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Hydrogen adsorption in metal-doped highly ordered mesoporous carbon molecular sieve

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ABSTRACT

In this study, highly ordered mesoporous carbon molecular sieve with high surface area and pore volume have been modified by Ni doping. The surface modified mesoporous carbon was characterized by BET surface area, also XRD analysis (low and wide angle). Adsorption data of H_2 on the ordered mesoporous carbon were collected with PCT method for a pressure range up to 100 bar at 303 K. Enhanced hydrogen adsorption was observed on the carbon adsorbents doped with 0.8 wt% of Ni doping due to the combined effects of hydrogen adsorption on the carbon surface and the spill over of hydrogen molecules into carbon structures.

1. Introduction

Development of hydrogen fueled vehicles can bring economical and environmental benefits through a decrease in using oil, and, consequently, a decrease in air pollution and other greenhouse gases [1]. However, one of the most important drawbacks of the use of hydrogen as a fuel is that it has to be stored. There are different techniques to store hydrogen. All those techniques have to meet the provisional Department of Energy of the United States (DOE) criterion. The DOE has established different targets for onboard hydrogen storage systems, including the minimum "gravimetric" and "volumetric" capacity and the reversibility of the charging/discharging processes. For the 2010 year, the storage system should have a gravimetric capacity of 2 kWh/kg (6 wt% of H_2) and a volumetric capacity of 1.5 kWh/l (0.045 kg H_2/l). In the case of the European Hydrogen & Fuel Cell Technology Platform, it requested energy density values of 1.1 kWh/l in its strategic research agenda (SRA) and deployment strategy (DS) documents, that it published at the end of 2004, and were reviewed in 2005 [2]. These energy density values are equivalent to a volumetric hydrogen storage capacity of about 33 g H_2/l. It is important to remark that, in the case of materials-based technologies, to achieve system-level capacities, the gravimetric and volumetric capacities of the material alone must clearly be higher than the system-level targets (depending on the material and on the system design, material capacities may need to be a factor of 1.2–2 times higher than system capacity targets [3]). These values are referred to the whole system, including the storage medium, the vessel, the refueling infrastructure, any regulators, electronic controllers, sensors, and so on.

There are basically six different storage technologies that have been investigated: compression, liquefaction, physisorption, metallic and complex hydrides and storage through oxidation of reactive metals with water [4–6]. However, the hydrogen physisorption has been considered as the most promising hydrogen storage method [6,7]. Generally, adsorption mechanisms can be classified into two types; physisorption and chemisorption. For physisorption, adsorbate molecules are held on the surface of the adsorbent by only the adsorption potential. In that case, adsorption is reversible. For chemisorption, chemical bonds are formed between the adsorbent and adsorbate molecules, and adsorption may be irreversible. In terms of hydrogen storage, the adsorption mechanism in hydrogen adsorbing metal alloys can be regarded as chemisorption, while that in carbon is physisorption. As for organic materials, crown ethers and phenyl groups have been examined for their hydrogen adsorption capability [8,9]. They have confirmed that these types of organic molecules and groups are probable candidates for hydrogen storage materials.

In recent years, physisorption of hydrogen on carbon-based nanomaterials or other porous materials have attracted greatly scientific interests. Nanostructured carbons are among the major candidates of physisorption for their lightweight, abundant natural

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precursors and low cost. The activated carbons have been reported to have relatively high hydrogen storage capacity at 77 K [10,11], but the pore size distribution is generally wide and more than half of the total porous volumes come from macropores, which contribute less to the uptake of hydrogen.

Recently, mesoporous carbons with well-ordered pore systems offered great potential in hydrogen storage [12–15]. The carbons were obtained via the template method, which involved the introduction of suitable carbon precursors into the ordered pores of the template followed by carbonization and finally removal of the template [16–18]. These carbon materials usually have large specific surface areas and high pore volumes, which are useful for effective physisorption of H_2. Besides, the ordered networks may provide fast transportation in the materials, a noticeable volume of micropores can efficiently adsorb hydrogen, and the micro- and the mesoporosity can be adjusted by changing the template, the carbon precursor and the amount of carbon infiltrated in the template [19]. As a matter of fact, hydrogen adsorption on carbon materials is strongly ascribed to surface heterogeneity, depending in its turn on their preparation and formulation. Surface heterogeneity can arise not only from surface irregularities, including bound impurities and functional groups, but also from nanopore polydispersity (structural heterogeneity).

In this work, we prepared novel high-specific-surface area porous carbons from highly ordered mesoporous silica template by using nanocasting pathway, and investigated the effects of specific surface area and surface functional group on hydrogen uptake. Herein, The H_2 sorption densities of the materials were measured at 303 K over the hydrogen pressure range up to 100 bar. Moreover, we attempted to find out the key factors in hydrogen storage, surface functional groups and also the amount of that, which may help to understand the H_2 adsorption mechanism and direct the design of carbon-based hydrogen adsorbents.

2. Experimental

2.1. Materials

The reactants used in this study were tetraethoxysilane (TEOS, 98%, Acros) as a silica source, non-ionic oligomeric alkyl-ethylene oxide surfactant (Pluronic 123) as a surfactant, HCl (35 wt%), ethanol and deionized water for synthesis of mesoporous silica (SBA-15), sucrose as a carbon source, sulfuric acid as a catalyst for synthesis of mesoporous carbon, nickel nitrate ($NiNO_3$) as fictionalization agent. All chemicals were of analytical grade from Merck.

2.2. Adsorbent preparation

2.2.1. Mesoporous silica and unmodified mesoporous carbon samples

SBA-15 silica was prepared according to the procedure reported by Zhao et al. [20] by using a non-ionic oligomeric alkyl-ethylene oxide surfactant (Pluronic 123) as a structure directing agent, after that template removal by means of calcinations at 500 °C in flowing air. Ordered porous carbon was synthesized via a two step impregnation of the mesopores of SBA-15 with a solution of sucrose using an incipient wetness method [18]. Briefly, 1.0 g of the as-prepared SBA-15 was impregnated with an aqueous solution obtained by dissolving 1.1 g of sucrose and 0.14 g of H_2SO_4 in 5.0 g of deionized water. The mixture was then dried at 100 °C for 6 h, and subsequently at 160 °C for 6 h. The silica sample, containing partially polymerized and carbonized sucrose, was treated again at 100 and 160 °C after the addition of 0.65 g of sucrose, 90 mg of H_2SO_4 and 5.0 g of deionized water. The sucrose–silica composite was then heated at 900 °C for 4 h under nitrogen to complete the carbonization. The silica template was dissolved with 5 wt% hydrofluoric acid at room temperature. The template-free carbon product thus obtained was filtered, washed with deionized water and ethanol, and dried.

2.2.2. Nickel doped samples

The mesoporous carbon samples were impregnated with nickel nitrate ($NiNO_3$) acetone solutions by a vacuum decomposition process using the incipient wetness impregnation method [21]. In this study, a nickel nitrate solution (analytical grade) of a low concentration (5 mM) was selected for the vacuum impregnation process in different times from 1 to 5 h (1-Ni-OMC to 5-Ni-OMC). Mesoporous carbon impregnated with the acetone solution were then filtered and dried at 60 °C for 4 h. The resultants mesoporous carbon doped with Ni were then heated at 100 °C for 1 h under hydrogen atmosphere to reduce the nickel salt to nanoparticles. The activation temperature was 1033 K and optimum N_2 gas flow rates (250 cc/min) were used [22].

2.3. Textural and structural studies

The porous structure of the surface modified samples was estimated by powder XRD (Philips 1830 diffractometer) using graphite monochromated Cu Ka radiation. Adsorption isotherms of the mesoporous carbon samples were obtained using a N_2 gas microporosimeter (micromeritics model ASAP 2010 sorptometer) at 77 K. Pore size distribution and specific surface area were calculated by Dollimore–Heal [23] and BET [24] methods. Pore volume was estimated from the amount of adsorbed N_2 gas at 0.963 in relative pressure, which derives from 25 nm radii pores. Micropore volume was calculated by *t*-plot.

2.4. Hydrogen adsorption

Hydrogen adsorption capacities at 303 K over the hydrogen pressure range up to 100 bar were measured by the PCT method (AnySorb 7) with an automatically controlled apparatus for high-pressure adsorption. The hydrogen adsorption capacities were measured after all samples were pretreated at 423 K for 90 min in helium flow and sequentially reduced in situ in a hydrogen/nitrogen mixture flow. The dead volume was calibrated with helium gas at room temperature. High-purity hydrogen (99.999%) was used in this study. The amounts of hydrogen adsorbed were calculated using the Redlich/Kwong equation. Steps were taken to ensure the accuracy of the experimental results. The principal part of the apparatus was held in an air thermostat to keep its temperature at 303 K. The apparatus was previously tested for leakage and calibrated with the empty sample cell and well-known standard samples. The time adopted for equilibration was 30 min at each step. About 300 mg of the mesoporous carbon samples were used for hydrogen adsorption.

3. Results and discussion

3.1. Textural characterization

Nitrogen physisorption is the method of choice to gain knowledge about mesoporous materials. This method gives information on the specific surface area and the pore diameter. Calculating pore diameters of mesoporous materials using the BJH method is common. Former studies show that the application of the BJH theory gives appropriate qualitative results which allow a direct comparison of relative changes between different mesoporous materials.

As shown in Fig. 1, all OMC samples show type IV isotherms with obvious hysteresis loops, indicating that OMC samples are typical mesoporous materials. It also can be seen from the inset of Fig. 1 that the pore sizes of OMC and 1-Ni-OMC, 3-Ni-OMC and 5-Ni-OMC locate in mesopore size range and their most probable pore diameter are 3.7, 3.65, 3.62 and 3.55 nm, respectively. From the nitrogen

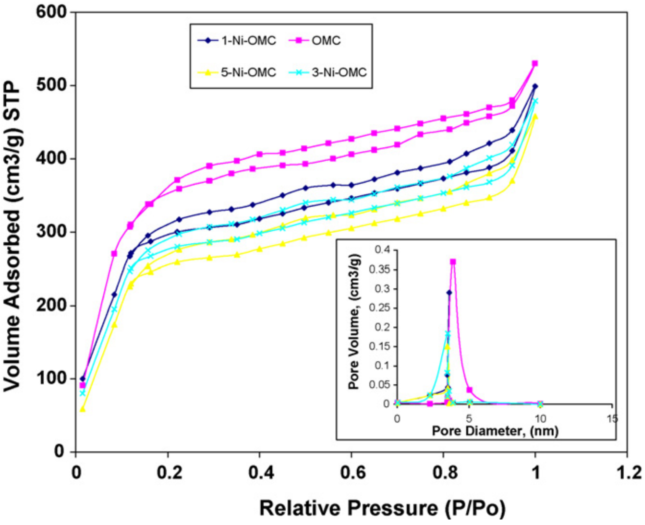

Fig. 1. Adsorption–desorption isotherms of nitrogen at 77 K on OMC, 1-Ni-OMC, 3-Ni-OMC and 5-Ni-OMC. The insert shows the BJH pore size distribution calculated from the desorption branch of the isotherm.

Table 1
Textural parameters of the OMC, 1-Ni-OMC, 3-Ni-OMC and 5-Ni-OMC employed in this study.

Adsorbent	*d* spacing (nm)	A_{BET} ($m^2 g^{-1}$)	V_p ($cm^3 g^{-1}$)
OMC	3.7	1530	0.73
1-Ni-OMC	3.65	1467.4	0.72
3-Ni-OMC	3.62	1434.1	0.69
5-Ni-OMC	3.55	1421.9	0.64

sorption isotherms of mesoporous carbon type carbons before and after chemical modification, it can be seen that after chemical modification the obtained carbons still have type IV isotherms, indicating that mesoporosity is preserved. The textural parameters listed in Table 1 clearly confirm the structural changes of nickel modified mesoporous carbon.

In order to check the structural degradation, XRD data of carbonaceous adsorbents were obtained on Philips 1830 diffractometer using Cu Kα radiation of wavelength 0.154 nm. Fig. 2 reports low angle XRD patterns of the parent mesoporous silica and of samples OMC, 1-Ni-OMC, 3-Ni-OMC and 5-Ni-OMC. With SBA-15, three well-resolved peaks are observed, corresponding to the (1 0 0), (1 1 0) and (2 0 0) reflections typical of the 2D hexagonal space group *p*6*mm*. With all replicas, the main reflection peak is well maintained, indicating that rather ordered mesoporous materials with hexagonal structures were obtained. With respect to the parent silica, a shift of the *d*1 0 0 peak towards higher 2θ values is observed, in agreement with the literature [20].

The wide-angle XRD patterns of nickel modified mesoporous adsorbent (3-Ni-OMC) in Fig. 3 exhibit two resolved diffraction peaks at 44.59° (1 1 1) and 51.90° (2 0 0) 2θ, characteristic of metallic nickel with a cfc structure but the same XRD pattern of pristine mesoporous carbon adsorbent does not show any diffraction peak. It reveals that the nickel species in the mesoporous carbon matrix exists in metallic form.

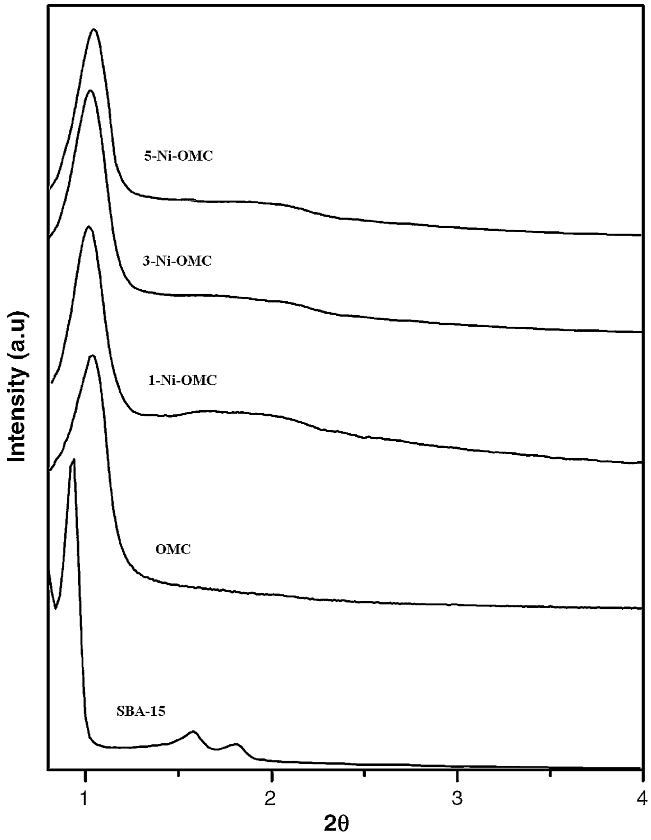

Fig. 2. Low angle XRD patterns of the parent SBA-15 and of carbonaceous mesoporous adsorbents (OMC, 1-Ni-OMC, 3-Ni-OMC and 5-Ni-OMC).

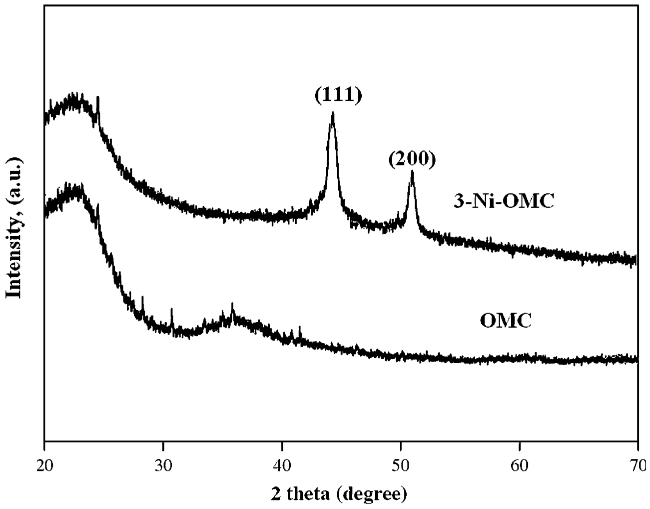

Fig. 3. Wide angle XRD patterns of the mesoporous carbon adsorbents (pristine mesoporous carbon and 3-Ni-OMC).

3.2. Hydrogen adsorption study

We estimated the hydrogen storage capacity of modified mesoporous carbon with the PCT method. Fig. 4 shows hydrogen adsorption isotherms of mesoporous carbons (OMC and 3-Ni-OMC) studied over hydrogen pressure up to 100 bar at 303 K. We have obtained similarly shaped of hydrogen adsorption isotherms in spite of surface modification for mesoporous carbon adsorbent studied. Hydrogen adsorption capacity is a linear function of pressure, which can be explained by Henry's law. These results indicated that nickel was well dispersed on the surface of mesoporous carbon adsorbent. The amount of hydrogen adsorbed increased with increasing pressure. The amounts of hydrogen adsorbed on nickel doped mesoporous carbon adsorbent (3-Ni-OMC) were much larger than parent mesoporous carbon adsorbent (OMC). In the data shown in Fig. 4, the effect of activation of nickel is more prominent, and thus led to more hydrogen storage. It could be confirmed that surface modification of mesoporous carbon adsor-

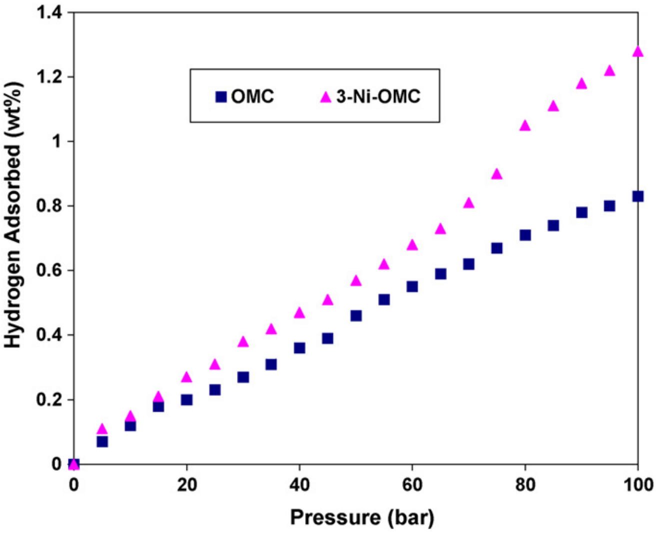

Fig. 4. Hydrogen adsorption isotherm of the unmodified (OMC) and modified mesoporous carbon (3-Ni-OMC) at 303 K.

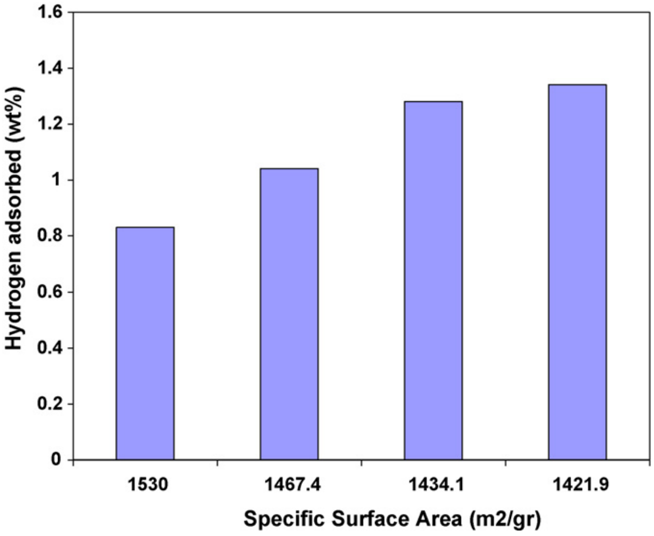

Fig. 5. The effect of specific surface area on the hydrogen adsorption capacity of unmodified and modified mesoporous carbon adsorbents at 100 bar, 303 K.

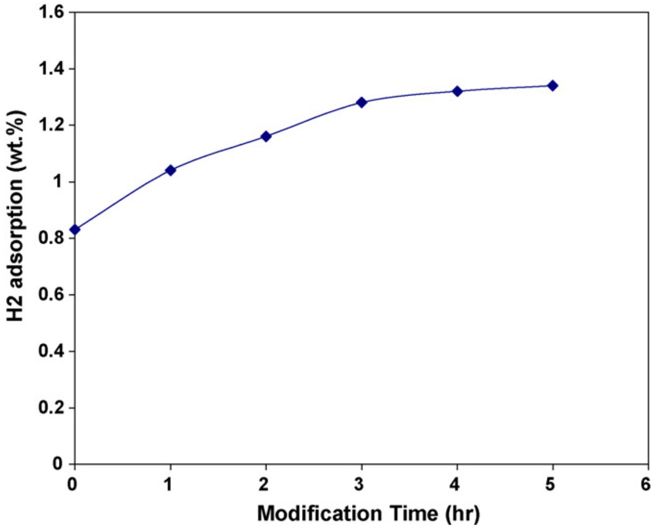

Fig. 6. Effect of modification time on hydrogen adsorption on ordered mesoporous carbon adsorbent at 100 bar, 303 K.

bents plays an important role in determining the porous structure and amounts of hydrogen adsorbed. Fig. 5 shows the effect of specific surface area on the hydrogen adsorption capacity of the all mesoporous carbon adsorbents studied at 100 bar, 303 K. As the BET surface area increases, the hydrogen adsorption of the materials also increases [25]. In this study, though the specific surface areas of modified mesoporous carbon adsorbents are decreased, their hydrogen adsorption are improved as compared with unmodified mesoporous carbon adsorbents due to the enhancement of hydrogen affinity by Ni doping.

Fig. 6 shows the hydrogen-storage volume as a function of the modification time. The as-received sample showed only a low hydrogen-storage capacity, 17.3 $cm^3 g^{-1}$ (hydrogen uptake: 0.14 wt%) at 100 bar. The hydrogen-storage capacity of the 1-Ni-OMC samples, in stark contrast, was found to be 200% more than that of the as-received sample. The 5-Ni-OMC sample was found to store 84.7 $cm^3 g^{-1}$ (hydrogen uptake: 0.69 wt%) of hydrogen, fully 500% that of the as-received sample. Yang et al. [26] reported that hydrogen-uptake capacity can be remarkably enhanced in the presence of transition metals, as a result of the spill over of hydrogen molecules into carbon structures. The presence of Ni particles can also encourage the hydrogen uptake of Ni-OMCs by means of hydrogen-molecule spill over.

4. Conclusions

SBA-15 carbon replicas were synthesized by using a sucrose solution as carbon source. The structural order and textural properties of the modified and unmodified mesoporous adsorbents was studied by XRD and nitrogen adsorption analyses. The Ni modified ordered mesoporous carbons prepared in this work are suitable for the hydrogen storage in contrast with other novel carbonaceous adsorbents. Enhanced hydrogen adsorption was observed on the carbon adsorbents doped with 0.5 wt% and 0.75 wt% of nickel at hydrogen pressures about 100 bar, 303 K.

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