

REFERENCES

- [1] Peters EC, Svec F, Fréchet JMJ. Rigid macroporous polymer monoliths. Adv Mater 11 (1999): 1169-1181.
- [2] Svec F, Huber CG. Monolith materials; promises, challenges, achievements. Anal Chem 1 (2006): 2101-2107.
- [3] Leinweber FC, Tallarck U. Chromatographic performance of monolithic and particulate stationary phase: hydrodynamic and adsorption capacity. J Chromatogr A 1006 (2003): 207-228.
- [4] Ishizuka N, Minakuchi H, Nakanishi K, Soga N, Tanaka N. Designing monolithic double-pore silica for high-speed liquid chromatography. J Chromatogr A 797 (1998): 133-137.
- [5] Mihelič I, Nemeč D, Podgornik A, Koloini T. Pressure drop in CIM disk monolithic column. J Chromatogr A 1065 (2005): 59-67.
- [6] Kato M, Inuzuka K, Sakai-Kato K, Toyooka T. Monolithic bioreactor immobilization trypsin for high-throughput analysis. Anal Chem 77 (2005): 1813-1818.
- [7] Nakanishi K, Minakuchi H, Soga N. Double pore silica gel monolith applied to liquid chromatography. J Sol-Gel Sci Techn 8 (1997): 547-552.
- [8] Ikegami T, Tanaka N. Monolithic columns for high-efficiency HPLC separations. Curr Opin Chem Biol 8 (2004): 527-533.
- [9] Fuchigami T, Toki M, Nakanishi K. Membrane emulsification using sol-gel derived macroporous silica glass. J Sol-Gel Sci Techn 19 (2000): 337-341.
- [10] Chen SX, Zhang X, Shen PK. Macroporous conducting matrix: Fabrication and application as electrocatalyst support. Electrochem Commun 8 (2006): 713-719.
- [11] Klodzińska E, Moravcova D, Jandera P, Buszewski B. Monolithic continuous beds as a new generation of stationary phase for chromatographic and electro-driven separations. J Chromatogr A 1109 (2006): 51-59.

- [12] Podgornik A, Jančar J, Merhar M, Kozamernik S, Glover D, Čuček K, et al. Large-scale methacrylate monolithic columns: design and properties. J Biochem Bioph Meth 60 (2004): 179-189.
- [13] Zhou X, Xue B, Bai S, Sun Y. Macroporous polymeric ion exchanger of high capacity for protein adsorption. Biochem Eng J 11 (2002): 13-17.
- [14] Eeltink S, Herrero-Martinez JM, Rozing GP, Schoenmakers PJ, Kok WT. Tailoring the morphology of methacrylate ester-based monoliths for optimum efficiency in liquid chromatography. Anal Chem 77 (2005): 7342-7347.
- [15] Nakanishi K, Takahashi R, Nagakane T, Kitayama K, Koheiya N, Shikata H, et al. Formation of Hierarchical Pore Structure in Silica Gel. J Sol-Gel Sci Techn 17 (2000): 191-210.
- [16] Konishi J, Fujita K, Nakanishi K, Hirao K. Phase-separation-induced titania monoliths with well-defined macropores and mesostructured framework from colloid-derived sol-gel systems. Chem Mater 18 (2006): 864-866.
- [17] Nakanishi K. Sol-gel process of oxides accompanied by phase separation. Bull Chem Soc Jpn 79 (2006): 673-691.
- [18] Hanai T. Separation of polar compounds using carbon columns. J Chromatogr A 989 (2003): 183-196.
- [19] Williams JL. Monolith structures, materials, properties and uses. Catal Today 69 (2001):3-9.
- [20] Liang C, Dai S, Guiochon G. A graphitized-carbon monolithic column. Anal Chem 75 (2003): 4904-4912.
- [21] Shi ZG, Feng YQ, Xu L, Da SL, Zhang M. A template method to control the shape and porosity of carbon materials. Carbon 42 (2004): 1677-1682.
- [22] Lu AH, Smått JH, Backlund S, Lindén M. Easy and flexible preparation of nanocasted carbon monoliths exhibiting a multimodal hierarchical porosity. Micropor Mesopor Mat 72 (2004): 59-65.
- [23] Wang X, Bozhilov KN, Feng P. Facile preparation of hierarchically porous carbon monoliths with well-ordered mesostructures. Chem Mater 18 (2006): 6373-6381.
- [24] Taguchi A, Smått JH, Lindén M. Carbon monoliths processing a hierarchical, fully interconnected porosity. Adv Mater 15 (2003): 1209-1211.

- [25] Yuan ZY, Su BL. Insights into hierarchically meso-macroporous structured materials. *J Mater Chem* 16 (2006): 663-667.
- [26] Yang T, Lua AC. Characteristics of activated carbons prepared from pistachio-nut shells by physical activation. *J Colloid Interf Sci* 267 (2003): 408-417.
- [27] Maria JH, Katarzyna K. Comparison of molecular sieve properties in microporous chars from low-rank bituminous coal activated by steam and carbon dioxide. *Carbon* 43 (2005): 944-953.
- [28] Hayashi J, Kazehaya A, Muroyama K, Watkinson AP. Preparation of activated carbon from lignin by chemical activation. *Carbon* 38 (2000): 1873-1878.
- [29] Okada K, Yamamoto N, Kameshima Y, Yasumori A. Porous properties of activated carbons from waste newspaper prepared by chemical and physical activation. *J Colloid Interf Sci* 262 (2003): 179-193.
- [30] Miyamoto J, Kanoh H, Kaneko K. The addition of mesoporosity to activated carbon fibers by a simple reactivation process. *Carbon* 43 (2005): 855-894.
- [31] Lei S, Miyamoto J, Kanoh H, Nakahigashi Y, Kaneko K. Enhancement of the methylene blue adsorption rate for ultramicroporous carbon fiber by addition of mesopores. *Carbon* 44 (2006): 1884-1890.
- [32] Lauterborn W, Schmitz E, Judt A. Experimental approach to a complex acoustic system. *Int J Bifurcat Chaos* 3 (1993): 635-642.
- [33] Rinkevichius BS, Stepanov AV, Tolkachev AV. Fiber optics LDA and laser knife simultaneous use for flow investigation. In: Groot PJ, editor, *Fifth International Conference on Laser Anemometry: Advances and Applications* Vol 2025, 359-364. New York: SPIE Publishing, 1993.
- [34] Tsochatzidis NA, Guiraud P, Wilhelm AM, Delmas H. Determination of velocity, size and concentration of ultrasonic cavitation bubbles by phase-Doppler technique. *Chem Eng Sci* 56 (2001): 1831-1840.
- [35] Burdin F, Tsochatzidis NA, Guiraud P, Wilhelm AM, Delmas H. Characterization of the acoustic cavitation cloud by two laser techniques. *Ultrason Sonochem* 6 (1999): 43-51.
- [36] Pekala RW. Organic aerogels from the polycondensation of resorcinol with formaldehyde. *J Mater Sci* 24 (1989): 3221-3227.

- [37] Hebalkar N, Arabale G, Sainkar SR, Pradhan SD, Mulla IS, Ayyub P, Kulkarni SK. Study of correlation of structural and surface properties with electrochemical behaviour in carbon aerogels. J Mater Sci 40 (2005): 3777 – 3782.
- [38] Elsayed MA, Hall PJ, Heslop MJ. Preparation and structure characterization of carbons prepared from resorcinol-formaldehyde resin by CO₂ activation. Adsorption 13 (2007): 299 – 306.
- [39] Pasto DJ, Johnson CR. 1969. Organic Structure Determination. New Jersey: Prentice-Hall Englewood Cliff
- [40] Gomez-Serrano V, Pastor-Villegas J, Perez-Florindo A, Duran-Valle C, Valenzuela-Calahorra C. FT-IR study of rockrose and of char and activated carbon. J Anal Appl Pyrol 36 (1996): 71 – 80.
- [41] Zawadzki J. IR spectroscopy in carbon surface chemistry. In: Thrower PA, editor. Chemistry and physics of carbon, vol. 21, 180-200. New York: Dekker, 1989.
- [42] Biniak S, Szymanski G, Siedlewski J, Swiatkowski A. The characterization of activated carbons with oxygen and nitrogen surface groups. Carbon 35 (1997): 1799-810.
- [43] Dollimore D, Heal GR. An improved method for the calculation of pore size distribution from adsorption data. J Appl Chem 14 (1964): 109 – 113.
- [44] Bel Japan Inc. Analysis software user's manual for BELSORP-mini. 9-1, 1-Chome, Haradanaka, Toyonaka-City, Osaka 561-0807 Japan: Bel Japan, Inc, 2007.
- [45] Sing KSW, Gregg SJ. Adsorption, Surface Area and Porosity, 2nd edition. New York :Academic Press. 1982: 287
- [46] Kalderis D, Bethanis S, Paraskeva P, Diamadopoulos E. Production of activated carbon from bagasse and rice husk by a single-stage chemical activation method at low retention times. Bioresource Technol 99 (2008): 6809-6816
- [47] Fuente E., Menéndez J.A., Diez M.A., Suárez D. and Montes-Morán M.A. Infrared spectroscopy of carbon materials: A quantum chemical study of model compounds. J Phys Chem B 107 (2003): 6350 – 6359.

- [48] Buczek B., Biniak S., Świątkowski A. Oxygen distribution within oxidized active carbon granules. Fuel 78 (2008): 1443 - 1448.
- [49] Domingo-García M., López-Garzón F.J. and Pérez-Mendoza M. Effect of some oxidation treatments on the textural characteristics and surface chemical nature of an activated carbon. J. Colloid Interf Sci. 222 (2000):233 - 240.
- [50] Zhou J.H., Sui Z.J., Zhu J., Li P., Chen D., Dai J.H., and Yuan W.K. Characterization of surface oxygen complexes on carbon nanofibers by TPD, XPS and FT-IR. Carbon 45 (2007): 785-796.
- [51] Moreno-Castilla C., Carrasco-Marín F., Maldonado-Hódar F.J. and Rivera-Utrilla J. Effect of non-oxidant and oxidant acid treatments on the surface properties of an activated carbon with very low ash content. Carbon 36 (1998): 145-151.
- [52] Moreno-Castilla C., López-Ramón M.V. and Carrasco-Marín F. Changes in surface chemistry of activated carbons by wet oxidation. Carbon 38 (2000): 1995-2001.
- [53] Boehm, H.P. Surface oxides on carbon and their analysis: a critical assessment. Carbon 40 (2002): 145-149.
- [54] Gomez-Serrano V., Pastor-Villegas J., Perez-Florindo C., Duran-Valle C. and Valenzuela-Calahorro C. FT-IR study of rock rose and of char and activated carbon. J. Anal. Appl. Pyrol 36 (1996): 71-80.
- [55] López-Garzón F.J., Domingo-García M., Pérez-mendoza M., Alvarez P.M. and Gómez-Serrano V. Textural and chemical surface modifications produced by some oxidation treatments of a glassy carbon. Langmuir 19 (2003): 2838-2844.
- [56] Burg P, Cagniant D. 2007. Characterization of carbon surface chemistry. edited by Radovic LA, Chemistry and physics of carbon Vol. 30, 150 -153. New York: CRS Press,
- [57] Fanning, P.E. and Vannice, M.A. A DRIFTS study of the formation of surface groups on carbon by oxidation. Carbon 31 (1993): 721-730.
- [58] Pekala RW. Organic aerogels from the polycondensation of resorcinol with formaldehyde. J Mater Sci 24 (1989): 3221 - 3227.

- [59] Ruben GC, Pekala RW, Tillotson TM, Hrubesh LW. Imaging aerogels at the molecular level. *J Mater Sci* 27 (1992): 4341-4349.
- [60] Gebert MS, Pekala RW. Fluorescence and light-scattering studies of sol-gel reactions. *Chem Mater* 6 (1994): 220 – 226.
- [61] Al-Muhtaseb SA, Ritter JA. Preparation and properties of resorcinol-formaldehyde organic and carbon gels. *Adv Mater* 15 (2003): 101 – 114.
- [62] Yamamoto T, Mukai SR, Endo A, Nakaiwa M, Tamon H. Interpretation of structure formation during the sol-gel transition of a resorcinol-formaldehyde solution by population balance. *J Colloid Interf Sci* 264 (2003): 532 – 537.
- [63] Yamamoto T, Yoshida T, Suzuki T, Mukai SR, Tamon H. Dynamic and Static Light Scattering Study on the Sol-Gel Transition of Resorcinol-Formaldehyde Aqueous Solution. *J Colloid Interf Sci* 245 (2002): 391 - 396.
- [64] Gavalda S, Kaneko K, Thomson KT, Gubbins KE. Molecular modeling of carbon aerogels. *Colloids and Surface A: Physicochemical and Engineering Aspects* 187 (2001): 531 – 538.
- [65] Tamon H. and Ishizaka H. SAXs study on gelation process in preparation of resorcinol-formaldehyde aerogel. *J Colloid Interf Sci* 206 (1998): 577 – 582.
- [66] Petrićević R, Reichenauer G, Bock V, Emmerling A, Fricke J. Structure of carbon aerogels near the gelation limit of the resorcinol-formaldehyde precursor. *J Non-Cryst Solids* 225 (1996): 41 – 45.
- [67] Durairaj RB. 2005. Resorcinol: Chemistry, Technology and Applications. Germany: Springer Berlin Heidelberg,
- [68] Marsh H, Rodríguez-Reinoso F. 2006. Activated Carbon. United States: Elsevier,
- [69] Rodríguez-Reinoso F. Plenary lecture: the role of carbon materials in heterogeneous catalysis. *Carbon* 36 (1998): 159 – 157.
- [70] Hassler JW. 1974. Purification with activated carbon: industrial, commercial and environmental. New York: Chemical Pu. Co,
- [71] Mohamed F Sh, Khater WA, Mostafa MR. Characterization and sorptive properties of carbon activated by sulphuric acid. *Chem Eng J* 116 (2006): 47-52.

- [72] Molina-Sabio M, Rodríguez-Reinoso F. Textural and chemical characterization of microporous carbons. Adv Colloid Interfac 76-77 (1998): 271-294.

APPENDIX

PUBLICATIONS FROM THIS DISERTATION

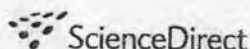
1. **Adisak Siyasukh**, Patompong Maneeprom, Siriporn Larпкиattaworn, Nattaporn Tonanon, Wiwut Tanthapanichakoon, Hajime Tamon, Tawatchai Charinpanitkul. *Preparation of a carbon monolith with hierarchical porous structure by ultrasonic irradiation followed by carbonization, physical and chemical activation*. Carbon 46 (10), 2008: 1309-1315. (I.F. in 2007; 4.260)
2. Nattaporn Tonanon, **Adisak Siyasukh**, Yunyong Wareenin, Tawatchai Charinpanitkul, Wiwut Tanthapanichakoon, Hiroto Nishihara, Shin R. Mukai, Hajime Tamon. *3D interconnected macroporous carbon monoliths prepared by ultrasonic irradiation*. Carbon 43 (13) 2005: p.2808-2811. (I.F. in 2005; 3.419)
3. Nattaporn Tonanon, Yunyong Wareenin, **Adisak Siyasukh**, Wiwut Tanthapanichakoon, Hiroto Nishihara, Shin R. Mukai, H. Tamon. *Preparation of resorcinol formaldehyde (RF) carbon gels: Use of ultrasonic irradiation followed by microwave drying*. Journal of Non-Crystalline Solids 352 (52-54), 2006: 5683-5686. (I.F. in 2006; 1.362)

INTERNATIONAL PROCEEDING

1. Patompong Maneeprom, Ukrit Kijchareanchai, **Adisak Siyasukh**, Siriporn Larпкиattaworn, Tawatchai Charinpanitkul, Nattaporn Tonanon. The generation of micropore and/or mesopore on 3D – interconnected macroporous carbon monolith by physical activation. Proceedings of Regional Symposium on Chemical Engineering 13th, pp. 99-100. December 3 – 5, 2006, Singapore, 2006.

CONFERENCE

1. **Adisak Siyasukh**, Nattaporn Tonanon, Tawatchai Charinpanitkul, Wiwut Tanthapanichakoon. *Macroporous monolith gels and carbons synthesizing by sol-gel polycondensation with ultrasonic irradiation* / Oral presentation / NSTDA Annual Conference 2007 (NAC2007) / NSTDA/ 29 Mar 2007, Bangkok, Thailand

available at www.sciencedirect.comjournal homepage: www.elsevier.com/locate/carbon

Preparation of a carbon monolith with hierarchical porous structure by ultrasonic irradiation followed by carbonization, physical and chemical activation

Adisak Siyasukh^a, Patompong Maneeprom^a, Siriporn Larpkittaworn^d,
Nattaporn Tonanon^{a,*}, Wiwut Tanthapanichakoon^b, Hajime Tamon^c,
Tawatchai Charinpanitkul^a

^aDepartment of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand

^bNational Nanotechnology Center, 111 Thailand Science Park, Klong Luang, Pathumthani 12120, Thailand

^cDepartment of Chemical Engineering, Kyoto University, Katsura, Kyoto 615-8510, Japan

^dThailand Institute of Scientific and Technological Research, 196 Phahonyothin Road, Chatuchak, Bangkok 10900, Thailand

ARTICLE INFO

Article history:

Received 18 March 2008

Accepted 8 May 2008

Available online 16 May 2008

ABSTRACT

A two-step direct and simple method for the preparation of a hierarchical porous carbon monolith with micropores, mesopores and macropores is described. The two stages give more flexibility in the preparation of a porous carbon monolith. In step I a macroporous interconnected carbon monolith is prepared by ultrasonic irradiation during sol-gel polycondensation. The effects of sol-gel temperature, catalyst concentration and ultrasonic power on the structure of the monolith are investigated. In step II, mesopores are induced in the monolith by $\text{Ca}(\text{NO}_3)_2$ impregnation followed by CO_2 activation. The effect of activation temperature is also studied. A hierarchical interconnected carbon monolith with mean pore size diameter of 1.2 μm , BET surface area of 624 m^2/g , mesopore volume of 0.38 cm^3/g and micropore volume of 0.22 cm^3/g has been obtained from $\text{Ca}(\text{NO}_3)_2$ impregnation of the macroporous carbon monolith followed by CO_2 activation at 850 $^\circ\text{C}$.

© 2008 Published by Elsevier Ltd.

1. Introduction

A hierarchical porous material has an interesting structure which contains the combination pores of micropore or mesopore throughout a macroporous monolith. The macropore structure allows fluid flow under low back pressure and high convective mass transfer, which is an explanation for high column efficiency and high-speed separation under continuous flow conditions [1–5]. Therefore, the hierarchical porous monolith has a great potential for many applications such as enzyme immobilization for high-throughput bioreactor [6], HPLC monolithic column for high-speed separation [7,8], membrane emulsification [9], electro catalyst support [10]

etc. Furthermore, one good example in the application of the hierarchical porous monolith is to use this material for a capillary column which is suitable for sample analysis in a very small amount [11].

Most hierarchical porous monoliths are generally produced from two main materials; one is an organic polymer [1,2–14] and the other is an inorganic polymer [15–17]. However, there are some limitations of the both materials. An organic polymer exhibits insufficient mechanical strength, especially for swollen polymer gels, while an inorganic polymer cannot resist strong acidic and alkaline conditions [18,20]. Regarding these drawbacks, the hierarchical porous carbon monolith is considered as a promising alternative. The hierarchical porous

* Corresponding author. Fax: +66 2 218 6877.

E-mail address: nattaporn.t@chula.ac.th (N. Tonanon).

0008-6223/\$ - see front matter © 2008 Published by Elsevier Ltd.
doi:10.1016/j.carbon.2008.05.006

carbon monolith has an interesting structure which can be fitted in any applications of activated carbon [19] such as air and water purification, adsorption, separation and catalyst support. The hierarchical porous carbon monolith can usually be produced through polymerization or sol-gel processes of various polymeric materials, such as resorcinol-formaldehyde gel [20,21], polymer of sucrose [22], furfuryl alcohol [23,24] etc., with template replication of, for instance, hierarchical porous silica monolith [20,22,23], suspension of silica beads [21], powdery silica [24] and so on [25], and followed by carbonization under inert gas. Hence, the pores structure and macroscopic shape of the carbon monoliths are determined by the morphology of these templates. In addition, this preparation method is quite complicate because removing the templates from carbon skeleton is needed.

In this work, the complete preparation of the hierarchical interconnected porous carbon monolith without using any template is introduced. This method is a simple and direct way to produce tailor-made carbon monolith via 2 steps individually, step I to design and control the interconnected macroporous structure of the carbon monolith and step II to develop and control micropores and/or mesopores within the internal structure of the interconnected macroporous carbon monolith. The preparation of macroporous carbon monolith has been reported for the first time in our previous work [26] that an irradiation of high intensity ultrasonic wave into the RF solution during sol-gel process under suitable condition could generate the network of macropores in the obtained RF monolithic gel. Step II, $\text{Ca}(\text{NO}_3)_2$ -impregnation followed by CO_2 activation of interconnected macroporous carbon monolith, was used to produce the hierarchical porous carbon monolith. For the control of micropores and/or mesopores in the macroporous carbon monolith, metal-catalyst-loaded and followed by CO_2 activation on macroporous carbon monolith will be applied. The design and control of mesoporosity is very desirable both for the improvement of activated carbon and for the development of its new application fields. Porosity of carbon can be controlled by many factors such as reaction condition, precursor, activation gas and catalyst [27]. Various catalysts such as Fe, Ni and TiO_2 together with activating gas such as CO_2 and steam are used in catalyst activations [28]. There are many studies on the effect of the activating gas (CO_2 and steam) and catalysts. A successful development of mesoporosity is prepared by CO_2 activation of char by using calcium as a catalyst [27]. The effect of temperature and activating gases (CO_2 and steam) on calcium-catalyzed polymer is also studied [29]. Calcium is suitable for both gases used in chemical activation but more efficiency can be found in CO_2 activation. A good distribution of calcium in carbon is another key factor in the promotion of good mesoporosity. From above information and our preliminary activation results, calcium is used as a catalyst for micro-/mesopore generation in this work.

Two separate steps give more flexibility to the tailor-made preparation of the hierarchical porous carbon monolith. The design and control of synthesis in each step can be done more conveniently and effectively. For examples, step I is responsible for the strength, macropore size, macropore size distribution and the pore through properties of macroporous carbon monolith. Individually, step II is responsible for surface area and micro-/mesopore volumes which directly effect adsorp-

tion, separation, catalyst support, and enzyme immobilization applications.

The objectives of this work are (1) to have more investigation on the effects of catalyst concentration, sol-gel ultrasonic irradiation time and ultrasonic power in the preparation of the macroporous carbon monolith and (2) to study the effects of catalyst and activation condition on the generation of meso/micropores on the interconnected macroporous carbon monolith.

2. Experimental

2.1. Synthesis of macroporous carbon monolith precursors

The macroporous carbon precursor, resorcinol-formaldehyde (RF) gel, in a monolithic form was synthesized via irradiation of high intensity ultrasonic wave during gel formation process. At first, the resorcinol ($\text{C}_6\text{H}_4(\text{OH})_2$) (R) (Fluka) was initially dissolved in deionized water, followed by adding sodium carbonate (Na_2CO_3) (C) (Ajax Finechem) as a catalyst and formaldehyde (HCHO) (F) (Ajax Finechem) into the solution, respectively, and the RF solution was obtained by stirring it with magnetic stirrer for 15 min. The molar ratios of resorcinol to formaldehyde, R/F, and resorcinol to catalyst, R/C, were fixed at 0.5 and 800, respectively, with various ratios of catalyst to water, C/W, as shown in Table 1. Next, the RF solution of 10 cm^3 was filled into the ultrasonic reactor glass tube, 2.5 cm in diameter. And then, the RF solution was irradiated by ultrasonic wave, generated from ultrasonic generator (Sonic&Material, VibraCell 120 Model) with titanium alloy transducer probe (20 kHz) at different temperature of sol-gel polycondensation during ultrasonic irradiation. T_{US} and ultrasonic power, P_{US} , as shown in Table 1. The ultrasonic irradiation was stopped when the viscosity of RF solution became high. Then RF solution was transferred into the cylindrical glass tube (inner diameter = 3 mm, length = 40 mm) where RF gel was formed. After that the gel was sealed at the ends of the tube, followed by 3 days for aging in the oven at temperature of 75°C . After aging the gel was moved from the tube and washed by distilled water daily for 3 day, followed by drying with hot air at 75°C until the weight was constant. The interconnected macroporous carbon precursor in a monolithic form was obtained.

2.2. Preparation of micropores with interconnected macropores of carbon monolith

The micropores with interconnected macropores of the carbon monolith were prepared by two methods. The first is the carbonization of the interconnected macroporous carbon precursors with N_2 gas, and the second is from CO_2 activation.

For the carbonization, the carbon precursors were carbonized with N_2 gas flow of 50 cm^3 (at STP)/min in a quartz tube reactor at a heating rate of $10^\circ\text{C}/\text{min}$, until the desired temperature, T_{D} , was reached and followed by maintaining the keeping time for 30 min. The carbon precursors with interconnected macropore in their structure for carbonization with N_2 were synthesized via different factors of C/W (A30, B30, C30 and D30), T_{US} (C20, C25, C30 and C45) and P_{US} (B30 and B30-30W) as shown in the Table 1.

Table 1 – Synthesis condition to prepare the hierarchical porous carbon monoliths

Samples	Conditions of RF monolith synthesis			Conditions of carbon synthesis		
	^a C/W (mol/m ³)	^a T _{US} (°C)	^a P _{US} (Watt)	Carbonization with N ₂		T _D (°C)
				Carbonization with N ₂	Activation with CO ₂ ^d CO ₂ -Ca(NO ₃) ₂	
A30	6	30	22			
B30	8	30	22	Yes		850
C30	10	30	22	Yes		850
D30	15	30	22	Yes		850
^b C45	10	45	22	Yes		850
C25	10	25	22	Yes		850
C20	10	20	22	Yes		850
B30-30W	8	30	30	Yes		850
C30-CO ₂	10	30	22	Yes		850
C30-Ca700	10	30	22		Yes	850
C30-Ca800	10	30	22			850
C30-Ca850	10	30	22		Yes	700
^c C30-Ca900	10	30	22		Yes	800
					Yes	850
					Yes	900

Remarks:

a The abbreviation of C/W, T_{US} and P_{US} are denoted as ratio of catalyst to water, temperature of sol-gel polycondensation during ultrasonic irradiation and ultrasonic power, respectively.

b The interconnected macropore cannot be formed within monolith structure.

c Final form of the carbon monolith is cracked by activation process.

d The RF monolith gel is impregnated with Ca(NO₃)₂ before CO₂-activation.

For the CO₂ activation, the carbon precursor, C30-CO₂, was activation with CO₂ gas flow of 50 cm³ (at STP)/min in a quartz tube reactor at a heating rate of 10 °C/min until the desired temperature, T_D, was reached and followed by maintaining the keeping time for 30 min.

2.3. Development of micropores and mesopores of carbon with impregnation of Ca(NO₃)₂ followed by CO₂ activation

The hierarchical porous carbon monoliths were obtained by an impregnation of the interconnected macroporous carbon precursors with calcium nitrate, Ca(NO₃)₂, followed by CO₂ activation. All of carbon precursors were prepared under the same condition (C/W = 10 mol/m³, T_{US} = 30 °C and P_{US} = 22 W) at different activation temperature, the obtained carbon monolith were C30-Ca700, C30-Ca800, C30-Ca850 and C30-Ca900 as shown in the Table 1. First the carbon precursors were soaked into the solution of 0.4 M Ca(NO₃)₂ for 3 day. After that, the carbon precursors were dried at 75 °C until the weight was constant. Activation was conducted in a quartz tube reactor with CO₂ flow at 50 cm³/min. The reactor was heated at the heating rate of 10 °C/min until the temperature reached the desired temperature, T_D, as shown in Table 1, and then they were kept at this temperature for 30 min.

2.4. Characterization of interconnected carbon monolith

The texture of interconnected pore in monolithic forms of both RF gels and carbons are revealed by scanning electron microscope (JEOL, JSM-6700 F). The macropore size distribution of the macroporous monolithic carbon is obtained by mercury porosimeter (Micromeritics, Pore-Sizer-9320). The micro/meso porosities are obtained from the adsorption and desorption isotherms of N₂ at 77 K measured by adsorption apparatus (BEL, mini-BEL Sorp.). A decrease in weight of the

obtained carbon monoliths, % burn-off, was measured after carbonization and both physical and chemical activations.

3. Results and discussion

3.1. Effects of mol ratio of catalyst to water, temperature of sol-gel polycondensation during ultrasonic irradiation and ultrasonic power on texture of carbon monolith

The effects of mol ratio of catalyst to water (C/W), temperature of sol-gel polycondensation during ultrasonic irradiation (T_{US}) and ultrasonic power (P_{US}) on texture of the carbon monolith were studied. The effect of T_{US} on the interconnected macroporous textures of the carbon monoliths, C20, C25, C30 and C45, is observed by the SEM micrographs in Figs. 1a–d. The SEM micrographs reveal that at the T_{US} of 20, 25 and 30 °C, C20, C25 and C30, respectively, the interconnected macroporous textures of the carbon monoliths are in a range of micrometer, whereas at the T_{US} of 45 °C, C45, the interconnected macroporous texture in a range of micrometer cannot be observed but monolith structure can be formed. Therefore, the suitable T_{US} to the formation of interconnected macroporous carbon monolith is not exceeding of 45 °C. These results correspond with the macropore size distributions as shown in the Fig. 2a. The macropore size distributions of carbon monoliths get narrower when T_{US} increases. The mean macropore diameter (from Table 2) of C20 (T_{US} = 20 °C), C25 (T_{US} = 25 °C) and C30 (T_{US} = 30 °C) are 3.9, 2.3, and 1.4 μm, respectively, as shown in Table 2, while macropores cannot be observed in the sample C45 (T_{US} = 45 °C).

In our previous work [30] the suitable C/W ratio range for the preparation of the interconnected macroporous carbon monolith has not been reported, therefore further investigation on the effect of C/W ratios is conducted in this work. Low C/W ratio (<5 mol/m³) results in aggregating of carbon particles without monolith formation, while the interconnected macroporous

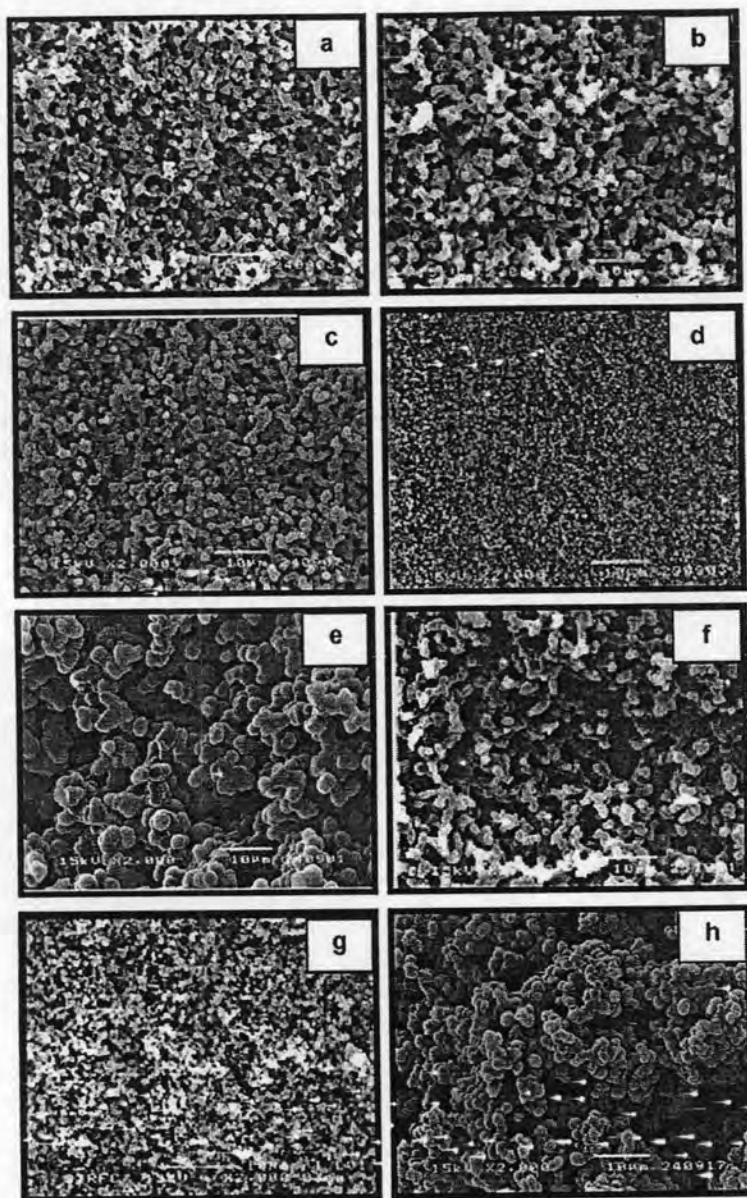


Fig. 1 – SEM images of macropore texture of carbon monoliths: (a) C20, (b) C25, (c) C30, (d) C45, (e) A30, (f) B30, (g) D30 and (h) B30-30W.

structure cannot be formed in the carbon monolith prepared from high C/W ratio ($>15 \text{ mol/m}^3$). They clearly exhibit that the interconnected macroporous texture depends on the starting C/W value. The effect of the starting C/W ratios is studied by SEM, and the micrographs of the interconnected macroporous texture of the carbon monoliths. A30, B30, C30 and D30, are shown in Figs. 1e, f, c and g. The SEM micrographs clearly indi-

cate that an increase in the starting C/W ratio can result in size reduction of the interconnected macropores. The particle size of A30 ($C/W = 6$) is around $4 \mu\text{m}$ which each of the particles appears to be globular and connecting with the others. On the contrary, B30 ($C/W = 8$), C30 ($C/W = 10$) and D30 ($C/W = 15$) exhibit the interconnected macroporous texture, and their macropore sizes tend to decrease with an increase in starting C/W ratios.

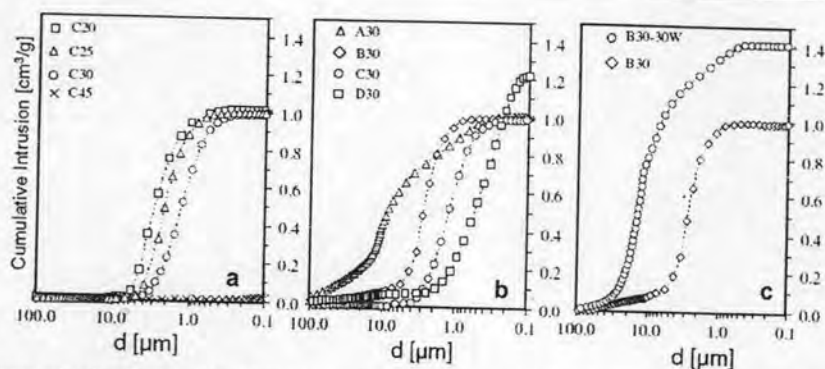


Fig. 2 – Macropore size distributions of macroporous carbon monoliths: (a) effect of T_{US} , (b) effect of C/W and (c) effect of P_{US} .

Table 2 – Macropore diameters of carbon monoliths prepared under various conditions

Samples	Mean pore diameter (μm)
A30	10.7
B30	3.1
C30	1.4
D30	0.3
C20	3.9
C25	2.3
C45	ND
B30-30W	12.1
C30-Ca850	1.2

Remark: ND = not determined.

From Fig. 2b, the interconnected macropore size of the carbon monoliths increase with decreasing starting C/W ratios, corresponding with the SEM micrographs. The mean pore diameters of the macropore in the structure of A30, B30, C30 and D30 listed in Table 2 are 10.7, 3.1, 1.4 and 0.3 μm , respectively.

The effect of P_{US} on the interconnected macroporous texture of the obtained carbon monoliths is shown by SEM micrographs in Figs. 1h and f. As the result, the internal structure of the carbon sample B30-30W ($P_{US} = 30\text{ W}$) exhibits the aggregation of 2 μm size-globular particles. While the carbon sample B30 ($P_{US} = 22\text{ W}$) exhibit the interconnected macropore throughout in its monolithic form. Fig. 2c shows macropore size distribution of these carbon monoliths which indicates that the macropore size distribution of B30-30W is broader than B30. From Table 2, the mean pore diameters are 12.1 and 3.1 μm for the sample B30-30W and B30 respectively. In addition, the macroporous volume of B30-30W (1.4 cm^3/g) is also higher than B30 (1.0 cm^3/g).

3.2. Effects of $\text{Ca}(\text{NO}_3)_2$ impregnation and activation condition on mesoporosity and microporosity of carbon monolith

3.2.1. Effects of $\text{Ca}(\text{NO}_3)_2$ impregnation

The effects of N_2 carbonization, CO_2 activation and $\text{Ca}(\text{NO}_3)_2$ impregnated CO_2 activation on the interconnected macropo-

rous texture and the micro-/mesoporosities of the carbon monolith were studied on C30, C30- CO_2 and C30-Ca850, respectively. The preparation conditions are shown in Table 1.

The SEM micrographs in Figs. 3b and c which show the interconnected macroporous texture in the carbon monoliths of C30-Ca850 (prepared by impregnation of $\text{Ca}(\text{NO}_3)_2$ followed by CO_2 activation) and C30 (prepared by carbonization with N_2), respectively suggest that the interconnected macroporous texture of the carbon monolith can be maintained in both samples. The macropore size distributions of both samples, as shown in Fig. 3a-outset, are slightly different. In addition, the macropore volume of C30-Ca850 is smaller than C30.

From the isotherms of C30 and C30- CO_2 as shown in Fig. 3a-inset and Fig. 4, respectively, they are classified by IUPAC as type I which means that these samples have only the micropore on the macroporous wall of its monolithic structure. Whereas the isotherm of C30-Ca850, shown in Fig. 3a-inset, exhibits in combination forms of type I and type IV and includes the hysteresis loop as type H3 which indicates that the sample has micropore, slit-pore shape of mesopore and not well-defined mesopore size distribution [31]. According to Table 3, it suggests that there are only microporous structure on C30 and C30- CO_2 (micropore volume, V_{mic} = 0.20 and 0.23 cm^3/g , respectively) while the mesoporous and microporous structure appear on C30-Ca850 (mesopore volume, V_{mes} = 0.38 cm^3/g and micropore volume, V_{mic} = 0.22 cm^3/g). The BET specific surface area, S_{BET} , of C30-Ca850 (624 m^2/g) is much larger than C30 (423 m^2/g) as a result of additional mesopores. In order to % burn-off for C30, C30- CO_2 and C30-Ca850 are 54%, 55% and 71%, respectively. These values of % burn-off correspond with the development of micro- and mesoporosity of the carbon monoliths.

These results indicate that the micropores on the interconnected macroporous carbon monolith can be created by either N_2 carbonization or CO_2 activation at 850 $^\circ\text{C}$, whereas the presence of $\text{Ca}(\text{NO}_3)_2$ in the structure of the RF monolith gel is needed to generate mesopores on the interconnected macroporous carbon monolith.

3.2.2. Effects of activation condition

Fig. 4 shows the N_2 adsorption-desorption isotherms at 77 K on the carbon monoliths which obtained from RF monolith

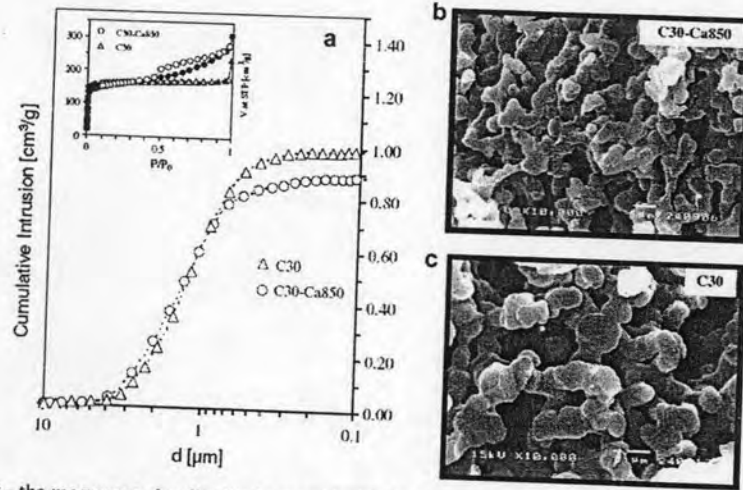


Fig. 3 - (a) Outset - the macropore size distributions and inside the N_2 adsorption-desorption isotherms, (b) and (c) SEM images showing the macroporous texture of the carbon monolith samples C30 and C30-Ca850.

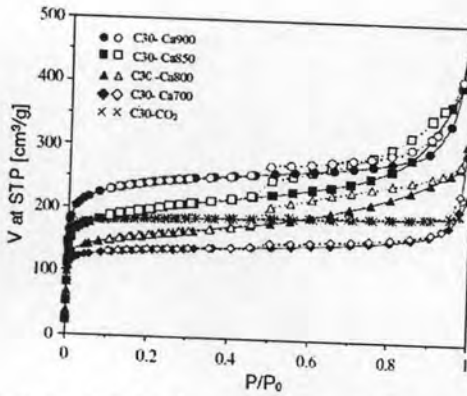


Fig. 4 - N_2 adsorption-desorption isotherm at 77 K on macroporous carbon monoliths prepared via $Ca(NO_3)_2$ -impregnation followed by CO_2 activation.

gels activation with $Ca(NO_3)_2$ -impregnation in their structure and the subsequent activation with CO_2 for 30 min under different activating temperatures, T_D . The activated carbon monoliths are C30-Ca700, C30-Ca800, C30-Ca850 and C30-Ca900 with the T_D of 700, 800, 850 and 900 °C, respectively, as shown in Table 1. C30-Ca800, C30-Ca850 and C30-Ca900 show combination forms of type I and type IV isotherms, while C30-700 exhibits type I isotherm. The V_{mes} of the samples C30-Ca800, C30-Ca850 and C30-Ca900 are 0.25, 0.38 and 0.27 cm^3/g , respectively. These results indicate that mesopores can be generated on the macroporous carbon monolith when the T_D is higher than 800 °C. However when the T_D reaches 900 °C, carbon monolith cannot be obtained by cracking. Table 3 shows that V_{mic} of C30-Ca700, C30-Ca800, C30-Ca850 and C30-Ca900 are 0.16, 0.19, 0.22 and 0.34 cm^3/g , respectively. These results indicate that the micropore volume is increase with increasing T_D . From % burn-off of C30-Ca700, C30-Ca800, C30-Ca850 and C30-Ca900 are 51%, 65%, 71% and 78%, respectively. The result suggests the development of micropores and mesopores of the obtained carbon monoliths. However, it is generally difficult to control microporosity by changing activation temperature.

Table 3 - Porous properties of the macroporous carbon monoliths prepared by various activation methods

samples	% burn-off	Type of isotherm	Pore volume (cm^3/g)		S_{BET} (m^2/g)	Final form
			V_{micro}	V_{meso}		
C30	54	I	0.2	ND	423	Monolith
C30- CO_2	55	I	0.23	ND	474	Monolith
C30-Ca700	51	I	0.16	ND	352	Monolith
C30-Ca800	65	IV+I	0.19	0.25	457	Monolith
C30-Ca850	71	IV+I	0.22	0.38	624	Monolith
C30-Ca900	78	IV+I	0.34	0.27	739	Cracking

Remark: ND = not determined.

4. Conclusions

In this work, the hierarchical carbon monolith (3 mm × 40 mm) successfully prepared by two separating steps, has $S_{\text{BET}} = 624 \text{ (m}^2/\text{g)}$, $V_{\text{micro}} = 0.22 \text{ (cm}^3/\text{g)}$, $V_{\text{mes}} = 0.38 \text{ (cm}^3/\text{g)}$ with macropore mean diameter = 1.2 μm. Step I is important for pore through property and strength of macroporous carbon monolith. The macropore size of the carbon monoliths increases with decreasing C/W ratios. Higher ultrasonic power leads to broader macropore size distribution, larger mean pore diameter and larger macropore volume of interconnected carbon monolith while Step II plays crucial role on surface properties such as surface area and pore volume. In Step II, mesopore can be successfully generated on macroporous interconnected carbon monolith by $\text{Ca(NO}_3)_2$ -impregnation and CO_2 activation. The suitable activation temperatures, T_D , are 800 °C or higher whereas cracking of carbon monolith occurs at 900 °C.

Acknowledgements

This work has been partially supported by the Thailand Graduate Institute of Science and Technology (TGIST)/NSTDA and the 90th Anniversary of Chulalongkorn University Fund (Ratchadaphiseksomphot Endowment Fund).

REFERENCES

- [1] Peters EC, Svec F, Fréchet JM. Rigid macroporous polymer monoliths. *Adv Mater* 1999;11(14):1169–81.
- [2] Svec F, Huber CG. Monolith materials; promises, challenges, achievements. *Anal Chem* 2006;1:2101–7.
- [3] Leinweber FC, Tallarek U. Chromatographic performance of monolithic and particulate stationary phase: hydrodynamic and adsorption capacity. *J Chromatogr A* 2003;1006(1–2):207–28.
- [4] Ishizuka N, Minakuchi H, Nakanishi K, Soga N, Tanaka N. Designing monolithic double-pore silica for high-speed liquid chromatography. *J Chromatogr A* 1998;797(1–2):133–7.
- [5] Mihelič I, Nemeč D, Podgoršek A, Koloini T. Pressure drop in CIM disk monolithic column. *J Chromatogr A* 2005;1065(1):59–67.
- [6] Kato M, Inazuka K, Sakai-Kato K, Toyooka T. Monolithic bioreactor immobilization trypsin for high-throughput analysis. *Anal Chem* 2005;77(6):1813–8.
- [7] Nakanishi K, Minakuchi H, Soga N. Double pore silica gel monolith: applied to liquid chromatography. *J Sol-Gel Sci Technol* 1997;8:547–52.
- [8] Ikegami T, Tanaka N. Monolithic columns for high-efficiency HPLC separations. *Curr Opin Chem Biol* 2004;8:527–33.
- [9] Fuchigami T, Toki M, Nakanishi K. Membrane emulsification using sol-gel derived macroporous silica glass. *J Sol-Gel Sci Technol* 2000;19:337–41.
- [10] Chen SX, Zhang X, Shen PK. Macroporous conducting matrix: fabrication and application as electrocatalyst support. *Electron Commun* 2006;8:713–9.
- [11] Klodzińska E, Moravcova D, Jandera P, Buszewski B. Monolithic continuous beds as a new generation of stationary phase for chromatographic and electro-driven separations. *J Chromatogr A* 2006;1109(1):51–9.
- [12] Podgoršek A, Jančar J, Merhar M, Kozamernik S, Glover D, Čuček K, et al. Large-scale methacrylate monolithic columns: design and properties. *J Biochem Biophys Meth* 2004;60:179–89.
- [13] Zhou X, Xue B, Bai S, Sun Y. Macroporous polymeric ion exchanger of high capacity for protein adsorption. *Biochem Eng J* 2002;11:13–7.
- [14] Eeltink S, Herrero-Martínez JM, Rozing GP, Schoenmakers PJ, Kok WT. Tailoring the morphology of methacrylate ester-based monoliths for optimum efficiency in liquid chromatography. *Anal Chem* 2005;77:7342–7.
- [15] Nakanishi K, Takahashi R, Nagakane T, Kitayama K, Koheiya N, Shikata H. Formation of hierarchical pore structure in silica gel. *J Sol-Gel Sci Technol* 2000;17:191–210.
- [16] Konishi J, Fujita K, Nakanishi K, Hirao K. Phase-separation-induced titania monoliths with well-defined macropores and mesostructured framework from colloid-derived sol-gel systems. *Chem Mater* 2006;18:864–6.
- [17] Nakanishi K. Sol-gel process of oxides accompanied by phase separation. *Bull Chem Soc Jpn* 2006;79(5):673–91.
- [18] Hanai T. Separation of polar compounds using carbon columns. *J Chromatogr A* 2003;989(1):183–96.
- [19] Williams JL. Monolith structures, materials, properties and uses. *Catal Today* 2001;69(1):3–9.
- [20] Liang C, Dai S, Guiochon G. A graphitized-carbon monolithic column. *Anal Chem* 2003;75:4904–12.
- [21] Shi ZG, Feng YQ, Xu L, Da SL, Zhang M. A template method to control the shape and porosity of carbon materials. *Carbon* 2004;42(8–9):1677–82.
- [22] Lu AH, Småt JH, Backlund S, Lindén M. Easy flexible preparation of nanocasted carbon monoliths exhibiting a multimodal hierarchical porosity. *Micropor Mesopor Mater* 2004;72:59–65.
- [23] Wang X, Bozhilov KN, Feng P. Facile preparation of hierarchically porous carbon monoliths with well-ordered mesostructures. *Chem Mater* 2006;18:6373–81.
- [24] Taguchi A, Småt JH, Lindén M. Carbon monoliths processing a hierarchical, fully interconnected porosity. *Adv Mater* 2003;15(4):1209–11.
- [25] Yuan ZY, Su BL. Insights into hierarchically meso-macroporous structured materials. *J Mater Chem* 2006;16:663–7.
- [26] Tonanon N, Siyasukh A, Wareenin Y, Charinpanitkul T, Tanthapanichakoon W, Nishihara H, et al. 3D interconnected macroporous carbon monoliths prepared by ultrasonic irradiation. *Carbon* 2005;43(13):2808–11.
- [27] Cazorla-Amorós D, Ribes-Pérez DDM, C.Román-Martínez, Linares-Solano A. Selective porosity development by calcium-catalyzed carbon gasification. *Carbon* 1996;34(7):869–78.
- [28] Kyotani T. Control of pore structure in carbon. *Carbon* 2003;38(2):209–86.
- [29] Salinas-Martínez de Lecea C, Almela-Alarch M, Linares-Solano A. Calcium-catalysed carbon gasification in CO_2 and steam. *Fuel* 1990;69(1):21–7.
- [30] Tonanon N, Siyasukh A, Tanthapanichakoon W, Nishihara H, Mukai SR, Tamon H. Improvement of mesoporosity of carbon cryogels by ultrasonic irradiation. *Carbon* 2005;43(3):525–31.
- [31] Sing SW, Gregg SJ. Adsorption, surface area and porosity. 2nd ed. New York: Academic Press; 1982. p. 287.

Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Carbon 43 (2005) 2808–2813

CARBON

www.elsevier.com/locate/carbon

3D interconnected macroporous carbon monoliths prepared by ultrasonic irradiation

Nattaporn Tonanon ^{a,*}, Adisak Siyasukh ^a, Yunyong Wareenin ^a,
Tawatchai Charinpanitkul ^a, Wiwut Tanthapanichakoon ^b, Hiroto Nishihara ^c,
Shin R. Mukai ^c, Hajime Tamon ^c

^a Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand

^b National Nanotechnology Center, 111 Thailand Science Park, Klong Luang, Pathumthani 12120, Thailand

^c Department of Chemical Engineering, Graduate School of Engineering, Kyoto University, Katsura, Kyoto 615-8510, Japan

Received 4 February 2005; accepted 26 May 2005

Available online 11 July 2005

Abstract

A new method in preparation of 3D interconnected macroporous carbon monolith has been introduced. Ultrasonic irradiation (ultrasonic intensity 78 W/cm²) and low catalyst concentration (C/W = 10 mol/m³) of RF solution are used as an interesting and unique preparation method for 3D interconnected macroporous sonogel (gel irradiated by ultrasound at gelation stage) and/or 3D interconnected macroporous carbon monolith without using templates.
© 2005 Elsevier Ltd. All rights reserved.

Keywords: Porous carbon; Pyrolysis Adsorption; Scanning electron microscopy; Porosity

Macroporous monolith is an interesting structure that has interconnected skeletons in a single column, and this unique structure allows flow paths (through-pores) through the monolithic columns [1,2]. Carbon monolith has high potential to be good candidates for applications such as columns for chromatography, catalyst supports, adsorbents and porous electrodes under continuous flow conditions. Macroporous carbon monoliths are mostly prepared by using carbon precursors and macroscopic shape templates [3–7]. In general, macroscopic shape templates are interconnected skeleton such as silica template, zeolite, stable emulsions, polymer latex and the interstitial volume of other porous structures. Carbon precursors are polymeric materials or precursor of polymeric materials such as sucrose

some thermoplastics, phenolic resin, copolymerization of resorcinol Fe(II) complex [2] and other thermosetting. There are some reports on macroporous carbon aerogels prepared by using metal catalyst [8] or acid catalyst [9].

In this work, a new method in preparation of 3D interconnected macroporous carbon monolith has been introduced. In general, ultrasonic irradiation has outstanding effects in many chemical reactions such as increasing reaction rates and yields of products, shortening reaction time, altering the reaction path and making milder reaction conditions possible [10,11]. An interesting role of ultrasonic irradiation on mesoporous properties of RF carbon gel when the ratio of catalyst to water C/W or pH is high was also reported [10]. To the best of our knowledge, this study is the first to report on the work of ultrasonic irradiation (ultrasonic intensity 78 W/cm²) together with low catalyst concentration (C/W = 10 mol/m³) of RF solution as an interesting

* Corresponding author. Tel.: +66 2 218 6865; fax: +66 2 218 6877.
E-mail address: nattaporn.t@chula.ac.th (N. Tonanon).

and unique preparation method for 3D interconnected macroporous sonogel (gel irradiated by ultrasound at gelation stage) and/or carbon monoliths without using templates.

Macroporous sonogel monolith, precursors for macroporous carbon monolith, were prepared from resorcinol–formaldehyde (RF) solutions which were composed of resorcinol ($C_6H_4(OH)_2$) (R), formaldehyde (HCHO) (F), sodium carbonate (Na_2CO_3) (C) and distilled water (W). All chemicals were research grades from Wako Pure Chemical Industries. Na_2CO_3 and distilled water were used as a basic catalyst and a diluent respectively. The ratios of resorcinol to formaldehyde (R/F), resorcinol to water (R/W) and catalyst to water (C/W) were fixed at 0.5 mol/mol, 8100 mol/m³ and 10 mol/m³ respectively. Gelation temperature was 308 K. Ultrasonic wave was applied into RF solution right from the start by Vibra Cell model VC 130 (frequency 20 kHz) with a titanium alloy transducer at intensity 78 W/cm². When it was close to the gelation time, the ultrasonic irradiation was stopped and the RF solution was then poured into the cylindrical glass tube (inner diameter = 3 mm, length = 40 mm) followed by aging for 7 days at 348 K in the oven. Before freeze drying, water in RF sonogel monolith was replaced by solvent exchange with *t*-butanol for three times. After that, RF sonogels were freeze-dried at 263 K for 3 h to obtain freeze dried macroporous RF sonogel monolith. Macroporous carbon sonogel monoliths were obtained by pyrolyzing macroporous RF sonogel monoliths at 1023 K. Pyrolysis was conducted under a 200 cm³/STP/min flow of nitrogen gas. At first, the freeze-dried sonogels were heated to 523 K at a constant heating rate of 523 K/h, and were kept at this temperature for 2 h. Then they were heated to 1023 K at a constant heating rate of 523 K/h and were kept at 1023 K for 4 h.

The structures of RF gel and RF sonogel monoliths were observed by scanning electron microscope (SEM). Macropore size distribution was measured by using mercury porosimeter. Porous properties, BET surface area (S_{BET}), mesopore volume (V_{mes}) and micropore volume (V_{mic}), were determined from the N_2 adsorption method using an adsorption apparatus.

The effect of ultrasonic irradiation at gelation stage can be seen as followed. In gelation process, gelation time is shortened outstandingly with ultrasonic irradiation. Gelation time obviously decreases from 48 h (RF gel monolith) to 8 h (RF sonogel monolith). The shrinkages of 3D interconnected macroporous RF gel monolith and RF sonogel monolith, after freeze drying, are 21% and 1% respectively. It is obvious that ultrasonic irradiation leads to small shrinkage in RF gel sonogel monolith compared to RF gel monolith. In Fig. 1, the cross section of RF sonogel monolith observed by SEM shows 3D interconnected macroporous structure which is totally different from mesoporous structure of

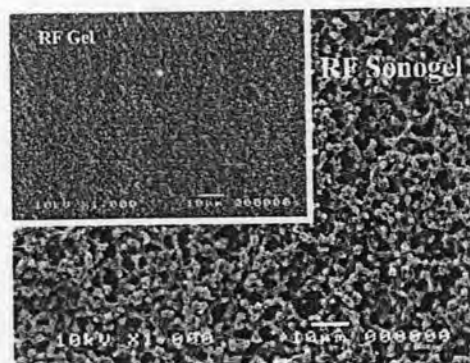


Fig. 1. SEM micrographs (cross section at 1000x) of RF gel and RF sonogel monolith.

RF gel monolith. S_{BET} are 228 (RF gel monolith) and 5 (RF sonogel monolith) m²/g. V_{mic} and V_{mes} of RF gel are 0.02 and 0.32 cm³/g respectively. For RF sonogel monolith, V_{mic} and V_{mes} cannot be detected.

After pyrolysis of RF sonogel monolith, no change in macroporous structure and very low shrinkage are observed. After pyrolysis S_{BET} and V_{mic} of sonogel increases from 5 to 366 m²/g and N/D to 0.11 cm³/g respectively (V_{mes} cannot be detected). It can be seen from SEM micrograph in Fig. 2 together with porous properties that RF carbon monolith can keep 3D interconnected macroporous structures. The macropore size distributions of carbon monolith are narrow, the average macropore size around 1–3 μ m as shown in Fig. 3.

In this work, new synthesis method for 3D interconnected macroporous sonogel and/or carbon monolith is proposed with some advantages to other methods such as shorter gelation time of polymer monolith, small

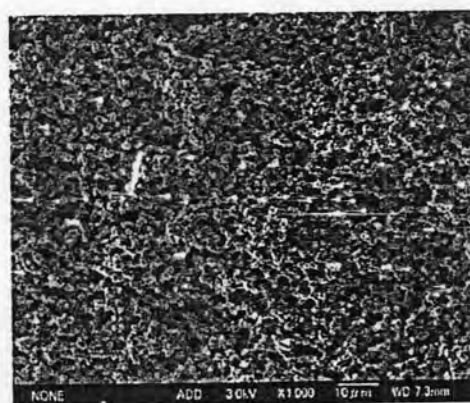


Fig. 2. SEM micrographs (cross section at 1000x) of RF carbon monolith.

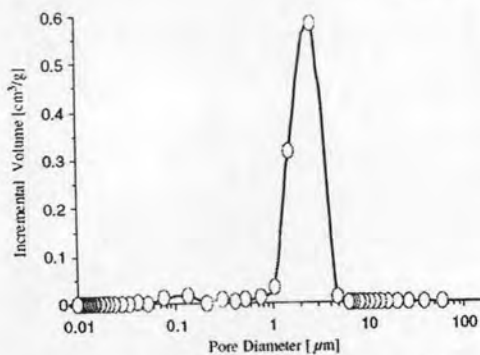


Fig. 3. Macropore size distribution of RF carbon monolith.

shrinkage percentage, no template preparation and template removal.

In addition to this preliminary work, the effect of R/C on the structure of 3D interconnected macroporous carbon monolith (microwave drying at 200 W after solvent

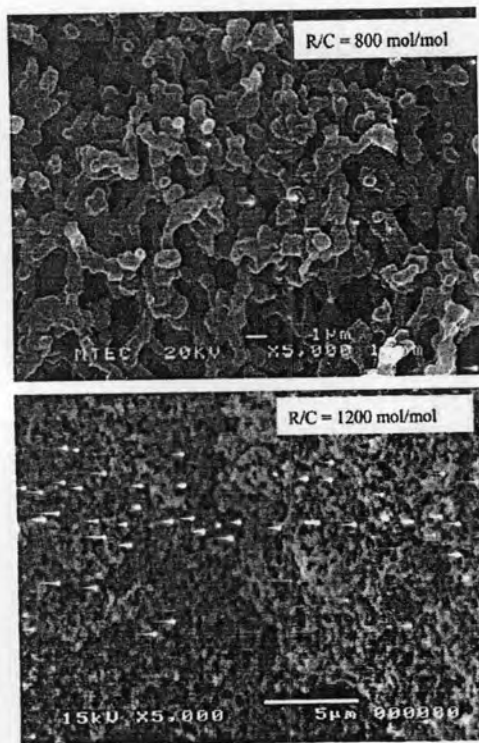


Fig. 4. SEM micrograph (cross section at 5000x) of RF carbon monolith (C/W 10 mol/m³, microwave drying).

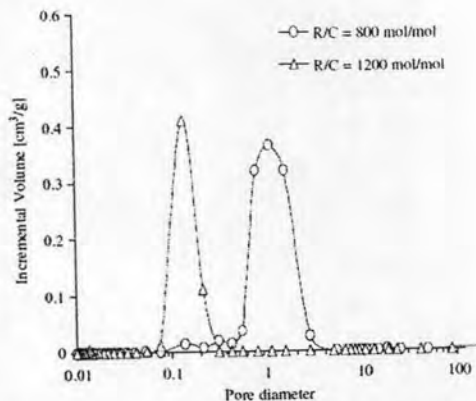


Fig. 5. Macropore size distribution of RF carbon monolith (C/W 10 mol/m³, microwave drying).

exchange with *t*-butanol) has been investigated. In Figs. 4 and 5, R/C = 1200 mol/mol gives 3D interconnected macroporous carbon monolith with smaller pore diameters than R/C = 800 mol/mol. 3D interconnected macroporous carbon monolith from both R/C = 800 and 1200 mol/mol show narrow pore size distributions as shown in Fig. 5. It is obviously seen that R/C has effects on the structure of interconnected macroporous carbon monolith.

These results suggest that there is a possibility to tailor pore structure of 3D interconnected macroporous soanogel monolith (precursor of 3D interconnected macroporous carbon monolith) directly and effectively at gelation stage with suitable reactant ratios of RF solution and ultrasonic intensity.

Acknowledgements

This research was partially supported by the Thai Government (Matching Fund), the Thailand Research Fund (Senior Researcher Scholarship), Thai-Japan Technology Transfer Project (TJTTP)/Chulalongkorn University, Silver Jubilee Research Fund/Chulalongkorn University, National Metal and Materials Technology Center (MTEC)/Thailand's National Science and Technology Development Agency (NSTDA) and the Thailand Graduate Institute of Science and Technology (TGIST)/NSTDA.

References

- [1] Tanaka N, Kobayashi H, Nakanishi K, Minakuchi H, Ishizuka N. A new type of chromatographic support could lead to higher separation efficiencies. *Anal Chem* 2001;421A:9A.

- [2] Liang C, Dai S, Guiochon G. A graphitized-carbon monolithic column. *Anal Chem* 2003;75:4904–12.
- [3] Taguchi A, Smatt JH, Linden M. Carbon monoliths possessing a hierarchical, fully interconnected porosity. *Adv Mater* 2003;15:1209–11.
- [4] Shi ZG, Feng YQ, Xu L, Da SL, Zhang M. Synthesis of carbon monolith with trimodal pores. *Carbon* 2003;41:2657–89.
- [5] Bu H, Rong J, Yang Z. Template synthesis of polyacrylonitrile-based ordered macroporous materials and their derivatives. *Macromol Rapid Commun* 2002;23:460–4.
- [6] Kang S, Yu JS, Kruk M, Jaroniec M. Synthesis of an ordered macroporous carbon with 62 nm spherical pores that exhibit unique gas adsorption properties. *Chem Commun* 2002:1670–1.
- [7] Peters EC, Svec F, Frechet JMJ. Rigid macroporous polymer monoliths. *Adv Mater* 1999;11:1169–81.
- [8] Moreno-Castilla C, Maldonado-Hóda FJ, Rivera-Utrilla J, Rodríguez-Castellón E. Group 6 metal oxide-carbon aerogels. Their synthesis, characterization and catalytic activity in the skeletal isomerization of 1-butene. *Appl Catal A* 1999;183:345–56.
- [9] Brandt R, Petricevic R, Probstle H, Fricke J. Acetic acid catalyzed carbon aerogels. *J Porous Mater* 2003;10:171–8.
- [10] Tonanon N, Siyasukh A, Tanthapanichakoon W, Nishihara H, Mukai SR, Tamon H. Improvement of mesoporosity of carbon cryogels by ultrasonic irradiation. *Carbon* 2005;43:525–31.
- [11] Suslick KS, Price GJ. Applications of ultrasound to materials chemistry. *Annu Rev Mater Sci* 1999;29:295–326.

Available online at www.sciencedirect.com

Journal of Non-Crystalline Solids 352 (2006) 5683–5686

LETTER TO THE EDITOR

JOURNAL OF
NON-CRYSTALLINE SOLIDSwww.elsevier.com/locate/jnoncrystal

Letter to the Editor

Preparation of resorcinol formaldehyde (RF) carbon gels: Use of ultrasonic irradiation followed by microwave drying

Nattaporn Tonanon^{a,*}, Yunyong Wareenin^a, Adisak Siyasukh^a,
Wiwut Tanthapanichakoon^b, Hiroto Nishihara^c, Shin R. Mukai^c, H. Tamon^c

^a Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand^b National Nanotechnology Center, 111 Thailand Science Park, Klong Luang, Pathumthani 12120, Thailand^c Department of Chemical Engineering, Graduate School of Engineering, Kyoto University, Katsura, Kyoto 615-8510, Japan

Received 1 February 2006; received in revised form 6 September 2006

Abstract

In this work, ultrasonic irradiation (with suitable reactant ratios) during gelation of RF solution is a promising technique for maintaining porous properties of carbon gels prepared by microwave drying.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Carbon; Scanning electron microscopy; Porosity; Sol-gel; Aerogel and solution chemistry; Sol-gels (xerogels); Surface and interfaces; Adsorption

Ultrasonic irradiation and microwave drying are discussed in the preparation of mesoporous and 3D interconnected macroporous carbons. Microwave drying is an interesting way to prepare resorcinol and formaldehyde (RF) gels with a short drying time. However, the use of this drying method is limited because microwave dried gels have poor porous properties compared to freeze dried gels. In this work we report on: (1) how mesoporous structure can be maintained during microwave drying with the help of ultrasonic irradiation and (2) how the microwave drying can be applied to the preparation of 3D interconnected macroporous carbon monoliths. The interesting outcome of this work will lead to an increased use of microwave drying for RF carbon gels.

Mesoporous RF carbon gels are interesting porous carbon materials with moderately high BET surface areas (500–1200 m²/g) and large mesopore volume (>0.89 cm³/g). The carbon gels are suitable for many applications such as

column packing materials for high-performance liquid chromatography, electrode materials for electrical double layer capacitors, medical applications (controlled drug delivery system and drug targeting) and materials for catalyst supports [1,2]. In addition to mesoporous carbon, the 3D interconnected macroporous carbon monolith [3] is a carbon structure which is suitable for flow-through application and some special applications such as separation and catalyst support. The porous properties of carbon gels depend on many factors such as reactant ratios, ultrasonic irradiation and drying methods.

One of the production steps that consumes time and energy and also has an important effect on the porous properties of RF carbon gels is a gel drying process. Freeze drying was introduced as a more economical process and easy to operate alternative for supercritical drying while good porous properties can also be maintained [4]. Microwave drying caused by rapid dipole reaction of dielectric molecules under electromagnetic fields was used successfully in the preparation of RF gels and RF carbon gels, and good porous properties were obtained under certain catalyst concentrations [5]. Although microwave drying

* Corresponding author. Tel.: +66 2 218 6865; fax: +66 2 218 6877.
E-mail address: nattaporn.t@chula.ac.th (N. Tonanon).

LETTER TO THE EDITOR

5684

N. Tomason *et al.* / *Journal of Non-Crystalline Solids* 352 (2006) 5683–5686

has a gas-liquid interface unlike freeze drying, it has several advantages, including no heating from outside like hot air drying, very fast drying rate, lower operating cost, selective drying, no hot spot, no lost energy in the atmosphere and uniform product quality. Not only the drying mechanism but drying time and drying cost are also extremely important in the preparation of carbon gels. Supercritical drying is the best drying method for preventing the drying shrinkage of mesopores. However, it is difficult to apply this drying method to the industrial production of carbon gels from the viewpoint of a drying cost. It will be very convincing if the proper synthesis conditions of organic gels are selected so that freeze drying and evaporation drying can be used.

From previous work [6], ultrasonic irradiation shows an interesting effect on sol-gel polycondensation of resorcinol and formaldehyde. The degree of ultrasonic effect depends on the reactant ratios. It was explained in the literature [2] that during gelation a large amount of catalyst causes many clusters for small network formation. When the clusters are small, the pores between clusters are also small. On the contrary, with a small amount of catalyst, the clusters become larger and pores become larger. For ultrasonic irradiated carbon gels, when C/W (the ratio of sodium carbonate to water) = 20–80 mol/m³, the mesoporous properties of an RF carbon gel can be maintained during freeze drying. In contrast, $C/W = 10$ mol/m³ gives 3D interconnected macroporous carbon monolith [3]. The objectives of this work are to investigate: (1) the porous properties of ultrasonic irradiated RF carbon gel after microwave

drying and (2) the possibility of using microwave drying for 3D interconnected macroporous carbon monolith. The use of ultrasonic irradiation during gelation is a good method in the preparation of mesoporous carbon gels by microwave drying and the most original point of the present work. The success in the preparation of RF carbon gels by microwave drying is very convincing for the broad use of porous RF carbon gels in the near future.

In this work, RF carbon gels were synthesized via the sol-gel polycondensation of resorcinol (1,3-dihydroxybenzene) ($C_6H_4(OH)_2$) (R) and formaldehyde (HCHO) (F) in a slightly basic aqueous solution followed by 0 and 22 W ultrasonic irradiation. From the previous work [6], three different ultrasonic powers 16 W, 22 W and 30 W were used. Ultrasonic irradiation at 22 W was found to be an optimized one. Gelation temperature was 308 K. Sample size is 4 cm in length and 3 mm in diameter. Before drying process, RF gels were solvent-exchanged with *t*-butanol for three times. RF gels were dried by freeze drying at 263 K for 3 h [3,6] and microwave drying (200 W microwave oven TURBORA (model TRX-2021) at 1 atm with 10 min drying time). Pyrolysis temperature was 1023 K under nitrogen flow (200 cm³/min).

The porous properties of RF carbon gels were determined by the N₂ adsorption method using an adsorption apparatus (BEL Japan Inc.: BELSORP28). BET surface area (S_{BET}), mesopore size distribution, and mesopore volume (V_{mes}) were evaluated. The cross-sections of RF carbon gels were observed by a scanning electron microscope (JEOL, JSM-6700F).

Table 1
The porous properties of carbon gels prepared by microwave drying from different synthesis conditions

Reactant ratio	Ultrasonic irradiation	Drying method	Sample	V_{mes} (cm ³ /g)	S_{BET} (cm ² /g)
$C/W = 20$ (mol/m ³)	No	Microwave	A1	0.65 ± 0.03	610 ± 24
$R/C = 200$ (mol/mol)	Yes	Microwave	A2	0.99 ± 0.04	570 ± 23
$C/W = 40$ (mol/m ³)	Yes	Freeze	A3	0.75 ± 0.03	740 ± 30
$R/C = 200$ (mol/mol)		Microwave	A4	0.68 ± 0.03	670 ± 27
	No	Freeze	A5	0.61 ± 0.02	750 ± 30
		Microwave	A6	0.49 ± 0.02	520 ± 21
$C/W = 80$ (mol/m ³)	No	Microwave	A7	0.46 ± 0.02	730 ± 30
$R/C = 200$ (mol/mol)	Yes	Microwave	A8	0.59 ± 0.02	760 ± 30
$C/W = 80$ (mol/m ³)	Yes	Freeze	A9	0.65 ± 0.03	740 ± 30
$R/C = 100$ (mol/mol)		Microwave	A10	0.33 ± 0.01	640 ± 26
	No	Freeze	A11	0.08 ± 0.008	360 ± 14
		Microwave	A12	0.29 ± 0.01	620 ± 25
$C/W = 80$ (mol/m ³)	No	Microwave	A13	0.01 ± 0.001	6 ± 0.6
$R/C = 50$ (mol/mol)	Yes	Microwave	A14	0.02 ± 0.002	5 ± 0.5
$C/W = 10$ (mol/m ³)	Yes	Freeze	A15 ^a	ND	366 ± 15
$R/C = 800$ (mol/mol) (3D interconnected macroporous monolith)	Yes	Microwave	A16 ^b		

ND, not detected; C/W , ration of sodium carbonate to water; R/W , ratio of resorcinol to water; R/F , molar ratio of resorcinol to formaldehyde (0.5 mol/mol); V_{mes} , mesopore volume; V_{mac} , macropore volume; S_{BET} , BET surface area and d_p , pore diameter.

^a Freeze dried carbon monolith [3]; $V_{mes} = 1.01$ cm³/g, $d_p = 2.72$ μm.

^b Microwave dried carbon monolith [3]; $V_{mes} = 1.08$ cm³/g, $d_p = 1.06$ μm.

The synthesis conditions and porous properties of carbon gels prepared by ultrasonic irradiation during gelation process and microwave drying are shown in Table 1. The freeze dried carbon gels from previous works [3,6] are also used for comparison with microwave dried carbon gels. The pore size distributions shown in Fig. 1 indicate that when C/W is low (20 mol/m^3) microwave drying and freeze drying [6] can be applied for RF gels prepared without help from ultrasonic irradiation. On the contrary, when C/W is higher (40 mol/m^3 and 80 mol/m^3 ($R/C \geq 100$)) microwave drying and freeze drying [6] are applicable only for RF gels prepared under ultrasonic irradiation. The porous properties and the pore size distributions of carbon gels prepared by freeze drying and microwave drying under the conditions of $C/W = 80 \text{ mol/m}^3$, R/C (the molar ratio of resorcinol to sodium carbonate) = 100 mol/mol and $C/W = 40 \text{ mol/m}^3$, $R/C = 200 \text{ mol/mol}$ are shown in Table 1 and Fig. 1. From Table 1 and Fig. 1, one can see that with the help of ultrasonic irradiation mesoporous structure can be maintained during microwave drying.

In Fig. 1 it is more difficult to maintain mesopore size when R/C becomes smaller. Mesoporous structure cannot be obtained when $R/C = 50 \text{ mol/mol}$. The difference in R/C leads to the decrease in V_{mes} with decreasing R/C as shown in Table 1. S_{BET} can hardly be measured for $R/C = 50 \text{ mol/mol}$. This result can be confirmed by SEM micrographs in Fig. 2. Unlike carbon gels prepared at $R/C = 100$ and 200 mol/mol the mesoporous structure cannot be maintained when $R/C = 50 \text{ mol/mol}$.

In microwave drying, it is obvious that ultrasonic irradiation can make gel preparation conditions at high catalyst concentration ($C/W = 80 \text{ mol/m}^3$ with $R/C > 100 \text{ mol/mol}$) possible. The difference in C/W leads to the decrease in V_{mes} with increasing C/W ratios (no big difference in the S_{BET} of $520\text{--}760 \text{ cm}^2/\text{g}$). Ultrasonic irradiation does not greatly influence pore size distribution of carbon gels when $C/W = 80 \text{ mol/m}^3$ with small R/C . It was explained in the literature [2] that during gelation a large amount of catalyst causes many clusters for small network formation. When the clusters are small the pores between clusters are also small. On the contrary, with the small amount of catalyst the clusters become larger and pores become larger. In general after drying mesopore structure cannot be maintained when pores are small because of strong capillary force.

The good mesoporous structure of RF gels (22 W ultrasonic irradiation) which are the precursor of carbon gels is formed during gelation because ultrasonic irradiation together with catalyst probably results in the generation of more free radicals which leads to fast reaction time and larger primary particles [6]. Larger mesopores which can be kept after microwave drying may be formed by large clusters induced by ultrasonic irradiation.

The pore size distributions of 3D interconnected macroporous carbon monoliths prepared by freeze drying [3] and microwave drying are compared in Fig. 3. Freeze dried carbon monolith shows larger macropore size than microwave dried carbon monolith as shown in Table 1. Furthermore, the SEM micrographs of 3D interconnected macroporous

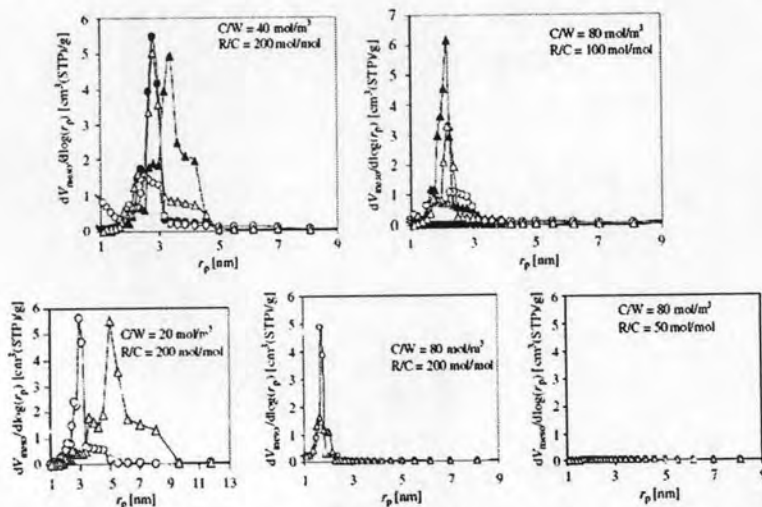


Fig. 1. The pore size distributions of A1–A4 in Table 1: (■) freeze dried carbon gels (0 W ultrasonic irradiation), (▲) freeze dried carbon gels (22 W ultrasonic irradiation), (○) microwave dried carbon gels (0 W ultrasonic irradiation), and (△) microwave dried carbon gels (22 W ultrasonic irradiation). The distributions are calculated by applying the Dollimore–Heal method to desorption isotherms. Lines are drawn as guides to the eyes.

LETTER TO THE EDITOR

5686

N. Tonanon et al. / Journal of Non-Crystalline Solids 352 (2006) 5683–5686

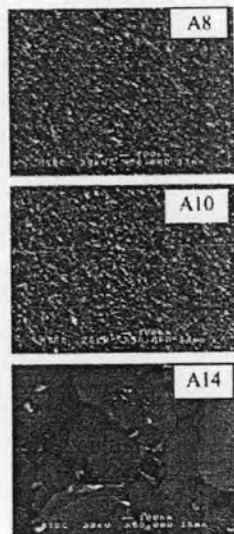


Fig. 2. SEM micrographs of ultrasonic irradiated carbon gels ($C/W = 80 \text{ mol/m}^3$) being dried by microwave.

monoliths prepared by freeze drying and microwave drying [3] also show similar structures. Therefore, from this study microwave can be used successfully in the drying of 3D interconnected macroporous carbon monolith ($C/W = 10 \text{ mol/m}^3$, $R/C = 800 \text{ mol/mol}$).

Although there are not enough data to explain the mechanism of microwave drying of RF gel at this moment, an interesting primary conclusion was obtained as follows. Ultrasonic irradiation with suitable reactant ratios during the gelation of RF solution is a promising technique for maintaining the mesoporous properties of carbon gels prepared by microwave drying.

In this way, the flexible synthesis conditions of RF gels for microwave drying can be selected. In the previous work [5] the mesoporous properties of carbon gels prepared by microwave drying can be maintained when C/W is $< 25 \text{ mol/m}^3$ ($R/C = 200 \text{ mol/mol}$). In this present work the mesoporous properties of RF gels (22 W ultrasonic irradiation) prepared by microwave drying can be maintained when catalyst concentration is high ($C/W < 80 \text{ mol/m}^3$, $R/C > 100 \text{ mol/mol}$). Furthermore it is an

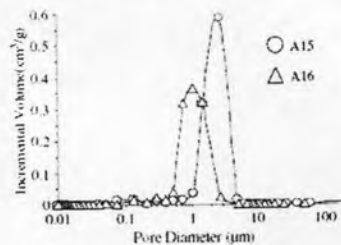


Fig. 3. Pore size distribution of macroporous carbon monolith: (○) freeze drying and (△) microwave drying ($C/W = 10 \text{ mol/m}^3$, $R/C = 800 \text{ mol/mol}$). The distributions are determined by mercury porosimetry. Lines are drawn as guides to the eyes.

additional benefit to find out that microwave drying can be successfully used for 3D interconnected macroporous carbon monoliths. In conclusion microwave drying is considered as an efficient drying method for production of both mesoporous and macroporous RF carbon gels in term of their porous properties, drying time, cost and convenience.

Acknowledgments

This research was partially supported by the Thai Government (Matching Fund), the Thailand Research Fund (Senior Researcher Scholarship), Thai-Japan Technology Transfer Project (TJTTP)/Chulalongkorn University, Silver Jubilee Research Fund/Chulalongkorn University, National Metal and Materials Technology Center (MTEC)/Thailand's National Science and Technology Development Agency (NSTDA) and the Thailand Graduate Institute of Science and Technology (TGIST)/NSTDA.

References

- [1] R.W. Pekala, C.T. Alviso, *Mater. Res. Soc. Proc.* 270 (1992) 3.
- [2] S.A. Al-Muhtaseb, J.A. Ritter, *Adv. Mater.* 15 (2003) 101.
- [3] N. Tonanon, A. Siyasukh, Y. Warennin, T. Charinpanitkul, W. Tanthapanichakoon, H. Nishihara, H. Tamon, *Carbon* 43 (2005) 2808.
- [4] H. Tamon, H. Ishizaka, T. Yamamoto, T. Suzuki, *Carbon* 37 (1999) 2049.
- [5] H. Tamon, S.R. Mukai, H. Nishihara, T. Yoshida, T. Yamamoto, N. Tonanon, T. Charinpanitkul, W. Tanthapanichakoon, in: *Proceedings of the third Asia-Pacific drying conference*, Asian Institute of Technology, Bangkok, Thailand, 2003, p. 123.
- [6] N. Tonanon, A. Siyasukh, W. Tanthapanichakoon, H. Nishihara, S.R. Mukai, H. Tamon, *Carbon* 43 (2005) 525.

VITAE

Mr. Adisak Siyasukh was born in Kanjanaburi, Thailand in 1979. He received his B.Eng and M.Eng in chemical engineering from Chulalongkorn University in 2001 and 2005, respectively. Subsequently, he continued to study in Doctoral Program at Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University under scholarship from Thailand Graduate Institute of Science and Technology (TGIST). His dissertation during graduation is focused on synthesis of the carbon material with hierarchical porous structure. He was awarded a D.Eng in chemical engineering in August 2008 from the dissertation in the article "Preparation of hierarchical porous carbon monolith without using templates".

