2,11-12]. For carbon samples derived from acetonitrile, the XRD patterns also show an additional weak peak at ca. 2θ = 6.2º, corresponding to the parent template and suggesting that zeolite-type pore ordering is replicated in the acetonitrile-derived carbons. For all m-PtY-P and m-PtY-AN carbon materials, a further peak is observed at ca. 2θ = 26º, which is attributed to the (002) diffraction from graphitic carbon. The intensity and sharpness of this peak increases when acetonitrile is used as a carbon source, implying that greater proportions of graphitic carbon are formed when the CVD is performed with acetonitrile which generally gives the high levels of graphitization in the acetonitrile-derived carbons. The diffraction peaks located at higher angle are ascribed to the Pt nano-particles.

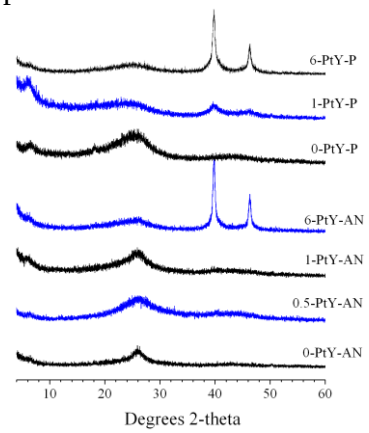

Fig. 1 XRD patterns of carbon samples

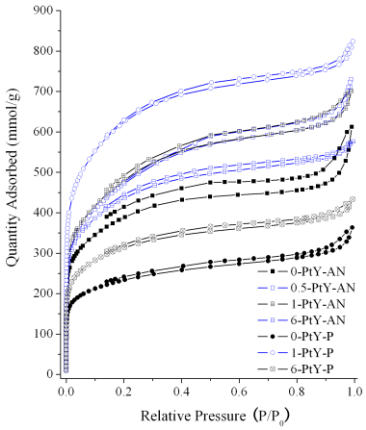

Fig. 2 Nitrogen sorption isotherms of carbon samples

The sorption isotherms of propylene- and acetonitrile-derived carbon materials are shown Fig. 2. These isotherms have a Type I shape which is classical for microporous materials. Micropore filling and capillary condensation are present in all carbons. The isotherms also exhibit nitrogen uptake at $P/P_0 > 0.2$, which may be attributed to adsorption into mesopores arising from interparticle voids. The textural characteristics of the templated carbons are summarized in Table 1. 1-PtY-P carbon sample has much higher total surface area (up to 2183 $m^2\ g^{-1}$) and pore volume (up to 1.229 $cm^3\ g^{-1}$), which is comparable to that previously reported for high surface area carbon templated using zeolite Y [7,11-13]. It is noted that the proportion of pore volume associated with micropores is much higher in the carbon materials prepared in our work (i.e. 67-94% and 77-94% for propylene- and acetonitrile-derived carbons, respectively) than that reported in the literature [11,14]. As expected, NaY-templated carbon samples that exhibit developed (according to XRD peak at 2θ = 6.2 º) zeolite-type long-range structural ordering generally have a higher proportion of micropore volume.

Table 1 Porosity parameters and elemental composition of carbon materials templating from zeolite NaY

Carbon sample	CVD temperature (ºC)	N content (wt%) [a]	BET surface area (m^2/g) [b]	Pore volume V_P (cm^3/g) [c]	DR V_{micro} (cm^3/g) [d]	Ratio of pore volume: micro/total	H_2 uptake at 77K (wt%)
0-PtY-P	700	–	827	0.524	0.351	0.67	1.19
1-PtY-P	700	–	2183	1.229	1.154	0.94	1.73
6-PtY-P	700	–	1107	0.641	0.486	0.76	1.12
0-PtY-AN	800	4.63	1362	0.859	0.673	0.78	1.60
0.5-PtY-AN	800	3.59	1762	1.058	0.990	0.94	1.71
1-PtY-AN	800	4.16	1668	1.036	0.793	0.77	1.64
6-PtY-AN	800	3.96	1524	0.882	0.744	0.84	1.69

[a] calculated by Elemental analysis carried on EA 1108 Carlo Erba Elemental Analyser; [b] calculated using the BET method based on adsorption data in the partial pressure (P/P_0) range (0.05-0.2); [c] calculated from the volume of gas adsorbed at $P/P_0 = 0.97$ for total pore volume; [d] calculated by Dubinin-Radushkevich equation for the total volume of micropores.

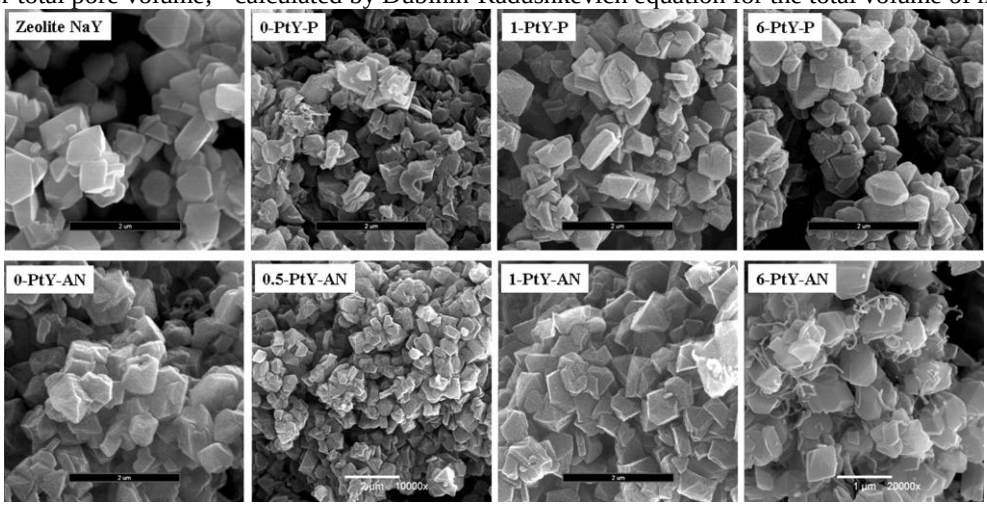

Fig. 3 SEM images of templated carbon samples

Fig. 3 shows representative scanning electron microscopy (SEM) images of zeolite NaY and carbon replicas. These carbon materials have been viewed as rhombic, cuboid, hexagonal and triangle crystal morphologies, very similar to their parent templates, implying that the morphology of zeolite NaY template was very well replicated in the m-PtY-P and m-PtY-AN carbons after removal of zeolite template. The particle size of the templated carbons is comparable to that of parent NaY. These observations suggest the consistency of the templating mechanism whereby the carbon is nanocasted within the pore channels of the zeolite and on the surface of the zeolite particles. However, for 6-PtY-AN carbon samples, carbon nanotubes are observed as by-products probably due to the easier graphitization of organic precursor acetonitrile source. It was also noted that higher Pt loading created higher graphitization, suggesting that graphitization is promoted by the presence of Pt.

Hydrogen Uptake Properties. Hydrogen adsorption isotherms at 77 K and 87K over the pressure range 0-1 bar for m-PtY-P (Fig. 4) and m-PtY-AN (Fig. 5) carbon samples, respectively, all show reversible desorption and no hysteresis loop, suggesting that physisorption phenomena occurs in our samples, except that 0.5-PtY-AN carbon has a slit-like loop at 77 K. The hydrogen uptake capacities of all the samples at 1 bar 77K are summarized in Table 1. 1-PtY-P carbon sample reaches a capacity of 1.73 wt% at 1 bar and 77 K. However, for 0.5-PtY-AN carbon samples with a lower specific area and micropore volume than 1-PtY-P carbon, it also reaches a high capacity of 1.71 wt%. It is observed that the trend in hydrogen uptake capacity appears to be closely related to the textural properties of the carbon materials [15]. It is also clear that hydrogen sorption does not reach saturation even at 1 bar, indicating that even greater uptake capacity is expected at higher pressure [14]. Micropore properties may determine the kinetics of hydrogen adsorption and the final uptake capacity. Considering that carbon samples studied here have high micropore volume and distinct pore size distribution < 2 nm, we conclude that hydrogen adsorption is mainly dependent on the micropore filling. We propose that

the high storage capacity for hydrogen of our carbon adsorbents might be due to the large volume of micropores.

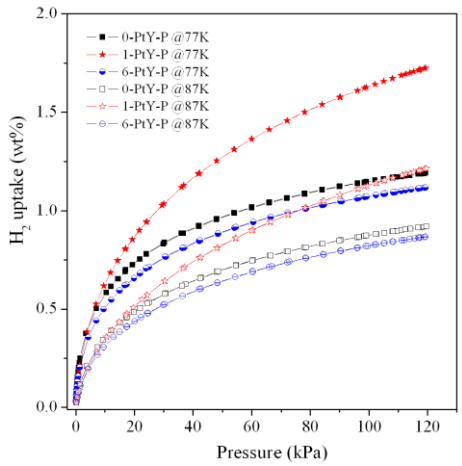

Fig. 4 Hydrogen sorption isotherms of carbon samples derived from propylene at 77K and 87K, respectively

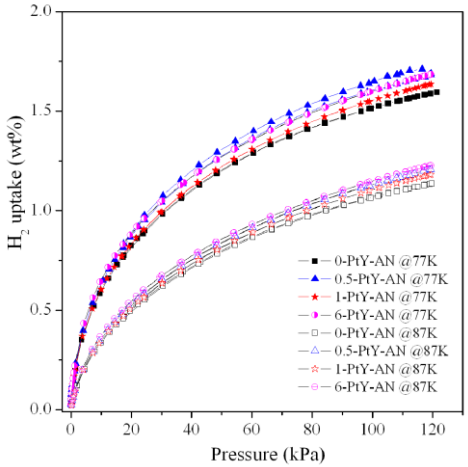

Fig. 5 Hydrogen sorption isotherms of carbon samples derived from acetonitrile at 77K and 87K, respectively

Summary

We have successfully demonstrated the preparation of graphitic N-free and N-doped carbon molecular sieves via one-step CVD method. The carbon molecular sieves prepared have very similar morphology and structure to the template NaY, indicating a faithful replication, with the best sample 1-PtY-P possessing a high surface area up to 2183 $m^2 g^{-1}$ and large micropore volume up to 1.154 $cm^3 g^{-1}$. A high hydrogen uptake up to 1.73 wt% at 77 K and 1 bar is observed. It shows that carbon materials prepared have relatively high capacity of hydrogen uptake. It might be mainly due to the greater proportions of micropore volume in our carbons. In particular, the use of acetonitrile as carbon source has allowed us to investigate the effect of functionalization (nitrogen doping) on both the textural properties and hydrogen sorption properties of the templated carbon materials.

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