

ORDERED POROUS CARBON/METAL COMPOSITES FOR HYDROGEN STORAGE

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Introduction

Hydrogen has attracted worldwide interest as the cleanest and environmentally friendly energy carrier, but the problems related to its storage and applications still have to be overcome. The physisorption on highly porous adsorbents has received great attention from the point of view of hydrogen uptake and release. Due to their low density, chemical stability, and variety of natural precursors to synthesise them, carbon materials are the most employed for hydrogen storage purposes in physisorbed state.

The importance of textural properties of these carbon materials in order to achieve high hydrogen storage capacities has already been demonstrated [1,2]. The hydrogen uptake seems to be proportional with both the specific surface area and the volume of micropores. Hence, a strict control of carbon porosity and pore size is required in order to optimise their performances. Another promising way to improve once more the hydrogen capacity of these carbon materials is to incorporate in their porosity metallic nanoparticles [3] to promote chemisorption reactions.

In this work, nanostructured microporous carbon materials with well-tailored pore size and structure were synthesised by replication of zeolite templates and their hydrogen storage capacities were evaluated at 77K and 298 K. Furthermore, the influence of palladium doping on the structural and textural properties and on hydrogen storage capacity of carbon was studied.

Experimental

Two types of ordered carbon materials were synthesized by template method using faujasite NaY and beta zeolites. The faujasite carbon template (FCT) and zeolite beta carbon template (BCT) were prepared by chemical vapour deposition with propylene at 700°C followed by thermal treatment in Ar at 900°C. For FCT material an impregnation with furfuryl alcohol was performed prior to the CVD process [4]. The obtained composites were washed with concentrated HF acid in order to dissolve the templates and to obtain the carbon materials. To obtain Pd/carbon composites, the carbon templates were impregnated with a solution of acid tetrachloropalladic (H_2PdCl_4) and subsequently thermally treated in Ar/ H_2 atmosphere at 573K. The textural properties of the materials were determined from nitrogen adsorption/desorption isotherms at 77K while the structural

characteristics were evaluated by X-ray diffraction. The hydrogen isotherms were measured at 77K and 298K in the pressure range from 0 to 10MPa.

Results and Discussion

The nitrogen isotherms for carbon and Pd/carbon materials (Figure 1) exhibit a typical type I curve revealing the presence of microporosity. All materials present high surface areas and narrow pore size distribution (Table 1 and inset Fig.1), the FCT having the highest surface area and pore volume. A decrease of the surface area and pore volume can be remarked after doping with 4wt% of Pd due to the increase of the weight and also to the pore blocking with metal nanoparticles.

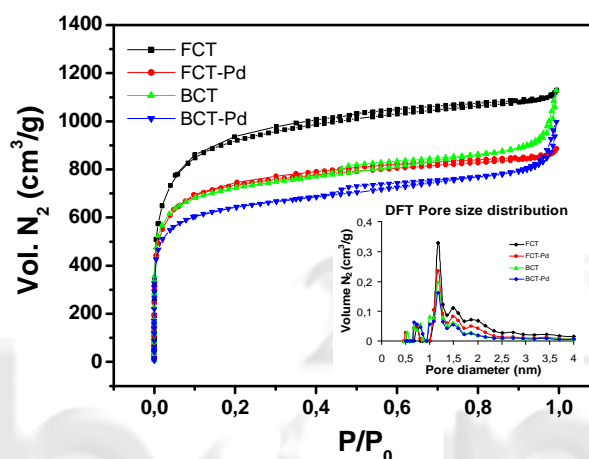


Fig. 1 Nitrogen isotherms of as-pristine and Pd-doped zeolite carbon templates.

Table 1. Textural and hydrogen storage properties of materials.

Material	S_{BET} (m^2/g carbon)	V_{DR} (cm^3/g)	V_T (cm^3/g)
FCT	3311	1.16	1.68
FCT-Pd	2889	0.97	1.32
BCT	2742	0.96	1.42
BCT-Pd	2531	0.85	1.27

The effect of the palladium doping on the carbon morphology and structure was also evaluated.

The TEM pictures (Fig. 2) of Pd/carbon composites reveal homogeneously distributed Pd nanoparticles in the carbon template with sizes of about 2-3 nm.

The presence of the well defined peaks in the small angle diffraction patterns (Fig. 3a) of pristine carbons prove the structural ordering in the materials and a good replication of the zeolite templates. The palladium insertion induces a decrease of the ordering.

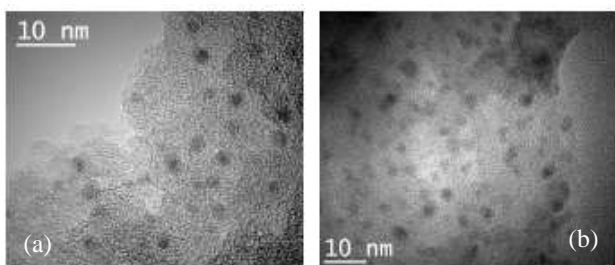


Fig. 2 TEM images of Pd nanoparticles embedded in the nanostructured zeolite (a) faujasite and (b) beta templated carbons.

Moreover, the wide angle diffraction patterns (Fig. 3b) exhibit specific patterns corresponding to a face centered cubic (fcc) structure of palladium. The broadness of the peaks suggests the nanometer size of the palladium particles in agreement with the TEM results.

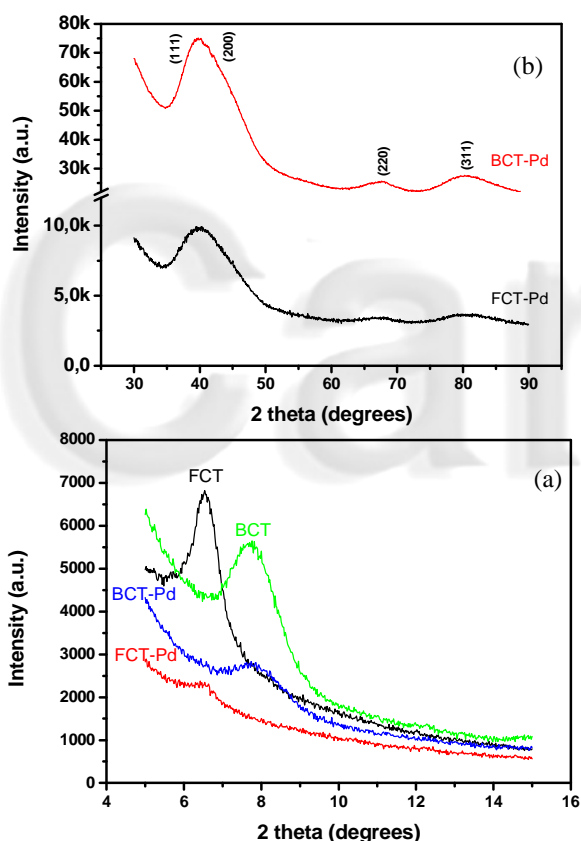


Fig. 3 Small (a) and wide (b) angle X-ray diffraction patterns of as-pristine and Pd-doped zeolite carbon templates.

The hydrogen isotherms for carbon and Pd/carbon composites were measured at liquid nitrogen and room temperature (Fig. 4). At 77K, the FCT and BCT adsorb 5.6 and 5 wt% H_2 respectively, at 4MPa. At this temperature the hydrogen storage capacity of FCT-Pd and BCT-Pd is lower (5 and 4.6 wt%) due mainly to the decrease of the surface area and porous volume. At room temperature, the hydrogen uptake is

lower than at 77K, and the hydrogen uptake is similar for all materials (0.35 wt%). Taking into account that the surface area of the Pd/carbon is inferior to that of pristine carbons and that their storage capacity is similar, the hydrogen storage mechanism is not only based on the physisorption but also based on a chemisorption process as showed by hydrogen adsorption at low pressures (not shown here). In order to improve the hydrogen storage at high pressures, the influence of the metal content and type in the carbon template must be evaluated.

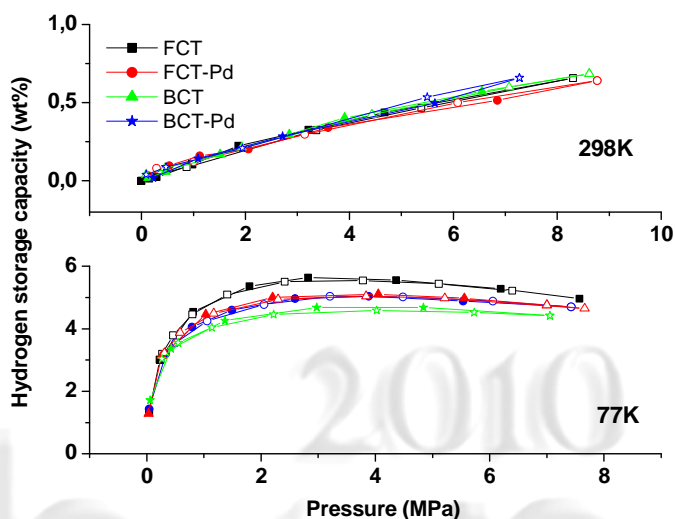


Fig. 4 Hydrogen adsorption isotherms at 77K and 298K of as-pristine and Pd-doped carbon templates (full symbols are in adsorption and open symbols are in desorption).

Conclusions

High surface area carbon materials with well defined structure and porosity were synthesized by replication of different zeolites. Homogeneously palladium nanoparticles were successfully embedded in the carbon templates. The hydrogen storage capacities of the materials at 77K were as high as 5.6wt% while at 298K an important decrease was noticed. Furthermore, the storage capacity was not improved by 4wt% Pd doping, hence, supplementary investigations are necessary to optimize the metal/carbon composition and structure for higher hydrogen storage capacities.

References

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