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ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

PREPARATION OF HIERARCHICAL POROUS CARBON MONOLITH  
WITHOUT USING TEMPLATES

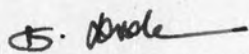
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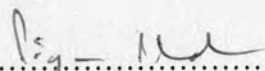
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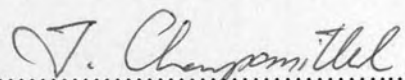
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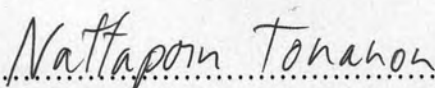
  
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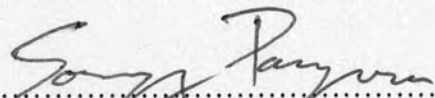
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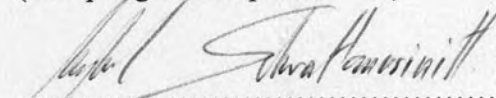
  
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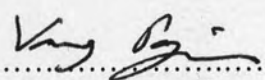
  
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อดิศักดิ์ ไสยสุข : การเตรียมคาร์บอน โมโนลิทที่มีรูพรุนแบบลำดับชั้นโดยไม่ใช้เทมเพลต. (PREPARATION OF HIERARCHICAL POROUS CARBON MONOLITH WITHOUT USING TEMPLATES)

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คาร์บอน โมโนลิทที่มีรูพรุนแบบลำดับชั้นประกอบไปด้วยโครงสร้างรูพรุนสองขนาดคือ โครงสร้างรูพรุนขนาดแมคโครพอร์ที่มีการเชื่อมทะลุถึงกันและโครงสร้างรูพรุนขนาดนาโนพอร์ ซึ่งโดยปกติสามารถเตรียมได้ด้วยการลอกแบบโครงสร้างรูพรุนแบบลำดับชั้นจากวัสดุอนินทรีย์ที่ใช้เป็นเทมเพลต อย่างไรก็ตามวิธีการดังกล่าวก็มีความซับซ้อนมากเนื่องด้วยจำเป็นต้องกำจัดเทมเพลตทิ้งในภายหลัง รวมไปถึงโครงสร้างรูพรุนของคาร์บอนที่ได้อยู่กับโครงสร้างรูพรุนของเทมเพลตอีกด้วย ดังนั้นในงานวิจัยนี้จึงได้มุ่งเน้นการค้นคว้าหาวิธีการเตรียมคาร์บอน โมโนลิทที่มีโครงสร้างรูพรุนแบบลำดับชั้นแบบใหม่โดยไม่จำเป็นต้องใช้เทมเพลตในกระบวนการเตรียม ซึ่งในงานวิจัยนี้จะนำเสนอสองวิธีแบบใหม่ ดังนี้

วิธีการเตรียมแบบแรก คือ การระดมยิงด้วยคลื่นเหนือเสียงที่มีความถี่ถึงที่ 20 กิโลเฮิร์ตซ์ ตลอดระยะเวลาที่เกิดปฏิกิริยาโซล เจล ของการสังเคราะห์ ริโซซินอล-ฟอร์มัลดีไฮด์ (อาร์-เอฟ) เจล ทำให้สามารถเตรียม อาร์-เอฟ เจล ที่มีลักษณะเป็นแท่งโมโนลิทซึ่งประกอบไปด้วยโครงสร้างรูพรุนขนาดแมคโครพอร์ที่เชื่อมทะลุถึงกัน หลังจากนั้น อาร์-เอฟ เจลที่ได้ถูกนำไปคาร์บอนไนซ์เซชันด้วยแก๊สไนโตรเจน ซึ่งจะทำได้คาร์บอน โมโนลิทซึ่งไม่ได้เพียงแต่มีโครงสร้างรูพรุนขนาดแมคโครพอร์ที่เชื่อมทะลุถึงกันเช่นเดียวกับ อาร์-เอฟ เจล เท่านั้น แต่ยังมีรูพรุนระดับไมโครพอร์อยู่บนผนังรูพรุนของแมคโครพอร์อีกด้วย ในงานวิจัยนี้ได้มีการศึกษาอิทธิพลของอุณหภูมิระหว่างการสังเคราะห์ อาร์-เอฟ เจล ค่าพีเอชในช่วงแรกของการละลาย อาร์-เอฟ และกำลังของคลื่นเหนือเสียงที่ระดมยิงว่ามีผลต่อโครงสร้างรูพรุนขนาดแมคโครพอร์ที่เชื่อมทะลุถึงกันของคาร์บอน โมโนลิทที่เตรียมได้อย่างไร ผลการศึกษาพบว่า ปัจจัยเหล่านี้ส่งผลอย่างมากต่อทั้งรูปร่างแบบ โมโนลิทและโครงสร้างรูพรุนขนาดแมคโครพอร์ที่เชื่อมทะลุถึงกันของคาร์บอนที่เตรียมได้ นอกจากนี้ แอคติเวตคาร์บอน โมโนลิทที่มีทั้งโครงสร้างรูพรุนแบบลำดับชั้นของไมโครพอร์บนแมคโครพอร์ และมีหมู่ฟังก์ชันที่เกี่ยวกับออกซิเจน ยังสามารถเตรียมได้ในเวลาที่สั้น (ประมาณ 30 นาที) โดยการกระตุ้นอาร์-เอฟ โมโนลิทด้วยความร้อนโดยตรงภายใต้บรรยากาศของคาร์บอนไดออกไซด์ ในขณะที่แอคติเวตคาร์บอน โมโนลิทที่มีทั้งโครงสร้างรูพรุนแบบลำดับชั้นของไมโครพอร์และมีโซพอร์บนแมคโครพอร์ และมีหมู่ฟังก์ชันที่มีออกซิเจนเป็นส่วนประกอบ ยังสามารถเตรียมได้ด้วยการแอคติเวตอาร์-เอฟ โมโนลิทโดยตรงในเวลาสั้น (ประมาณ 30 นาที) ด้วยวิธีการเคมิลแคลเซียมไนเตรตแล้วตามด้วยการกระตุ้นด้วยความร้อนภายใต้บรรยากาศของคาร์บอนไดออกไซด์

สำหรับวิธีการที่สองเป็นการเตรียม อาร์-เอฟ เจล ที่มีลักษณะเป็นแท่งโมโนลิทซึ่งประกอบไปด้วยโครงสร้างรูพรุนขนาดแมคโครพอร์ที่เชื่อมทะลุถึงกัน ด้วยการเหนี่ยวนำการตกตะกอนของสารละลายอาร์-เอฟ ในช่วงปลายของการกลายเป็นเจล ระยะเวลาที่เติมน้ำและปริมาตรของน้ำที่เติมเป็นปัจจัยหลักในการเตรียม อาร์-เอฟ เจล ที่มีโครงสร้างดังกล่าว จากนั้นสามารถเตรียมแอคติเวตคาร์บอน โมโนลิทที่มีโครงสร้างรูพรุนแบบลำดับชั้นได้ ด้วยวิธีการกระตุ้นโดยตรงทั้งแบบกระตุ้นด้วยความร้อนหรือใช้สารเคมีภายใต้บรรยากาศของคาร์บอนไดออกไซด์

ภาควิชา.....วิศวกรรมเคมี.....  
สาขาวิชา.....วิศวกรรมเคมี.....  
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ลายมือชื่อนิสิต.....  
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ลายมือชื่ออาจารย์ที่ปรึกษาร่วม.....  
ลายมือชื่ออาจารย์ที่ปรึกษาร่วม.....

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KEY WORD: ACTIVATED CARBON / HIERARCHICAL POROUS STRUCTURE/ MONOLITH / RESORCINOL-FORMALDEHYDE GEL / POROSITY

ADISAK SIYASUKH: PREPARATION OF HIERARCHICAL POROUS CARBON MONOLITH WITHOUT USING ANY TEMPLATES. THESIS ADVISOR: ASSOC. PROF. TAWATCHAI CHARINPANITKUL, D.Eng., THESIS COADVISORS: PROF. EMER. WIWUT TANTHAPANICHAKOON, Ph.D., ASST. PROF. NATAPORN TONANON, D.Eng., 108 pp.

Carbon monolith with hierarchical porous structure containing both interconnected macroporous and nanoporous structure are generally prepared by replicating from a hard template of inorganic material with similar porous structure. However, the preparing method is very complicate because of because the template removal is needed. Besides the porous structure of the carbon monolith is depended on the template. This research, therefore, focuses on the new effective method without using any templates for synthesis the monolithic carbon containing the hierarchical porous structure. Two effective methods are introduced.

The first method is an irradiation of ultrasonic wave at constant frequency of 20 kHz during sol-gel process of resorcinol-formaldehyde (RF) gel synthesis. Consequently, the RF monolith gel consisting of the interconnected macroporous structure can be obtained. Afterwards, the carbonization with N<sub>2</sub> is performed in order to prepare the carbon monolith from the RF monolith gel. The carbonized carbon monolith not only consists with the interconnected macropores as well as the RF monolith, but also has the microporosities on the macropore walls. Additionally, the effect of sol-gel temperature, initial pH value of the resorcinol-formaldehyde solution and ultrasonic power on the interconnected macroporous structure of the carbonized carbon monolith are also investigated. These parameters strongly result in both the obtained monolith shape and the interconnected macropores of the carbon monolith. Moreover, the activated carbon monolith containing both bi-modal microporosities on macropore structure and oxygenated functional groups can directly prepared at low retention time (~30min) by direct thermal activation with CO<sub>2</sub> of the interconnected macroporous RF monolith gel, whereas the activated carbon monolith containing both tri-modal micro-/meso-/ macropore structure and oxygenated functional groups can be prepared at low retention time by direct chemical activation by impregnation of Ca(NO<sub>3</sub>)<sub>2</sub> followed by activating with CO<sub>2</sub>.

The second method is an inducing the inverse-phase suspension of the RF solution at nearly complete gel-formation with adding water. The RF monolith gel with the interconnected macroporous structure can be obtained. Sol-gel keeping time and volume of adding water are the important key parameters for achievements of both obtained monolith shape and interconnected macropores. Afterwards, the direct thermal activation and the direct chemical activation are carried out under the same condition in order to generate the microporosities and mesoporosites in the obtained carbon monolith.

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## NOMENCLATURE

C	= Sodium carbonate
C/W	= Ratio of sodium carbonate to water [mol/m <sup>3</sup> ]
Ca(NO <sub>3</sub> ) <sub>2</sub>	= Calcium nitrate
CO <sub>2</sub>	= Carbon dioxide
d <sub>p</sub>	= Macropore size [μm]
F	= Formaldehyde
FT-IR	= Fourier Transform Infrared Spectroscopy
M	= Molar [mol/liter]
N <sub>2</sub>	= Nitrogen
ND	= Not determined
P/P <sub>0</sub>	= Relative pressure of N <sub>2</sub> gas [-]
pH <sub>Init</sub>	= Initial pH value of RF solution [-]
P <sub>US</sub>	= Power of ultrasonic irradiation [W]
R	= Resorcinol
R/F	= Mol ratio of resorcinol to formaldehyde [-]
R/W	= Mol ratio of resorcinol to water [-]
RF	= Resorcinol-formaldehyde gel
r <sub>p</sub>	= Peak value of mesopore size distribution [nm]
S <sub>BET</sub>	= Specific surface area determined by BET model [m <sup>2</sup> /g]
SEM	= Scanning electron microscopy
S <sub>sp</sub>	= Specific surface area determined by average from S <sub>BET</sub> and S <sub>t-plot</sub> [m <sup>2</sup> /g]
STP	= Standard temperature (0 °C) and pressure (1 atm)
S <sub>t-plot</sub>	= Specific surface area determined by t-plot model [m <sup>2</sup> /g]
t <sub>AD</sub>	= Gel keeping time before adding water [hr]
T <sub>D</sub>	= Activating temperature [°C]
t <sub>D</sub>	= Activating time [hr]
T <sub>US</sub>	= Gel-formation temperature during ultrasonic irradiation [°C]
t <sub>US</sub>	= Ultrasonic irradiation time [hr]
V	= Adsorption volume at STP of N <sub>2</sub> [cm <sup>3</sup> /g]
V <sub>macro</sub>	= Macropore volume [cm <sup>3</sup> /g]

$V_{\text{meso}}$	= Mesopore volume [ $\text{cm}^3/\text{g}$ ]
$V_{\text{micro}}$	= Micropore volume [ $\text{cm}^3/\text{g}$ ]
W	= Water
$W_{\text{AD}}/\text{RF}$	= Volume ratios of the adding water to RF solution [-]