



Synthesis of mesoporous carbon material by hard template method a comparative study of SBA-15 and MCF as templates

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ABSTRACT

Ordered mesoporous carbons (OMC) have been synthesized using mesoporous silica of SBA-15 (Santa Barbara Acid-15) and MCF (Mesoporous cellular foam) as hard templates. The synthesized carbon materials were characterized by different techniques such as the powder X-ray diffraction, transmission electron microscopy, N₂ adsorption–desorption measurements. From obtained results, it revealed that the average pore width of OMC(MCF) samples (5.7 nm) was higher than that of OMC(SBA-15) samples (4.5 nm). OMC samples also exhibited high Methylene Blue (MB) adsorption capacity with Q_{max} of 385 mg/g for OMC(SBA-15) and 625 mg/g for OMC(MCF). The mesoporous silica template allows controlling the textural properties, providing new possibilities for many applications in adsorption and catalysis.

Introduction

Porous carbon materials [1, 2, 3] have a great scientific and technologic importance thanks to their unique properties (high adsorption capacity of atoms, ions, molecules and supramolecules, high chemical and thermal stability, etc.). They are widely used in many applications such as gas separation [4], adsorbent [5, 6, 7, 8], gas storage [9], catalysis [10], electrochemical energy storage [11].... Most porous carbons have a high specific surface area with main contribution of large amount of micropores and mesopores, are usually obtained via carbonization carbon precursor. Porous

carbons are synthesized by hard – templating method using nanostructured silica as template to impregnate with an appropriate carbon source, followed by carbonization of the composite, and subsequent removal of the template [12].

In this paper, we report the synthesis of OMCs using hard template method with a comparative study of SBA-15 and MCF as templates. To the best of our knowledge, this is the first study about this comparison in MB adsorption capacities of OMC(SBA-15) and OMC(MCF) samples.

Experimental

Synthesis of OMC

SBA-15, MCF silica were synthesized with a triblock copolymer, EO₂₀PO₇₀EO₂₀ (Pluronic P123, Aldrich), as the surfactant, and liquid glass as the silica source. OMC(SBA-15) and OMC(MCF) were synthesized by calcinations of SBA-15 or MCF impregnated with an aqueous solution of carbon sources with sulfuric acid. Typically, 1g of sucrose was mixed with 1g SBA-15 or MCF and then added to a solution obtained by dissolving 0.14g of H₂SO₄ in 5g of H₂O. The mixture was placed in a drying oven for 6h at 100°C, and subsequently the oven temperature was increased to 160°C and maintained there for 6h. The sample turned dark brown or black during the treatment in the oven. We repeated this step at 100 and 160°C using the same oven after the addition of 1 g of carbon, 0.14 g of H₂SO₄, and 5g of H₂O. The carbonization was completed by pyrolysis with heating at typically 800°C under nitrogen flow. The carbon-silica composite obtained after pyrolysis was immersed in HF 40% solution and then washed with H₂O before being washed with a mixture of 50 vol% ethanol + 50 vol% H₂O. The final product was dried at 100°C for 3h.

Characterization.

The powder X-ray diffraction (XRD) patterns of the samples were recorded on a Shimadzu XRD-6100 analyzer with Cu K α radiation ($\lambda = 1.5417\text{\AA}$). Transmission electron microscopy (TEM) was recorded using JEOL1010 instrument operating at 80 kV with a magnification of 25,000 – 100,000. The surface area of samples was determined on Quantachrome Instruments version 3.0 at 77K and

using nitrogen as an adsorbent.

Results and discussion

X-Ray Diffraction (XRD)

XRD patterns of SBA-15, OMC(SBA-15), MCF and OMC(MCF) samples are showed in figure 1. From XRD patterns of SBA-15, it showed that three well-resolved XRD peaks, which are assigned to the (100), (110) and (200) reflections characteristic of the 2D hexagonal space group p6mm, in the case of OMC(SBA-15), only an intense peak assigned to (100) reflection was observed. This results confirmed OMC(SBA-15) had same the structure with SBA-15. From XRD patterns of MCF and OMC(MCF), it showed that OMC(MCF) had the same structure with MCF.

Transmission Electron Microscopy (TEM)

TEM images of OMC(SBA-15) and OMC(MCF) samples are compared in figure 2. As shown in figure 2, the ordered structures of OMC(SBA-15) and OMC(MCF) samples with hexagonal symmetry and uniform pore dimension were clearly observed. The mean pore sizes of OMC(MCF) are larger than that of OMC(SBA-15).

N₂ Adsorption–Desorption Isotherms (BET)

N₂ adsorption–desorption isotherms and pore-size distribution of OMC(SBA-15) and OMC(MCF) are presented in figure 3. As observed in figure 3, both OMC(SBA-15) and OMC(MCF) showed the isotherm curves of type IV with the hysteresis loop, characteristic for capillary condensation which is typical for mesoporous material.

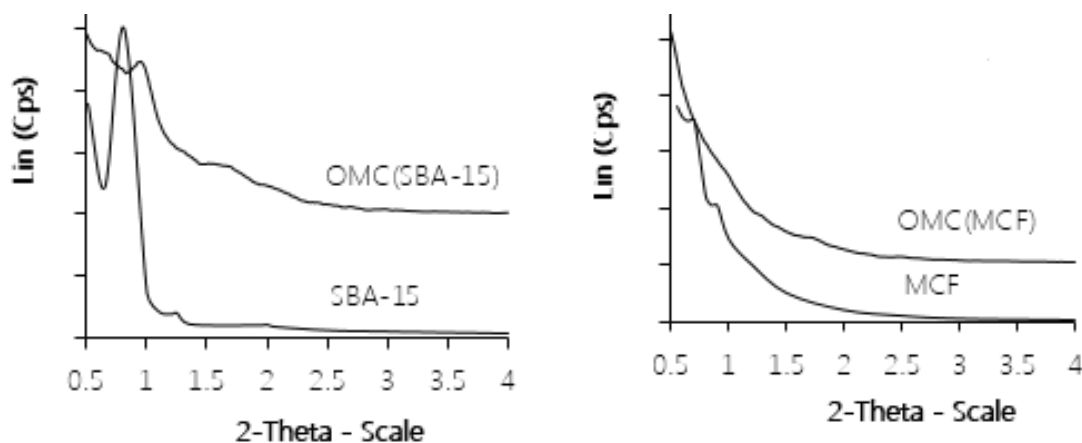


Fig 1. XRD patterns of SBA-15, OMC(SBA-15), MCF and OMC(MCF)

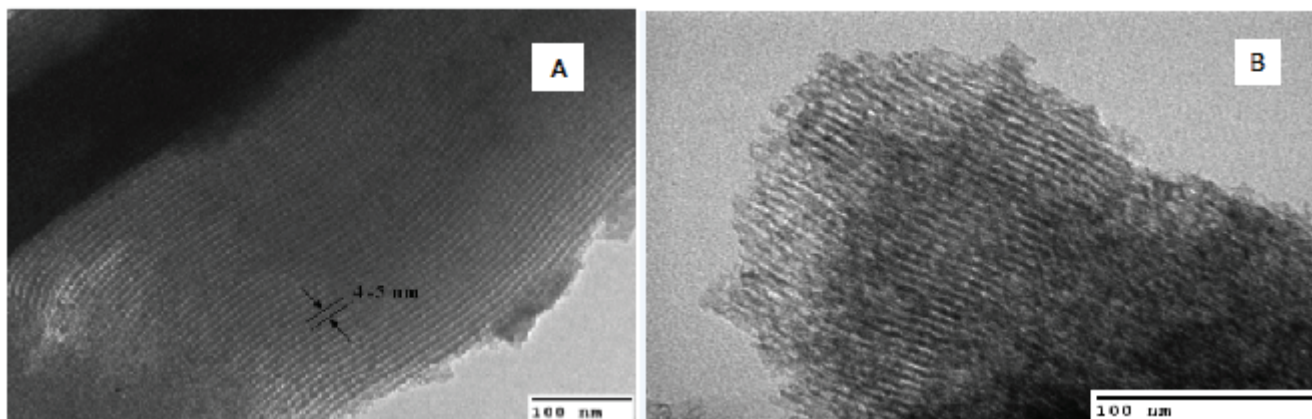
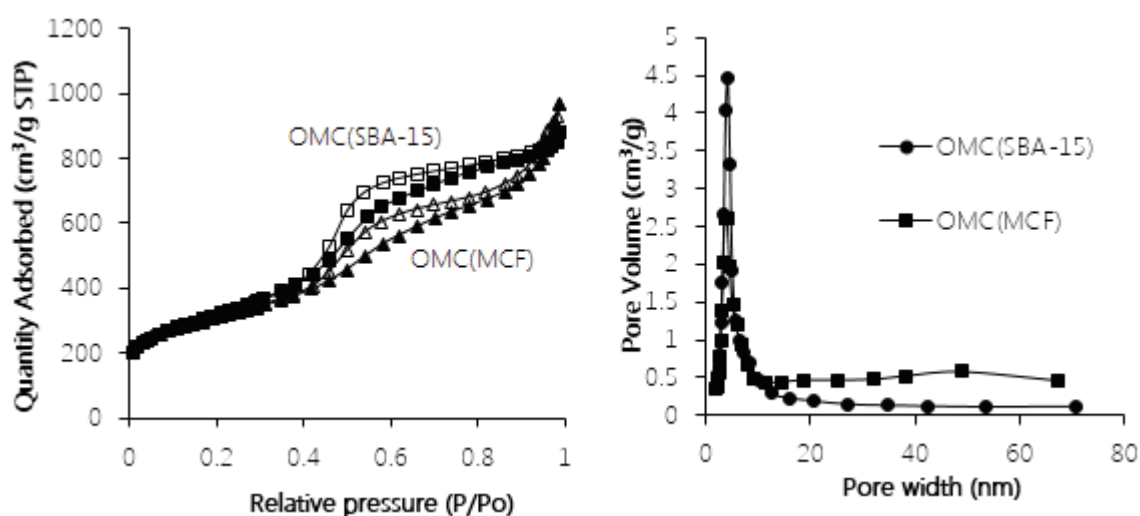


Fig 2. TEM images of OMC(SBA-15) and OMC(MCF)

Fig 3. N₂ adsorption-desorption isotherms (a) and pore-size distribution (b) of OMC(SBA-15) and OMC(MCF)

Textural properties of samples are shown in table 1. As observed in table 1, both OMC(SBA-15) and OMC(MCF) exhibited high surface areas. However, the pore size of OMC(MCF) is larger than that of OMC(SBA-15). Thus, surface area of OMC(SBA-15) (1,126 m²/g) is higher than that of OMC(MCF) (1,073 m²/g). The pore size of OMC(SBA-15) is distributed with the average pore width of 4.5 nm while pore size of OMC(MCF) is distributed with the average pore width of 5.7 nm. These results can explain that, OMC(SBA-15) was formed based on SBA-15. The pore size of SBA-15 is 6.5 nm. Opposite this, OMC(MCF) was formed base on MCF (Pore size of MCF is 16.9 nm), this is reason pore size of OMC(MCF) is bigger than that of OMC(SBA-15).

Table 1. Textural properties of samples

Sample	Textural properties		
	Average pore width (nm)	Pore volume (cm ³ /g)	Surface area (m ² /g)
OMC(SBA-15)	4.5	1.25	1,126
OMC(MCF)	5.7	1.35	1,073

OMC(MCF) exhibited high surface areas. However, the pore size of OMC(MCF) is larger than that of Methylene blue adsorption isotherms MB adsorption capacities of OMC(SBA-15) and OMC(MCF) are given in table 2. MB adsorption capacities of OMC(SBA-15) and OMC(MCF)

were very high with Q_{max} of 385 mg/g (mg methylene blue/g adsorbent) for OMC(SBA-15) and 625 mg/g for OMC(MCF). This can be explained that the average pore width and the pore volume of OMC(MCF) (5.7 nm and 1.35 cm^3/g) is greater than that of OMC(MCF) with the size ranging from 5.7 nm to 50 nm is wider than that of OMC(SBA-15). The pore volume of SBA-15 (4.5nm and 1.25 cm^3/g). In addition, Fig. 3b showed

that the pore-size distribution of OMC OMC(MCF) is 1.1 times higher that of OMC(SBA-15). The pore-size of OMC(MCF) is not significantly different from the pore-size of OMC(SBA-15). In addition, MB is adsorbed on OMC(MCF) and OMC(SBA-15) by electrostatic force. This is process of multi-layered physical adsorption. That is why the MB adsorption capacity OMC(MCF) is higher than of OMC(SBA-15).

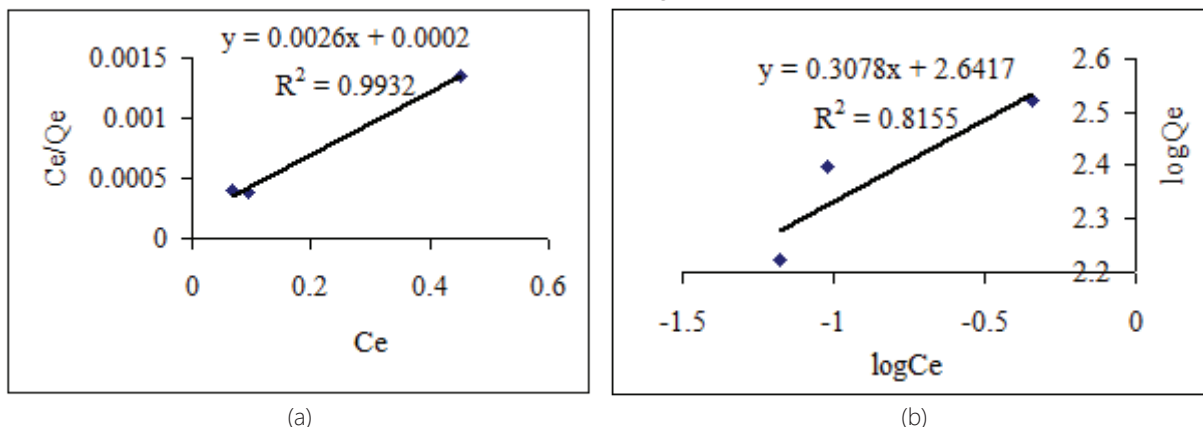


Fig 4. Experimental adsorption data fitted to different isotherm models (a) Langmuir and (b) Freundlich of OMC(SBA-15).

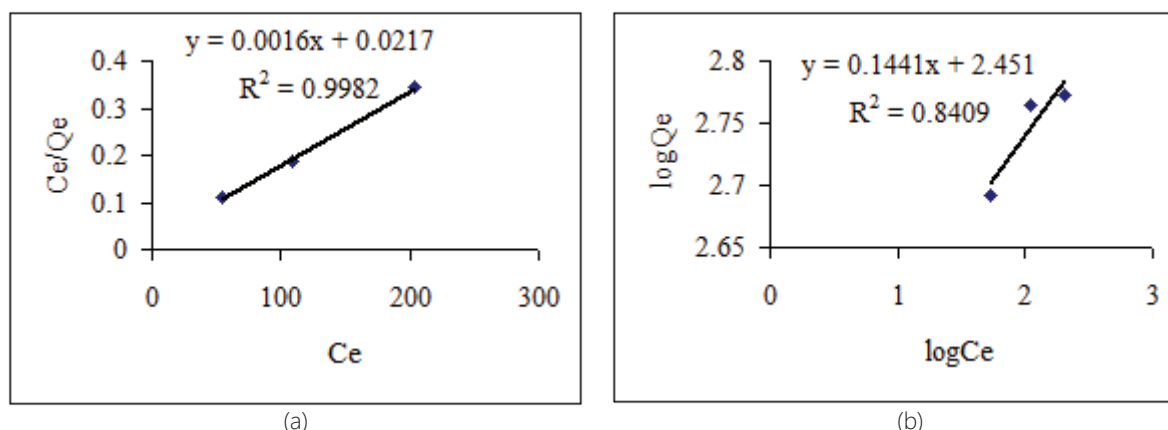


Fig 5. Experimental adsorption data fitted to different isotherm models (a) Langmuir and (b) Freundlich of OMC(MCF).

Langmuir and Freundlich isotherm constants of OMC (SBA-15)			
Langmuir isotherm		Freundlich isotherm	
Q_o ($mg \cdot g^{-1}$)	385	n	26
K_L ($L \cdot mg^{-1}$)	13	K_F [$(mg \cdot g^{-1})(mg^{-1})^{1/n}$]	438
R^2	0.993	R^2	0.815
Langmuir and Freundlich isotherm constants of OMC (MCF)			
Q_o ($mg \cdot g^{-1}$)	625	n	6.9
K_L ($L \cdot mg^{-1}$)	0.07	K_F [$(mg \cdot g^{-1})(mg^{-1})^{1/n}$]	1.76
R^2	0.998	R^2	0.841

Table 2. Langmuir and Freundlich isotherm constants of OMC(SBA-15) and OMC(MCF)

As observed in finger 4, 5 and table 2, the value of $R^2 = 0.993$ and 0.998 for Langmuir model with OMC(SBA-15) and OMC(MCF) is higher than that of $R^2 = 0.815$ and 0.841 for Freundlich model with OMC(SBA-15) and OMC(MCF), respectively. The results indicated that the Langmuir model fits much better than the Freundlich model for both samples.

Conclusion

Ordered mesoporous carbons were successful synthesized by using hard template methods. From XRD, TEM

and N₂ adsorption–desorption measurements results, it revealed that the obtained OMCs showed high surface area (>1000 m²/g) with uniform pores and large pore size (> 4 nm). Moreover, OMC(MCF) samples had bigger pore size than OMC(SBA-15). Thus, OMC(MCF) samples exhibited high MB adsorption capacity with Q_{max} of 625 mg/g bigger than OMC(SBA-15) with Q_{max} of 385 mg/g. The mesoporous silica template allows controlling the pore diameters and pore volume, leading the change of adsorption capacity of OMC.

References

1. Shinae Jun, Sang Hoon Joo, Ryong Ryoo, Michal Kruk, Mietek Jaroniec, Zheng Liu, Tetsu Ohsuna, Osamu Terasaki, Synthesis of New, Nanoporous Carbon with Hexagonally Ordered Mesostucture, *J. Am. Chem. Soc.* 122 (2000) 10712-10713.
2. Deicy Barrera, Mara Dávila, Valeria Cornette, J.C. Alexandre de Oliveira, Raúl H. López, Karim Sapag, Pore size distribution of ordered nanostructured carbon CMK-3 by means of experimental techniques and Monte Carlo simulations, *Microporous and Mesoporous Materials* 180 (2013) 71–78.
3. Enterria M., F. Suárez-García, A. Martínez-Alonso, JMD Tascon, Synthesis of ordered micro-mesoporous carbons by activation of SBA-15 carbon replicas, *Microporous and Mesoporous Materials*, 151 (2012) 390-396.
4. Farzin Nejad N, E. Shams, MK Amini, JC Bennett, Ordered mesoporous carbon CMK-5 as a potential sorbent for fuel desulfurization: Application to the removal of dibenzothiophene and comparison with CMK-3, *Microporous and Mesoporous Materials*, 168 (2013) 239- 246.
5. Yin Li, Bin Yuan, Jie Fu, Shuguang Deng, Xiuyang Lu, Adsorption of alkaloids on ordered mesoporous carbon, *Journal of Colloid and Interface Science*, 408 (2013) 181–190.
6. Jinghuan Chen, Feifei Cao, Songze Chen, Mingjiang Ni, Xiang Gao, Kefa Cen, Adsorption kinetics of NO on ordered mesoporous carbon (OMC) and cerium-containing OMC (Ce-OMC), *Applied Surface Science*, 317 (2014) 26–34.
7. Zeinab Ezzeddine, Isabelle Batonneau-Gener, Yannick Pouilloux, Hussein Hamad, Removal of methylene blue by mesoporous CMK-3: Kinetics, isotherms and thermodynamics, *Journal of Molecular Liquids* 223 (2016) 763–770.
8. Wannes Libbrecht, An Verberckmoes, Joris W. Thybaut, Pascal Van Der Voort, Jeriffa De Clercq, Soft templated mesoporous carbons: Tuning the porosity for the adsorption of large organic pollutants, *Carbon* 116 (2017) 528-546.
9. Chen-Chia Huang, Yi-Hua Li, Yen-Wen Wang, Chien-Hung Chen, Hydrogen storage in ordered mesoporous cobalt-embedded carbon, *International journal of hydrogen energy*, 38 (2013) 3994-4002.
10. Chi-Yeong Ahn, Jae-Yeong Cheon, Sang-Hoon Joob, Junbom Kim, Effects of ionomer content on Pt catalyst / ordered mesoporous carbon support in polymer electrolyte membrane fuel cells, *Journal of Power Sources*, 222 (2013) 477 - 482
11. Fu Ruo-wen, Li Zheng-hui, Liang Ye-ru, Li Feng, Xu Fei, Wu Ding-cai, Hierarchical Porous carbons: design, preparation, and performance in energy storage, *New Carbon Materials*, 26 (2011) 171-179.
12. Ryong Ryoo, Sang Hoon Joo, Michal Kruk and Mietek Jaroniec, Ordered Mesoporous Carbons, *Adv. Mater*, 13 (2001) 677 - 681.