

SYNTHESIS OF Ti/Mo-MCM-41 AND Bi₁₂TiO₂₀ AND THEIR ACTIVITIES

Nopporn Thanabodeekij

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Prof. Erdogan Gulari

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University, in partial fulfilment of the requirements for the Degree of Doctor of
Philosophy.

Nantaya Yanumet.
..... College Director
(Assoc. Prof. Nantaya Yanumet)

Thesis Committee:

Nantaya Yanumet.
.....
(Assoc. Prof. Nantaya Yanumet)

Sujitra Wongkasemjit
.....
(Assoc. Prof. Sujitra Wongkasemjit)

Erdogan Gulari
.....
(Prof. Erdogan Gulari)

Sumaeth Chavadej
.....
(Assoc. Prof. Sumaeth Chavadej)

dot Lu
.....
(Asst. Prof. Vachat Chuenchom)

ABSTRACT

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Metal alkoxides have been of interest in the past few years for production of advanced materials due to their hydrolyzable property for sol-gel application. Silatrane synthesized from inexpensive silica and triethanolamine (TEA) was used as the precursor for MCM-41 synthesis at low temperature because of its stability in aqueous solutions. Using cationic surfactant hexadecyltrimethyl ammonium bromide (CTAB) as a template, the resulting meso-structure mimics the liquid crystal phase. Variations of the surfactant concentration, ion concentration and temperature of the system, change the structure of the liquid crystal phase, resulting in different pore structures and surface area. After heat treatment, extremely high surface area mesoporous silica was obtained. The surface area was extraordinarily high, up to more than $2400 \text{ m}^2/\text{g}$ at pore volume of 1.29 cc/g . However, the pore volume is increased to 1.72 cc/g when the surface area was lower, $2100 \text{ m}^2/\text{g}$. The mesoporous MCM-41 was also used as a catalyst support for Ti, Mo. Titanium is successfully incorporated in hexagonal mesoporous silica to form Ti-MCM41 at low temperature using titanium glycolate precursor synthesized via the Oxide One Pot Synthesis (OOPS) process. The percentage of Ti loading was varied from 1 to 35%. The temperatures used to prepare were 60° and 80°C . After heat treatment, very high surface area mesoporous silica was also obtained. As for Mo-MCM-41, high dispersion of Mo onto MCM-41 was successfully prepared using molybdenum glycolate precursor. Impregnation process was used to load metal onto support before and after heat treatment. The %Mo dispersion was as high as 10 mol% or 0.265 g

MoO₃/g SiO₂ while the structure of MCM-41 was still retained. Bulk MoO₃ was observed in the case of Mo-loaded onto calcined support of MCM-41(c). Both Ti-MCM-41 and Mo-MCM-41 were used to study peroxidative reaction, showing impressive results. Titanium glycolate was also used to prepare bismuth titanate, Bi₁₂TiO₂₀. Pure phase of sillenite structure, Bi₁₂TiO₂₀, was directly synthesized using stoichiometric bismuth (III) nitrate pentahydrate and titanium glycolate by coprecipitation. The influence of pH on the structure of Bi₁₂TiO₂₀ was studied in the pH range of 3-10. Photo-degradation reaction of 4-nitrophenol (4-NP) was used to study photocatalytic activity of Bi₁₂TiO₂₀ as a function of the pH. The rate of decomposition was followed using UV-vis and TOC. The initial concentration of 4-NP, 44 ppm, was decreased to less than 1 ppm within 30 min for all prepared catalysts. It was found that the decomposition rate constant of Bi₁₂TiO₂₀ is six times higher than those of either TiO₂ or Bi₂O₃ under the same conditions.

บทคัดย่อ

นพพร ธนบดีกิจ : การสังเคราะห์และศึกษาสมบัติของสารเร่งปฏิกิริยา ไททาเนียม/โมลิบดีนัมบนตัวรองรับ MCM-41 และสารเร่งปฏิกิริยาบิสมาทไททาเนต ($\text{Bi}_{12}\text{TiO}_{20}$) (Synthesis of Ti/Mo-MCM-41 and $\text{Bi}_{12}\text{TiO}_{20}$ and Their Activities) อ. ที่ปรึกษา : รศ. ดร. สุจิตรา วงศ์เกษมจิตต์ และ ศ. ดร. เออร์โดแกน กุลาริ 133 หน้า ISBN 974-9937-34-1

สารประกอบประเภทโลหะแอลคอกไซด์เป็นสารประกอบที่น่าสนใจ เนื่องจากมีสมบัติของการไฮโดรไลซ์ซึ่งสามารถใช้ได้ในกระบวนการโซล-เจล โซลาเทรนเป็นสารที่สังเคราะห์ได้จากซิลิกาและไตรเอทานอลามีน มีความเสถียรต่อการไฮโดรไลซ์ จึงถูกนำมาใช้เป็นสารตั้งต้นในการสังเคราะห์สารรองรับ MCM-41 ที่อุณหภูมิต่ำ โดยใช้สารตั้งผิวชนิดประจุบวก ได้แก่ CTAB ซึ่งจะทำให้โครงสร้างของ MCM-41 มีลักษณะเป็นผลึก ปัจจัยต่างๆ ที่มีผลต่อโครงสร้าง และคุณภาพของตัวรองรับ ได้แก่ ความเข้มข้นของสารตั้งผิว ความเข้มข้นของอ็อกซิเจน และอุณหภูมิของระบบ เปลี่ยนโครงสร้างและพื้นที่ผิวของผลิตภัณฑ์ที่สังเคราะห์ได้ หลังจากผ่านกระบวนการให้ความร้อน ตัวรองรับที่สังเคราะห์ได้มีพื้นที่ผิวสูงถึง 2400 $\text{m}^2/\text{กรัม}$ ขณะที่ปริมาตรของรูพรุน 1.29 $\text{ซม}^3/\text{กรัม}$ อย่างไรก็ตาม ปริมาตรของรูพรุนสามารถเพิ่มขึ้นถึง 1.72 $\text{ซม}^3/\text{กรัม}$ เมื่อพื้นที่ผิวลดลงที่ประมาณ 2100 $\text{m}^2/\text{กรัม}$ ในงานวิจัยนี้ ได้นำเอา MCM-41 มาใช้เป็นสารรองรับโลหะทรานซิชัน ไททาเนียม และโมลิบดีนัม โดยใช้ไททาเนียม ไกลโคเลต และโมลิบดีนัม ไกลโคเลต เป็นสารตั้งต้น ผลการศึกษาพบว่า ไททาเนียมสามารถเข้าร่วมในโครงสร้างของสารรองรับได้ถึง 35% โดยใช้อุณหภูมิที่ 60 และ 80 องศาเซลเซียส ในการสังเคราะห์ ในส่วนของโลหะโมลิบดีนัมบน MCM-41 จากการศึกษาพบว่า โมลิบดีนัมมีการกระจายตัวสูงโดยลักษณะโครงสร้างรูพรุนแบบหกเหลี่ยมยังปรากฏให้เห็นแม้ว่าปริมาณของโลหะโมลิบดีนัมจะสูงถึง 0.265 กรัมต่อ MCM-41 1 กรัม ผลของการศึกษาปฏิกิริยาการเติมโบรมีน โดยใช้ฟีนอลเรดเป็นสารตั้งต้นของสารเร่งปฏิกิริยาทั้งสองชนิดพบว่า สารละลายสีแดงของฟีนอลเรดเปลี่ยนเป็นสารละลายสีน้ำเงินของโบรมิโนฟีนอลบลูเมื่อเกิดปฏิกิริยาการเติมหมู่โบรมีน นอกจากนี้ ได้ศึกษาการเตรียมสารเร่งปฏิกิริยา บิสมาทไททาเนต ($\text{Bi}_{12}\text{TiO}_{20}$) โดยใช้สารประกอบไททาเนียมไกลโคเลตตกตะกอนร่วมกับบิสมาทไนเตรต เพนตะไฮเดรต สารเร่งปฏิกิริยาชนิดนี้ใช้ในการศึกษาการสลายสารอินทรีย์ประเภทไนโตรฟีนอลด้วยแสง และพบว่า สามารถสลาย 4-ไนโตรฟีนอลให้มีความเข้มข้นต่ำกว่า 1 ในล้านส่วนภายในระยะเวลา 30 นาที ค่าคงที่ของอัตราการสลายสูงกว่าไททาเนีย หรือบิสมาทออกไซด์ประมาณ 6 เท่า

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ABBREVIATIONS

TEA	Triethanolamine
EG	Ethylene Glycol
CTAB	Cetyltrimethylammonium Bromide
HEPES	4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid
TETA	Triethylenetetramine
FTIR	Fourier Transform Infrared Spectroscopy
TGA	Thermogravimetric Analysis
XRD	X-ray Diffractometer
TEM	Transmission Electron microscope
DRUV	Diffuse Reflectance Ultraviolet Spectroscopy
EDS	Energy Dispersive X-ray Analysis
XRF	X-ray Fluorescence Spectroscopy
CMC	Critical Micelle Concentration