HYDROGEN STORAGE IN N-DOPED MESOPOROUS CARBONS

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ABSTRACT

An ordered mesoporous carbon CMK-3 was synthesized by replication using SBA-15 as a template and sucrose as carbon source. The synthesized CMK-3 was modified by immersion with chitosan solution or ammonia aqueous solution. The effect of CMK-3 surface modification on hydrogen storage capacity was investigated. The CMK-3 texture characteristics were determined by using small angle X-ray scattering analysis, transmission electron microscope and nitrogen adsorption analysis. The surface basic functional groups were analyzed by X-ray photoelectron spectroscope and determined by the Boehm method. Hydrogen capacity of the CMK-3 samples was measured by a volumetric adsorption apparatus at 77, 90 and 195K under 0.1 MPa. Experimental results showed that hydrogen storage capacity of modified CMK-3 by chitosan and ammonia at 77K and 0.1 MPa increased from 1.17 wt.% to 1.30 wt.% and to 1.31 wt.%, respectively. Although the specific surface areas and the micropore volumes of CMK-3 decreased after modification, the hydrogen storage capacity enhanced. The enhancement of hydrogen storage capacity might be attributed to the nitrogen doping on the surface of CMK-3.

Keywords: Ordered mesoporous carbon, hydrogen storage, surface modification.

1. INTRODUCTION

In the pursuing of a clean energy alternative, hydrogen as a fuel has received special attention of the scientific community. Hydrogen storage technology is one of the critical factors for the development of hydrogen based energy. Currently, the main methods of storing hydrogen have involved compressed hydrogen, liquefied hydrogen, chemisorption in the form of metal hydrides (Huang *et al*. 2009; Yoo *et al*. 2009) or complex hydrides (Kojima *et al*. 2004; Biniwalea *et al*. 2008), and physisorption of hydrogen on porous materials with large specific surface areas and high micropore volume (Strobel *et al*. 2006; Chen and Huang 2007; Yürüm *et al*. 2009; Huang *et al*. 2010; Guo and Gao 2010). However, none of hydrogen storage methods presently meets the storage targets (gravimetric capacity and volumetric capacity) set by the US Department of Energy (DOE) for vehicular storage systems (Satyapal *et al*. 2007).

Carbon-based materials are among the major candidates of physisorption. Recently, ordered mesoporous carbons synthesized by replication from silica templates have shown remarkable potential in hydrogen storage (Xia *et al*. 2007; Armandi *et al*. 2008). Xia *et al*. (2007) used CO_2 to activate CMK-3 for increasing the specific surface area and micropore volume to enhance hydrogen adsorption capacity. Recently, Zheng *et al*. (2010) used ethylenediamine and carbon tetrachloride as carbon precursor prepared mesoporous nitrogen-doped carbons (MCN-1). They found that though the surface area of MCN-1 is about as half that of CMK-3, the hydrogen uptake capacity of MCN-1 is larger than that of CMK-3. The MCN-1 was further activated using potassium hydroxide to obtain large surface area and high pore volume. They concluded that the small mesopores between the sizes 2 and 3 nm also make contributions to the hydrogen adsorption at high pressure. Yang *et al*. (2006) studied the influence of functionalization (nitrogen-doping) in zeolite-template acetonitrile-derived carbon on hydrogen storage and found the benefit of using acetonitrile rather than ethylene as carbon source. Wang *et al*. (2009) reported that the B- and N-doped microporous carbon had a 53% higher hydrogen storage capacity than the carbon materials with similar surface areas. However, Giraudet *et al*. (2010) studied the influence of nitrogen functional groups on hydrogen storage and found the texture of the adsorbent dominated the storage capability and the nitrogen groups had no significant influence. Obviously, the influence of the doping nitrogen on carbonaceous material on hydrogen storage capacity is needed to further study.

Nitrogen containing functionalities can be introduced through either reaction with nitrogen containing reagents or activation with nitrogen containing precursors (Shafeeyan *et al*. 2010). Chitosan is one of the most abundant biopolymer in nature and has one amino group in the repeating glucosamine unit. Huang and Shen (2012) used chitosan to modify CMK-3 for adsorption of carbon dioxide. They found nitrogen functional groups increased on the chitosan modified CMK-3 and the CO_2 capture capacity was enhanced. Several authors have studied thermal treatment of activated carbons with ammonia to increase their basicity (Jansen and van Bekkum 1994; Biniak *et al*. 1997). To the best of our knowledge, there is no report of chitosan or ammonia solution modified porous carbon materials as a hydrogen adsorbent.

In this paper, the ordered mesoporous carbon CMK-3 was synthesized by replication using SBA-15 as the template and

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sucrose as the carbon source (Ryoo *et al.* 1999). The synthesized CMK-3 was simply modified by immersing it with chitosan and ammonia aqueous solutions. The aim of this work is to examine the effect of immersed chitosan and ammonia on structure and texture as well as hydrogen storage of ordered mesoporous carbon.

2. MATERIALS AND METHODS

2.1 Materials

Pluronic 123 (P123), tetraethyl orthosilicate (TEOS), and sucrose (99%) were obtained from Aldrich. Sulfuric acid (98%), hydrochloric acid (37%), acetic acid (100%), nitric acid (65%), sodium hydroxide (99%), and ammonium solution (25%) were purchased from Merck. Chitosan powder (degree of deacetylation of 85%, 100 mesh size, and 50 kDa) was obtained from VA&G Bioscience Inc. All chemicals used in this study were of analytical reagent grade and were used without any further purification.

2.2 Synthesis of CMK-3 and Modification of Prepared CMK-3

The mesoporous silica template SBA-15 was synthesized using triblock copolymer Pluronic P123 as a template and tetraethoxytitane (TEOS) as a silica source (Chareonpanich *et al.* 2007). The CMK-3 was synthesized according to the process described in the literature (Ryoo *et al.*, 1999). In a typical synthesis of CMK-3, 1 g of calcined SBA-15 was added to a solution of 1.25 g sucrose and 0.14 g sulfuric acid in 5 g of de-ionized (DI) water, and the mixture was placed in an oven at 373K for 6 h. Subsequently, the oven temperature was raised to 433K and maintained for another 6 h. Next, 0.8 g of sucrose, 90 mg of sulfuric acid and 5 g DI water were again added to the pre-treated sample and the mixture was again subjected to the thermal treatment described above. The template-polymer composite was then pyrolyzed in a furnace under nitrogen atmosphere up to 1,173K by a heating rate of 5 K/min, at the holding temperature for 6 h for carbonization. After cooling to room temperature, the mesoporous carbon CMK-3 was recovered after dissolution of the silicon framework in 2 M NaOH solution, by filtration, washed several times with DI water and ethanol and dried at 393K.

The synthesized CMK-3 was modified by immersion with chitosan solution at 303K for 24 h. Chitosan solution was prepared by dissolving 3 wt.% of chitosan powder in acetic acid. After filtration the samples were dried at 373K for 24 h. The chitosan deposited CMK-3 is denoted as C-Chi. Parts of C-Chi samples were further submersed in a basic solution (1N NaOH) for 24 h. Then washed with large amounts of DI water and dried at 378K for 24 h. The chitosan modified CMK-3 with alkaline immobilization is denoted as C-Chi-b.

The synthesized CMK-3 was also modified by immersing in 25% ammonia aqueous solution at 303, 313, 323, and 353K and shaking for 24 h. Then, washed with DI water at room temperature and finally dried at 378K for 24 h. The ammonia modified CMK-3s are denoted as CN-n, where n is temperature.

2.3 Characterization of CMK-3s

The texture characteristics of the CMK-3 samples were determined by using a small angle X-ray scattering analyser (SAXS, Rigaku D/MAX-2500) and a transmission electron microscope (HRTEM, JEOL, JEM-2010 type). The element contents of the CMK-3 before and after modification were determined by X-ray photoelectron spectroscope (XPS). The amount of chitosan loaded on the CMK-3 was determined by a thermogravimetric analyzer (TA, TGA2050). The amounts of basic functional groups on the ammonia modified CMK-3 samples were determined by the Boehm titration method (Boehm 1994). The porous texture of the prepared CMK-3 samples was characterized by physical adsorption of nitrogen at 77K in a gas adsorption apparatus (Quantachrome Autosorb-1). Specific surface area (S_{BET}) was calculated using the BET equation at relative pressure between 0.005 and 0.3. The pore size was calculated using the BJH model in the range 1.4-200 nm and the DFT method in the micropore range.

2.4 Hydrogen Adsorption Measurement

The hydrogen adsorption in all CMK-3 samples was accurately measured by a volumetric adsorption apparatus. Ultrahigh purity grade hydrogen (99.9995%) was used through a moisture trap (packed SICAPENT powder, Merck) to eliminate moisture impurities. About 200 mg of CMK-3 samples were used for each measurement. The samples were outgassed under vacuum at 573K for 3 h prior to the experiment. After the pretreatment, adsorption measurements were carried out under pressure below 0.1 MPa and at 77K. The hydrogen isotherms were also determined at 90K and 195K controlled by liquid oxygen and dry ice, respectively. Prior to measurements, the samples were outgassed at 573K for 3 h under vacuum. The determined values were additionally cross-checked using the hydrogen adsorption data of a known amount of AX-21 (Lachawiec *et al.* 2008). The hydrogen adsorption data are reproducible. Typically, the variation in uptake capacity is less than 1.5% throughout the entire pressure range.

3. Results and Discussion

3.1 Characterization of CMK-3s

Figure 1 shows the TEM images for the CMK-3. It is very clear from the TEM images that the structure of the prepared CMK-3 material is a highly ordered hexagonal arrangement of cylindrical mesoporous channels with uniform pore size of 6 ~ 8 nm. From high-resolution TEM images, the CMK-3 exhibited well-organized pores parallel to each other. The above results are consistent with the results derived from the SAXS patterns (not shown) which showed that three well-resolved peaks with 2θ at 0.93°, 1.42°, and 1.56°, indexed as (100), (110), and (200) reflections associated with p6mm hexagonal symmetry, indicative of the well-ordered mesoporous structure (Bharat *et al.* 2002; Lázaro *et al.* 2007). From the TEM images and SAXS patterns, it is shown that the CMK-3 exhibited a highly ordered mesoporous structure with linear arrays of mesopores, originating from the mesoporous silica framework of the SBA-15.

(a)

(b)
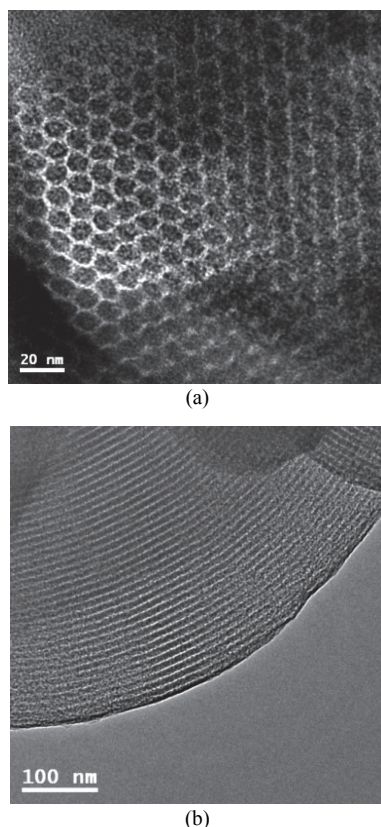
Fig. 1 **TEM images of CMK-3: (a) projection along the direction parallel to carbon rods; (b) projection along the direction perpendicular to carbon rods**

Nitrogen adsorption/desorption isotherms at 77K of CMK-3, C-Chi and C-Chi-b are illustrated in Fig. 2(a). The nitrogen adsorption isotherm of the CMK-3 samples were of Type VI in the IUPAC classification and exhibited an H1 hysteresis loop with capillary condensation at a relative pressure that ranged between 0.4 ~ 0.95. From the shape and hysteresis of the isotherm, it is plausible to suggest that CMK-3 shows a mesoporous structure. The pore size distributions of CMK-3, C-Chi and C-Chi-b obtained using the BJH and DFT methods are shown in Fig. 2(b). The results clearly indicate that the pore distribution of CMK-3, C-Chi and C-Chi-b are with tri-modal pores that range from 2 to 4 nm (mesopores), from 1 to 2 nm, and less than 0.9 nm (micropores). The pore distribution of CMK-3 samples was not apparently changed after chitosan modification. The specific surface area S_{BET}, the total pore volume, the micropore volume of SBA-15, CMK-3, and the modified CMK-3 samples were calculated from nitrogen isotherm data and listed in Table 1. The specific surface area and total pore volume of the CMK-3 are 1339 m^2/g and 1.73 cm^3/g, respectively. Xia *et al*. (2007) synthesized the CMK-3 using SBA-15 as the template and obtained the specific surface area and pore volume of 984 m^2/g and 1.09 cm^3/g, respectively. From Table 1, the surface areas and micropore volumes obviously decreased after chitosan modification due to the pore blockage. The BET specific surface area and total pore volume of the CMK-3 immersed by ammonia aqueous solution at different temperatures are also listed in Table 1. The surface area and pore volume are slightly decreased after socking with ammonia solution.

Table 1   Textural characters of SBA-15 and CMK-3s

| Sample	S_{BET} (m^{2}g^{-1})	V_{tot} (cm^{3}g^{-1})	V_{mic} [a] (cm^{3}g^{-1})	V_{meso} [b] (cm^{3}g^{-1})	d_{BJH} [c] (nm)
SBA-15	1044	1.90	0.36	1.54	7.3
CMK-3	1339	1.73	0.47	1.25	5.2
C-Chi	1170	1.37	0.42	0.95	4.7
C-Chi-b	954	1.21	0.39	0.83	5.1
CN-303	1128	--	--	--	--
CN-313	1120	1.44	--	--	5.1
CN-323	1114	1.49	--	--	5.3
CN-353	1122	1.39	--	--	5.0

[a] : micropore volume, calculate by the D-R equation
[b] : mesopore volume, $V_{meso} = V_{tot} - V_{mic}$
[c] : peak maxima of mesopore size distribution by the BJH method
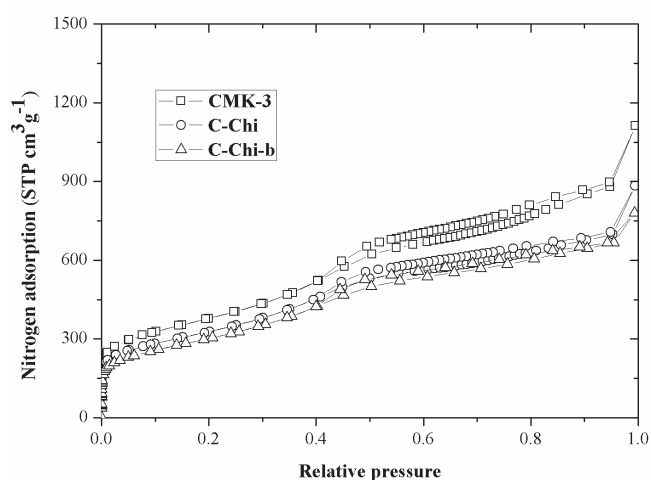
(a) N$_2$ adsorption-desorption isotherms at 77K
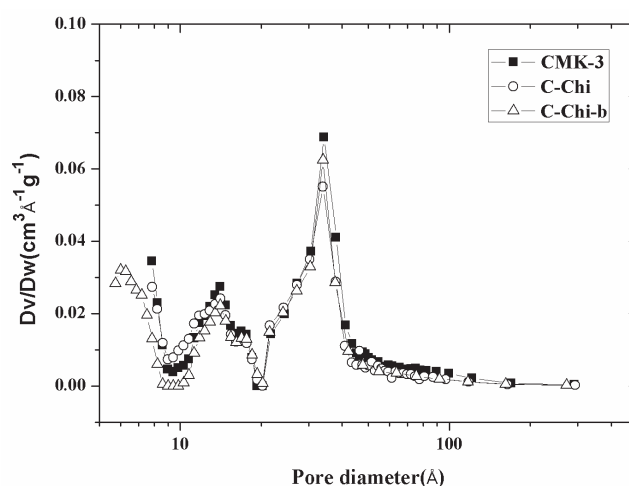
(b) Pore size distribution

Fig. 2   Nitrogen adsorption isotherms and pore size distribution of CMK-3 and chitosan modified CMK-3

Thermogravimetric behaviors of pure chitosan, CMK-3 and chitosan modified CMK-3 recorded in thermal stability tests under nitrogen atmosphere are shown in Fig. 3. There is about 0.2-3% weight loss below 100°C, and it can be attributed to the removal of physisorbed water. About 55% weight loss of pure
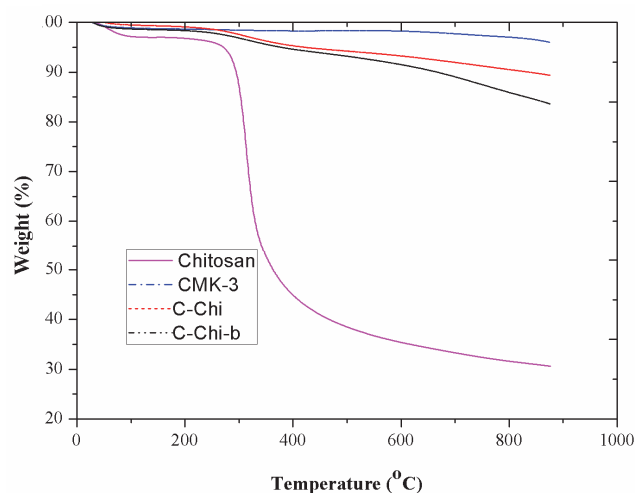
Fig. 3   Thermogrametric analysis of pure chitosan, CMK-3, C-Chi, and C-Chi-b

chitosan is found between 250 and 400°C due to its degradation. A similar result was reported by Huacai *et al*. (2006). For the CMK-3, there is no weight loss until 800°C under nitrogen atmosphere. The chitosan modified CMK-3 samples exhibit similar weight change patterns and start their main weight loss at 250°C. According to thermogravimetric analysis, the chitosan loading on C-Chi and C-Chi-b were determined as 6.0 and 6.04 wt.%, respectively.

Figure 4 presents the XPS C1s and N1s spectra of CMK-3 and chitosan modified CMK-3. From the C1s spectra (Fig. 4(a)), it is noticed that there is a slight shoulder at 286-287 eV (C-N bonding) shown after chitosan modification. By deconvolution, the slight shoulder represents the C-N bonding. From the N1s spectra (Fig. 4(b)), it is obvious that there is no peak around 400 eV for the CMK-3; however, there is an apparent peak observed after chitosan modification. The XPS analysis confirmed the deposition of chitosan on the CMK-3. The surface elemental composition of CMK-3 carbons is listed in Table 2. The surface nitrogen content of the C-Chi and C-Chi-b determined from XPS analysis increased from the trivial value of the pristine CMK-3 to 1.58 and 1.76 wt%, respectively. It is noted that nitrogen element of C-Chi and C-Chi-b is obviously greater than that of CMK-3, indicating chitosan indeed immobilized on the carbonaceous material. According to the study of Lawrie *et al*. (2007), the N1s spectra can be deconvoluted by curve fitting for three peaks: at 399.4 eV (amine), at 400.5 eV (amide), and at 401.4 eV (protonated amine). The relative content of surface functional groups deconvoluted from XPS N1s spectra is also listed in Table 2.
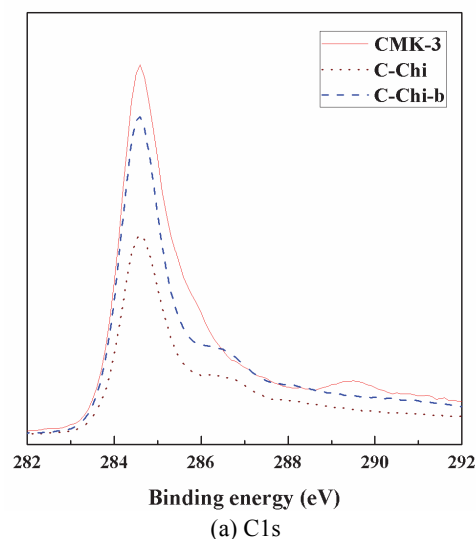
(a) C1s
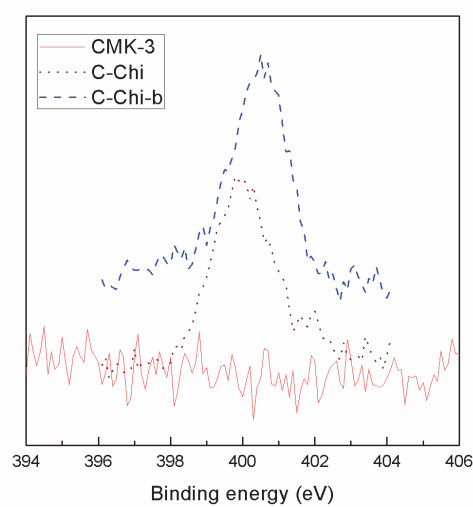
(b) N1s

Fig. 4   XPS spectra of CMK-3 and chitosan modified CMK-3

From Fig. 4(b), it is interesting to note that the main peak shifted from 399.5 eV for C-Chi to 400.5 eV for C-Chi-b, that is, the nitrogen functionality was changed from the amine to the amide group after alkaline solution treatment. As shown in Table 1, the decreases of surface area and pore volume of the C-Chi-b might be caused by the steric hindrance effect of amide group onto the C-Chi-b surface leading to a diminishing of the chance of nitrogen molecules entering into the micropores. In addition, the small shoulder at 401.4 eV of protonated amine for C-Chi disappeared after deprotonation by NaOH (for C-Chi-b).

Table 2   Surface elemental composition of CMK-3 carbons and relative content of surface functional groups determined from XPS N1s spectra

Samples	Elemental composition (wt%)				Surface concentration from N 1s spectra (at. %):		
	C	O	N	Si	Amine (399.4 eV)	Amide (400.5 eV)	Protonated amine (401.4 eV)
CMK-3	82.5	11.6	0.3	5.6	-	-	-
C-Chi	82.1	14.2	1.58	2.2	47.4	47.6	5.0
C-Chi-b	85.8	11.5	1.76	0.9	9.7	90.2	0.1

3.2 Hydrogen Adsorption Capacity

The hydrogen storage capacity of the CMK-3 at 77, 90, and 195K under 0.1 MPa are shown in Fig. 5. The hydrogen adsorption capacity decreases along with the increase of temperature which implies the physisorption process. To quantitatively evaluate the interation of the CMK-3 with hydrogen molecules, the isosteric heat of hydrogen adsorption was calculated by fitting 77, 90 and 195K isotherms to the Clausius-Clapeyron equation (Rouquerol *et al*. 1999). The slope of the plot of ln(p) versus 1/T at a given adsorption coverage gives the isosteric heat of adsorption in the range value 4.9-6.8 kJ/mol, where p is the saturation pressure of adsorption and T is absolute temperature of adsorption. It is noted that the initial isosteric heat of adsorption for CMK-3 is comparable to that of hydrogen physisorption on high surface area activated carbons (Zhou *et al*. 2004).

Table 3 lists the comparison of hydrogen adsorption capacity on various CMK-3s. The hydrogen adsorption capacity on CMK-3 ranged from 0.98 to 1.39 wt% at 77K and 0.1 MPa. The difference might be caused by various texture characteristics and methods of hydrogen uptake measurement. The hydrogen adsorption capacity of this work is comparable to the previous works reported in the literature (Xia *et al*. 2007).
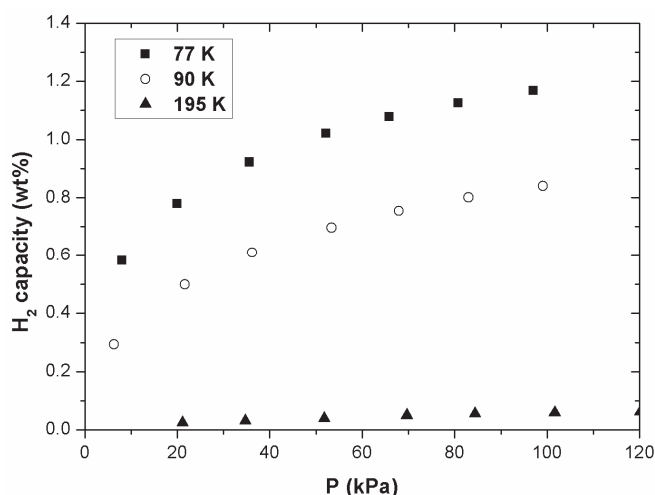

Fig. 5 Hydrogen adsorption isotherms of CMK-3 at 77K, 90K, and 195K

Table 3 Comparison of hydrogen adsorption capacity on various CMK-3s

S_{BET} (m²g⁻¹)	V_t (cm³g⁻¹)	V_{mic} (cm³g⁻¹)	adsorption capacity (wt.%) (temperature, pressure)	References
825	1.36	0.21	2.3 (77 K, 3 MPa)	Giraudet and Zhu, 2011
852	–	–	1.03 (77 K, 0.1MPa)	Jiang *et al*. 2010
984	1.09	0.37	0.98 (77 K, 0.1MPa)	Xia *et al*. 2007
1301	1.16	0.19	1.39 (77 K, 0.1MPa)	Kockrick *et al*. 2010
1323	1.10	0.25	2.2 (77 K, 1Mpa)	Juarez *et al*. 2017
1330	1.084	0.013	1.24 (77 K, 0.1MPa)	Giraudet *et al*. 2010
1339	1.73	0.47	1.17 (77 K, 0.095MPa)	This work

Figure 6 illustrates hydrogen storage capacities of CMK-3 and chitosan modified CMK-3 at 77K and under 0.1 MPa. It is found that the hydrogen storage capacity of both C-Chi and C-Chi-b is almost the same as that of CMK-3 at lower pressure (< 0.03 MPa) due to part of the pores of CMK-3 blocked by chitosan. However, the hydrogen storage capacity of C-Chi is larger than that of the pristine CMK-3 by about 10% at 0.1 MPa. As aforementioned, the hydrogen storage data are high reproducible (the measurement error < 1.5%). Therefore, the storage capacity difference between on the C-Chi and the CMK-3 samples is significant. It is well known that the key factors governing the hydrogen storage capacity of carbonanceous materials at cryogenic temperature are specific surface and micropore volume (Xia *et al*. 2007, Kockrick *et al*. 2010). The specific surface areas and the micropore volumes of C-Chi decreased after immersion of chitosan, however, the hydrogen storage capacity was enhanced. The surface chemistry should be considered as an important factor too. As above discussion on the XPS analysis, the nitrogen atomic concentrations of the C-Chi and C-Chi-b increased from the trivial value of pristine CMK-3 to 1.58 and 1.76 wt%, respectively. The enhancement of hydrogen storage capacity might be attributed to the addition of amine and amide groups on the surface of the C-Chi and C-Chi-b. Zheng *et al*. (2010) presumed that the doped heterogeneous nitrogen atoms into carbonaceous materials increase the adsorption heat of hydrogen which improves the hydrogen storage capacity. Giraudet *et al*. (2010) synthesized CMK-3 and enriched with nitrogen by exposing it to a flow of pure ammonia at different temperatures (400, 550, 700°C). The nitrogen contents determined by XPS were 1.2, 2.3, and 3.9 wt%, respectively. They obtained hydrogen capacity at 77K and 0.1 MPa increased about 8.9% for the CMK-3 doped with 2.3 wt% nitrogen. In summary, our experimental results show that a small amount of nitrogen content can increase the hydrogen storage capacity of carbonaceous materials. Furthermore, the hydrogen uptake on the C-Chi-b is slightly lower than that on the C-Chi can be attributed to the lower specific surface area.

Figure 7 presents hydrogen storage capacities of CMK-3 and ammonia modified CMK-3 at 77K and upto 100 kPa. The hydrogen storage capacity increases along with pressure. The hydrogen storage capacities of all ammonia modified CMK-3s are almost the same as that of CMK-3 at lower pressure (< 0.02 MPa).
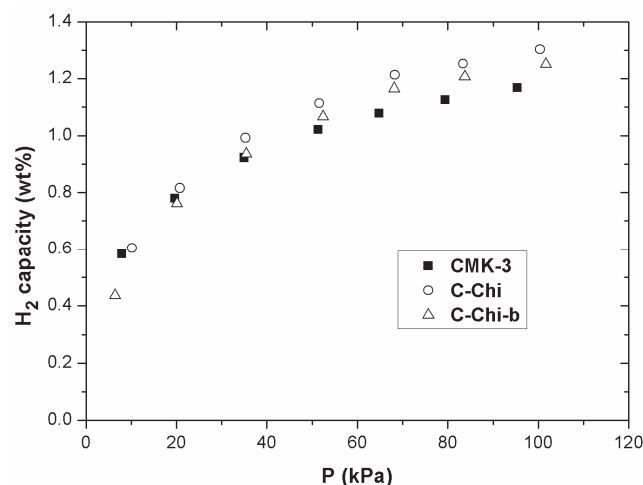

Fig. 6 Hydrogen storage capacities of CMK-3 and chitosan modified CMK-3 at 77K
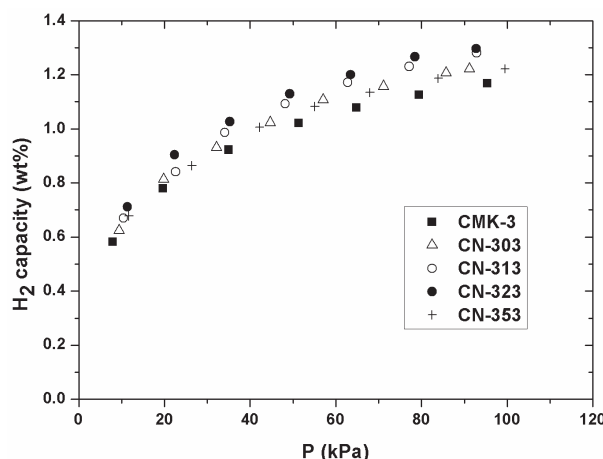
Fig. 7   Hydrogen storage capacities of CMK-3 and ammonia modified CMK-3 at 77K

At pressure of 100 kPa, however, the hydrogen storage capacity of CN-323 is larger than that of the pristine CMK-3 by about 10 %. Hydrogen storage capacity of ammonia-modified CMK-3 increases as the modification temperature increases. However, the hydrogen storage capacity of CN-353 is lower than that of CN-323. It is well known that the amount of hydrogen adsorbed on the porous carbon material depends on the pore characteristics (such as specific surface area, pore size, etc.) and the surface functional groups of the carbon material (Armandi *et al.* 2008; Giraudet and Zhu 2011; Wang *et al.* 2009). The effect of immersion temperature on hydrogen sorption onto ammonia-modified CMK-3 will be discussed in the next paragraph.

Figure 8 depicts the immersion temperature effect on hydrogen capacity, amount of basic groups, and BET surface area of ammonia modification CMK-3. The amount of basic functional groups on ammonia modified CMK-3 increased with increasing immersion temperatures. However, the basic groups were significantly reduced when the immersion temperature raised to 353K, the reason could be attributed to the emission of ammonia vapor at higher temperatures. It is noted that the initial boiling point of ammonia solution is 311K. When the temperature is higher than the initial boiling point, the ammonia vapor continuously evaporates from the aqu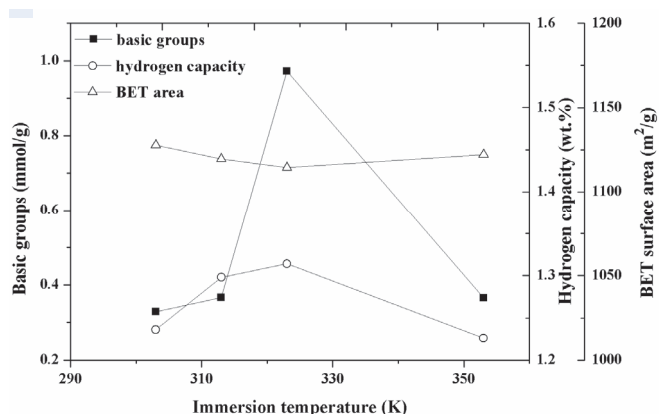eous solution. The ammonia in the aqueous solution decreases and its boiling point gradually rises until 373K. When CMK-3 is immersed in ammonia solution at 353K for 24 h, the ammonia in the aqueous solution has been greatly reduced because the temperature is much higher than its initial boiling point, and therefore the basic functional groups of the CN-353 is significantly reduced. The BET surface areas of the CMK-3 slightly decreased after ammonia modification. The hydrogen capacity of ammonia modified CMK-3 is higher than that of the pristine one. The CN-323 possesses the highest hydrogen capacity as well as the largest amount of basic functional groups. The experimental results showed that nitrogen-containing basic functional groups are favorable to adsorption of hydrogen.

4.   CONCLUSIONS

In this study, we have investigated the texture characteristics as well as hydrogen storage capacities of the ordered mesoporous carbon CMK-3 modified with chitosan or ammonia aqueous solution. Though the surface areas and pore volumes were decreased after 6.0 wt.% of chitosan deposition, hydrogen storage capacity increased about 10% from 1.17 wt.% to 1.29 wt.% at 77K and 0.1 MPa. This can be attributed to amine and amide functional groups existing on the surface of C-Chi and C-Chi-b. It is also noticeable that hydrogen storage capacity of the ammonia modified CMK-3 enhanced by about 10%. Experimental results confirmed that nitrogen-containing functional groups of porous carbonaceous materials enhanced the hydrogen storage capacity.

REFERENCES

Armandi, M., Bonelli, B., Karaindrou, E.I., Otero Arean, C., and Garrone, E. (2008). "Post-synthesis modifications of SBA-15 carbon replicas: Improving hydrogen storage by increasing microporous volume." *Catalysis Today*, **138**, 244-248.

Bharat, L., Komarneni, S.N., and Katsuki, H. (2002). "Rapid synthesis of mesoporous SBA-15 molecular sieve by a microwave–hydrothermal process." *Chemical Communications*, **23**, 89-90.

Biniak, S., Szymanski, G., Siediewski, J., and Swiatkowski, A. (1997). "The characterization of activated carbons with oxygen and nitrogen surface groups." *Carbon*, **35**, 1799-1810.

Biniwalea, R.B., Rayalua, S., Devottaa, S., and Ichikawa, M. (2008). "Chemical hydrides: A solution to high capacity hydrogen storage and supply." *International Journal Hydrogen Energy*, **33**, 360-365.

Boehm, H.P. (1994). "Some aspects of the surface chemistry of carbon blacks and other carbons." *Carbon*, **32**(5), 759-769.

Chareonpanich, M., Nantangern, A., and Limtrakul, J. (2007). "Short-period synthesis of ordered mesoporous silica SBA-15 using ultrasonic technique." *Materials Letters*, **61**, 5153-5156.

Chen, C.-H. and Huang, C.-C. (2007). "Hydrogen storage by KOH-modified multi-walled carbon nanotubes." *International Journal Hydrogen Energy*, **32**, 237-246.

Giraudet, S. and Zhu, Z. (2011). "Hydrogen adsorption in nitrogen enriched ordered mesoporous carbons doped with nickel nanoparticles." *Carbon*, **49**, 398-405.

Fig. 8   Effect immersion temperature on hydrogen capacity, amount of basic groups, and BET surface area of CMK-3 modified by ammonia aqueous solution

Giraudet, S., Zhu, Z., Yao, X., and Lu, G. (2010). "Ordered mesoporous carbons enriched with nitrogen: Application to hydrogen storage." *Journal Physical Chemistry C*, **114**, 8639-8645.

Guo, H. and Gao, Q. (2010)**. "**Cryogenic hydrogen uptake of high surface area porous carbon materials activated by potassium hydroxide." *International Journal Hydrogen Energy*, **35**, 7547-7554.

Huacai, G., Wan, P., and Dengke, L. (2006). "Graft copolymerization of chitosan with acrylic acid under microwave irradiation and its water absorbency." *Carbohydrate Polymers*, **66**(3), 372-378.

Huang, C.-C., Chen, H.-M., and Chen, C.-H. (2010). "Hydrogen adsorption on modified activated carbon." *International Journal Hydrogen Energy*, **35**, 2777-2780.

Huang, C.-C. and Shen, S.-C. (2012). "Adsorption of CO_2 on chitosan modified CMK-3 at ambient temperature." *Journal of the Taiwan Institute of Chemical Engineers*, **44**(1), 89-94.

Huang, Z., Cuevas, F., Liu, X., Jiang, L., Wang, S., Latroche, M., and Du, J. (2009). "Effects of Si addition on the microstructure and the hydrogen storage properties of $Ti_{26.5}V_{45}Fe_{8.5}Cr_{20}Ce_{0.5}$ BCC solid solution alloys." *International Journal Hydrogen Energy*, **34**, 9385-9392.

Jansen, R.J.J., and van Bekkum, H. (1994). "Amination and ammoxidation of activated carbons." *Carbon*, **32**(8), 1507-1516.

Jiang, J., Gao, Q., Zheng, Z., Xia, K., and Hu, J. (2010). "Enhanced room temperature hydrogen storage capacity of hollow nitrogen-containing carbon spheres." *International Journal Hydrogen Energy*, **35**, 210-216.

Juárez, J.M., Ledesma, B.C., Costa, M.G., and Beltramone, A.R. (2017). "Novel preparation of CMK-3 nanostructured material modified with titania applied in hydrogen uptake and storage." *Microporous and Mesoporous Materials*, **254**, 146-152.

Kockrick, E., Schrage, C., Borchardt, L., Klein, N., Rose, M., Senkovska, I., and Kaskel, S. (2010). "Ordered mesoporous carbide derived carbons for high pressure gas storage." *Carbon*, **48**, 1707-1717.

Kojima, Y., Suzuki, K., Fukumoto, K., Kawai, Y., Kimbara, M., Nakanishi, H., and Matsumoto, S. (2004). "Development of 10 kW-scale hydrogen generator using chemical hydride." *Journal Power Sources*, **125**, 22-26.

Lachawiec, Jr. A.J., DiRaimondo, T.R., and Yang, R.T. (2008). "A robust volumetric apparatus and method for measuring high pressure hydrogen storage properties of nanostructured materials." *Review Scientific Instruments*, **79**, 063906-12.

Lawrie, G., Keen, I., Drew, B., Chandler-Temple, A., Rintol, L., Fredericks, P., and GrØndahl, L. (2007). "Interactions between alginate and chitosan biopolymers characterized using FTI and XPS." *Biomacromolecules*, **8**, 2533-2541.

Lázaro, M.J., Calvillo, L., Bordejé, E.G., Moliner, R., Juan, R., and Ruiz, C.R. (2007). "Functionalization of ordered mesoporous carbons synthesized with SBA-15 silica as template." *Microporous and Mesoporous Materials*, **103**, 158-165.

Rouquerol, F., Rouquerol, J., and Sing, K. (1999). *Adsorption by Powders and Porous Solids: Principles, Methodology and Applications*, Academic Press, London.

Ryoo, R., Joo, S.H., and Jun, S. (1999). "Synthesis of highly ordered carbon molecular sieves via template-mediated structural transformation," *Journal Physical Chemistry B*, **103,** 7743-7746.

Satyapal, S., Petrovic, J., Read, C., Thomas, G., and Ordaz, G. (2007). "The US department of energy's national hydrogen storage project: progress towards meeting hydrogen-powered vehicle requirements." *Catalysis Today*, **120**, 246-256.

Shafeeyan, M.S., Daud, W.M.A.W, Houshmand, A., and Shamiri, A. (2010). "A review on surface modification of activated carbon for carbon dioxide." *Journal of Analytical and Applied Pyrolysis*, **89**, 143-151.

Ströbel, R., Garche, J., Moseley, P.T., Jörissen, L., and Wolf, G. (2006). "Hydrogen storage by carbon materials." *Journal Power Sources*, **159**, 781-801.

Wang, L., Yang, F.H., and Yang, R.T. (2009). "Hydrogen storage properties of B- and N-doped microporous carbon." *American Institute of Chemical Engineer Journal*, **55**(7), 1823-1833.

Xia, K., Gao, Q., Wu, C., Song, S., and Ruan, M. (2007). "Activation, characterization and hydrogen storage properties of the mesoporous carbon CMK-3." Carbon, **45**, 1989-1996.

Yang, Z., Xia, Y., Sun, X., and Mokaya, R. (2006). "Preparation and hydrogen storage properties of zeolite-templated carbon materials nanocast via chemical vapor deposition: Effect of the zeolite template and nitrogen doping." *Journal Physical Chemistry B*, **110,** 18424-18431.

Yoo, J.H., Shi, G., Park, C.N., Kim, W.B., and Cho, S.W. (2009). Influence of Mn or Mn plus Fe on the hydrogen storage properties of the Ti-Cr-V alloy, International Journal Hydrogen Energy **34**, 9116-9121.

Yürüm, Y., Taralp, A., and Veziroglu, T.N. (2009). "Storage of hydrogen in nanostructured carbon materials." *International Journal Hydrogen Energy*, **34**, 3784-3798.

Zheng, Z., Gao, Q., and Jiang, J. (2010). "High hydrogen uptake capacity of mesoporous nitrogen-doped carbons activated using potassium hydroxide." *Carbon*, **48**, 2968-2973.

Zhou, L., Zhou, Y., and Sun, Y. (2004). "A comparative study of hydrogen adsorption on superactivated carbon versus carbon nanotubes." *International Journal Hydrogen Energy*, **29**, 475-479.