Original Article

Synthesis of new ordered microporous mesoporous carbon sorbent, an investigation on hydrogen adsorption capacity

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Abstract : In the current research, ordered microporous mesoporous carbon molecular sieve with ultra high surface area and pore volume has been synthesized by KOH activation technique. The mesoporous carbon samples were characterized by BET surface area, also XRD analysis. Adsorption data of H_2 on the ordered mesoporous carbon were collected with PCT method for a pressure range up to 100 bar at 303K. The novel microporous mesoporous carbon has shown much better hydrogen capacity in respect to ordered mesoporous carbon and chemically oxidized mesoporous carbon due to the combined effects of hydrogen adsorption on the micro-mesoporous structure. **© Global Scientific Inc.**

Keywords : Microporous mesoporous carbon; KOH activation; Specific surface area; Hydrogen storage.

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[1-3]. Conventionally available methods to store hydrogen are: liquid hydrogen[3], compressed gas, metal hydrides[4,5] and sorption on different porous materials[6-16].

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 precursors and low cost. The activated carbons have been reported to have relatively high hydrogen storage capacity at 77K[17,18], 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[19-21]. 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[22-25]. These carbon materials usually have large specific surface areas and high pore volumes, which

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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[26]. In fact, hydrogen adsorption on carbon materials is strongly ascribed to surface porosity, depending in its turn on their preparation and formulation.

In the present work, we prepared high-specific-surface area microporous mesoporous carbon by using by KOH activation technique, and investigated the effects of specific surface area and surface structure 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 microporous surface area, which may help to understand the H_2 adsorption mechanism and direct the design of carbon-based hydrogen adsorbents.

EXPERIMENTAL SECTION

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, nitric acid as an oxidizer agent and potassium hydride (KOH) as activation agent. All chemicals were of analytical grade from Merck.

Adsorbent preparation

(a) Mesoporous silica and unmodified ordered mesoporous carbon (OMC) samples

SBA-15 silica was prepared according to the procedure reported by Zhao et al.[27]. A non-ionic oligomeric alky-ethylene oxide surfactant (Pluronic P123) was used as the structure-directing agent and tetraethyl orthosilicate (TEOS) of analysis grade was used as the silica source. After filtration and drying, the as-synthe-

sized product was calcinated at 823 K to obtain the SBA-15 structure. 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[25]. 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.

(b) Ordered microporous mesoporous carbon preparation

The ordered mesoporous carbon (1.67 g) was impregnated with KOH solution (36 g of KOH in 10 ml of water) at 80 °C over 4 h. The KOH-impregnated ordered mesoporous carbon was dried at 105 °C for 10 h. The KOH/carbon weight ratio in the dry product was 0.6. The activation process for the KOH-impregnated OMC was carried out by heating the sample to 700 °C under flowing nitrogen in a tube furnace at a rate of 10 °C/min and then maintaining this temperature for 45 min. After the resulting sample was cooled in flowing nitrogen, it was washed successively with 0.1 M HCl solution and deionized water to ensure that the KOH was completely removed. Finally, the activated microporous mesoporous carbon was dried at 105 °C for 12 h, and the final microporous-mesoporous carbon was denoted as OMMC.

(c) Chemical oxidation of OMC

To introduce oxygen-containing functional groups on the carbon surface, OMC was oxidized by nitric acid under optimal oxidation condition, such as nitric acid concentration, oxidation temperature[28]. 0.1 g of dried OMC powder was treated with 15mL of HNO_3 solution (2M solution) for 1 h in the 80 °C under refluxing. After oxidation, oxidized ordered mesoporous

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carbon samples (OOMC) were recovered and washed thoroughly with distilled water until the pH was close to 7.

Textural and structural studies

The porous structure of the surface modified samples was estimated by powder XRD (Philips 1830 diffractometer) using graphite monochromated CuKa 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[29] and BET[30] methods. Pore volume was estimated from the amount of adsorbed N_2 gas at 0.963 in relative pressure, which derives from 25nm radii pores. Micropore volume was calculated by t-plot.

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.

RESULTS AND DISCUSSION

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.

Nitrogen sorption isotherms at 77 K are reported in Figure 1 and the corresponding structural parameters being gathered in TABLE 1. OOMC still exhibits a type I isotherm, with a more pronounced hysteresis loop with respect to parent ordered mesoporous carbon samples. The oxidation by acid nitric caused a small decrease in BET surface area (1467 $m^2.g^{-1}$), total pore volume and micropores volume (0.67 and 0.11 $cm^3.g^{-1}$, respectively). With ordered microporous mesoporous carbon sample, a Type I isotherm is observed, typical of microporous systems: most of the total pore volume is in fact due to micropores (0.55 $cm^3.g^{-1}$ against 1.05 $cm^3.g^{-1}$). As to mesopores, activation with KOH leads to an increase in BET surface area (2432 $m^2.g^{-1}$). As we can see, activation of the OMC by KOH increased the fraction of micropores from 16.4% to 65.4%.

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. Low-angle XRD patterns of the activated samples OOMC and OMMC are reported in Figure 2, along with that of ordered mesoporous carbon, for comparison. With OOMC, the (100), (110) and (200) reflections peak is maintained, indicating that the hexagonal structural order is preserved, whereas with OMMC, the structural order is completely lost after chemical activation.

Hydrogen adsorption study

We estimated the hydrogen storage capacity of modified mesoporous carbon with the PCT method. Figure 3 shows hydrogen adsorption isotherms of mesoporous carbons (OMC, OMMC and OOMC) studied over hydrogen pressure up to 100 bar at 303 K. All of adsorption lines seem to be linear except OMMC. The reason of that was explained before simply due to the low amount of hydrogen uptake[31]. There is no hysteresis in all samples indicating that adsorbed hydrogen can be desorbed reversibly[32]. NaOH-activated samples showed the higher hydro-
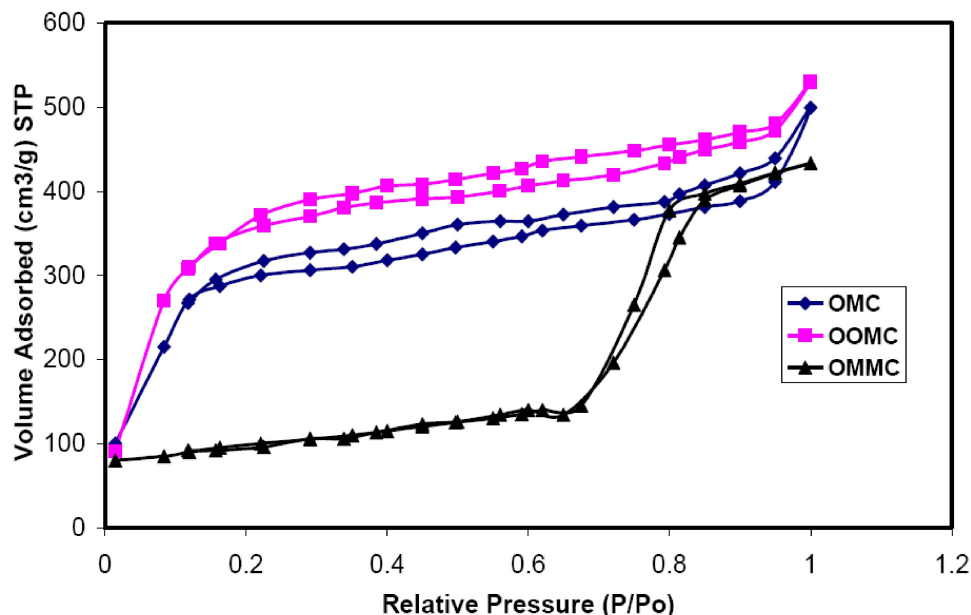
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Figure 1 : Adsorption-desorption isotherms of nitrogen at 77 K on OMC, OOMC and OMMC. The insert shows the BJH pore size distribution calculated from the desorption branch of the isotherm.

TABLE 1 : Textural parameters of the OMC, OOMC and OMMC employed in this study.

Adsorbent	A_{BET} $(m^2 g^{-1})$	Total pore volume $(cm^3.g^{-1})$	Micropore volume $(cm^3.g^{-1})$	% Micropore volume
OMC	1530	0.73	0.12	16.4
OOMC	1467	0.67	0.11	16.4
OMMC	2432	1.05	0.67	62.4

gen adsorption than OOMC samples. This is believed to be due to the higher specific surface area and micropore volume of ordered microporous mesoporous carbon than in acid nitric modified mesoporous carbon (OMMC).

Figure 4 shows the effect of specific surface area on the hydrogen adsorption capacity of the all mesoporous carbon adsorbents studied at 100 bar, 303
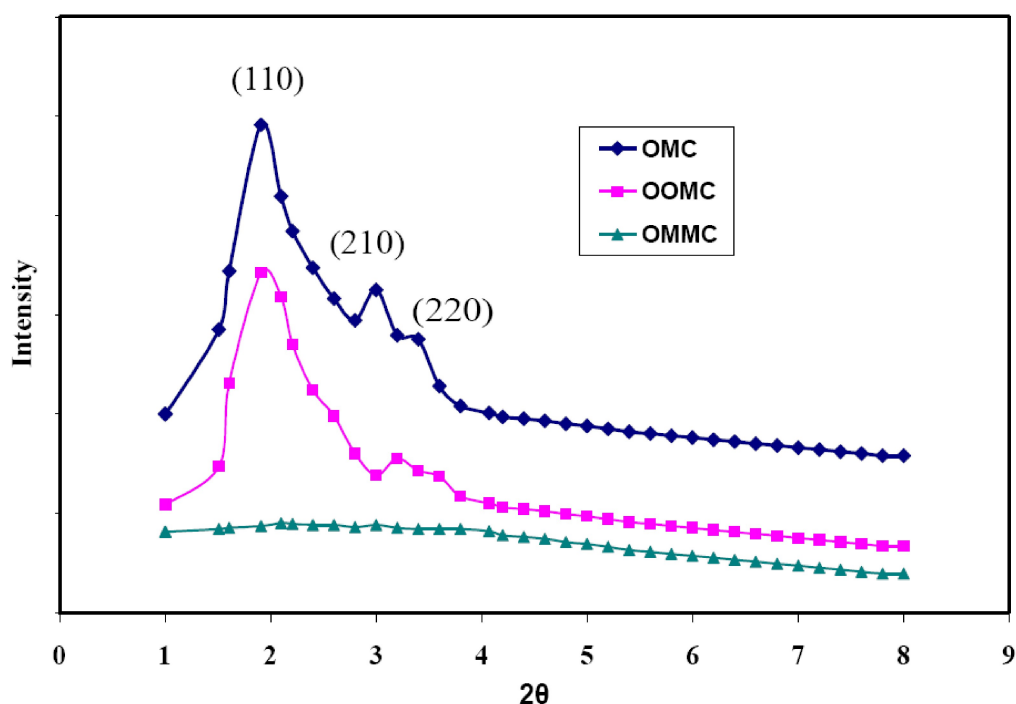

Figure 2 : Low angle XRD patterns of the parent ordered mesoporous carbon (OMC) and of OOMC and OMMC.

K. As the BET surface area increases, the hydrogen adsorption of the materials also increases. Comparing OMMC with OMC, even though OMMC has 1.6 times more specific surface area and 1.4 times more total pore volume, the hydrogen storage capacity of ordered microporous mesoporous carbon (OMMC) is 1.8 times higher than that of ordered mesoporous carbon. This may be due to the fraction of micropore volume (OMMC: 65.4%, OMC: 16.4%). This clearly suggests that micropore volume favors the capacity of hydrogen adsorption better than specific surface area and total pore volume.

In Figure 5, adsorbed volumes of hydrogen at 100 bar and 303 K are plotted as a function of samples microporous volumes. In the former case, the regular trend reported repeatedly in the literature for different
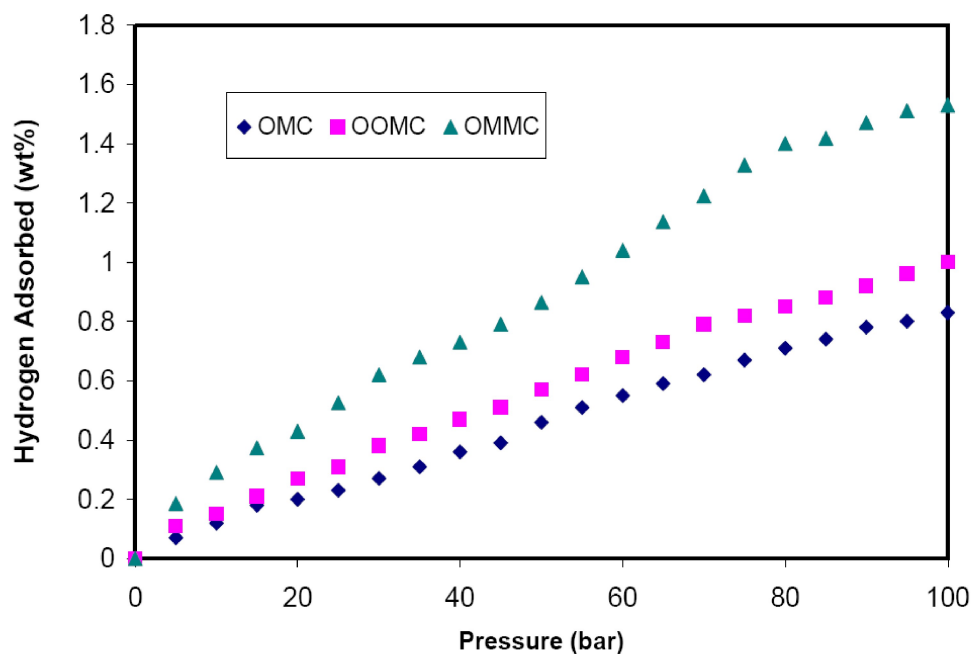

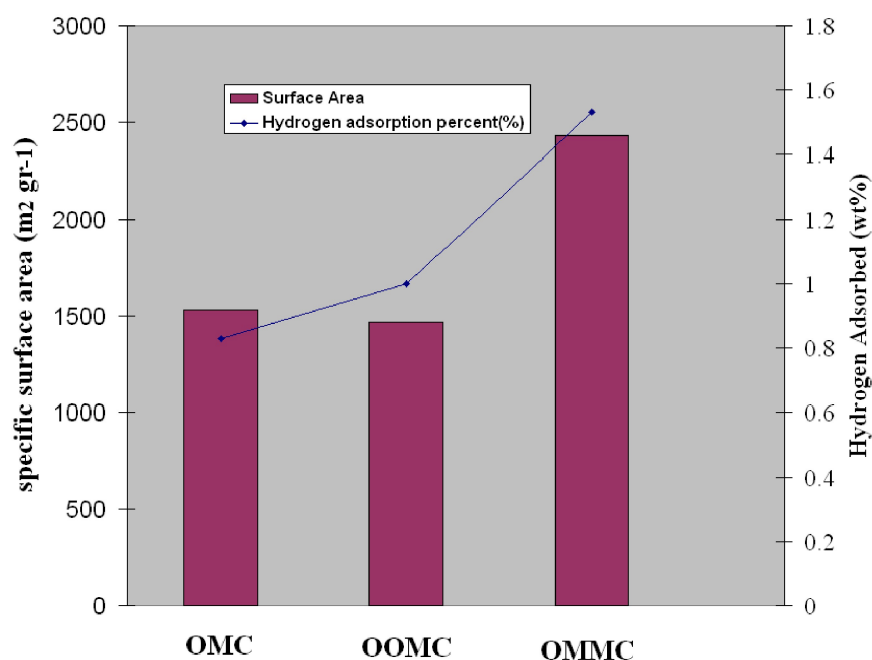**Figure 3 : Hydrogen adsorption isotherm of carbonaceous adsorbents (OMC, OOMC and OMMC) at 303 K.**

Figure 4 : The effect of specific surface area on the hydrogen adsorption capacity of mesoporous carbon adsorbents at 100 bar, 303 K.
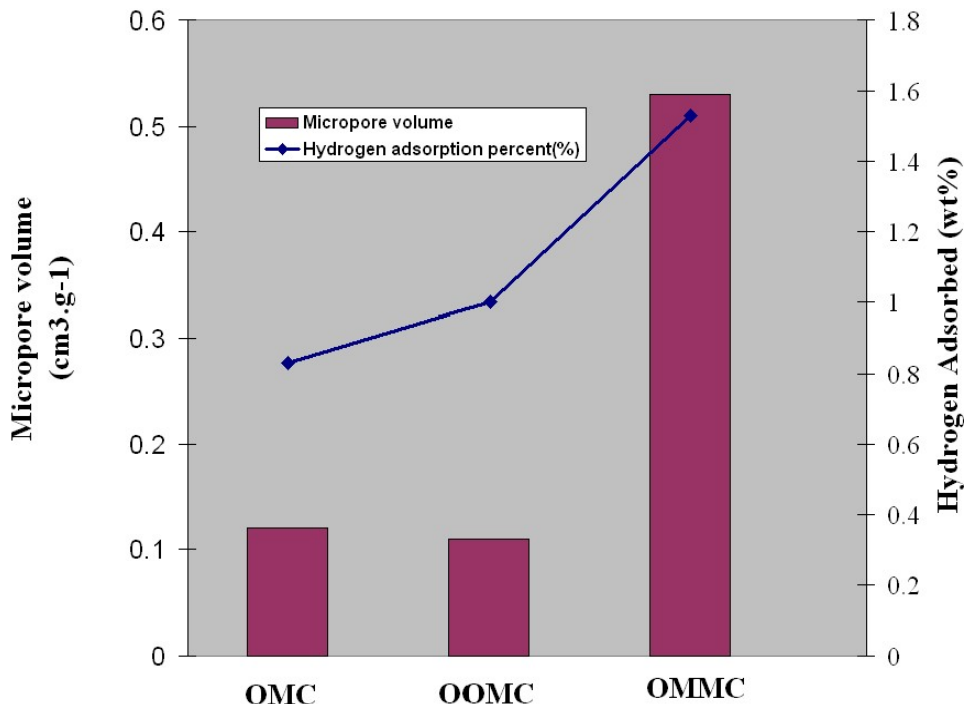
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Figure 5 : The effect of micropore volume on the hydrogen adsorption capacity of mesoporous carbon adsorbents at 100 bar, 303 K.

porous systems is observed[33-36]. In the latter case, instead, a linear behavior is observed for all samples, which definitely points out to the crucial role of microporosity in H_2 adsorption, as previously proposed with various kinds of ordered porous carbons, activated carbons[37,38]. But, OOMC in respect to lower BET surface areas and microporous volumes has shown much better hydrogen adsorption capacity than OMC, which is due to the chemically modified structure of OOMC.

CONCLUSIONS

In the present work, ordered mesoporous carbon has been modified to get high specific surface area and pore volume by activation for improved hydrogen storage. The structural order and textural properties of the modified and unmodified mesoporous adsorbents was studied by XRD and nitrogen adsorption analyses. The ordered microporous mesoporous carbons prepared in this work are suitable for the hydrogen storage in contrast with other novel carbonaceous adsorbents. Enhanced hydrogen adsorption (0.7 wt%) was observed on the microporous mesoporous carbon adsorbent at hydrogen pressures about 100 bar, 303 K.

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