

**MFI ZEOLITE SYNTHESIS VIA SOL-GEL PROCESS WITH MICROWAVE
TECHNIQUE AND APPLICATION AS OXIDATIVE DEHYDROGENATION
CATALYST**

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for the Degree of Doctor of Philosophy
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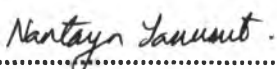
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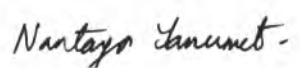
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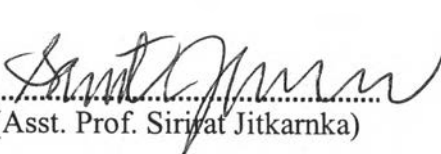
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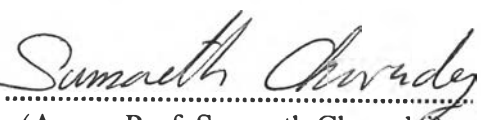

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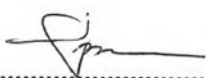

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ABSTRACT

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Silatrane and alumatrane were prepared via the oxide one-pot synthesis process and used as precursors for synthesis of MFI zeolite family, i.e., silicalite, ZSM-5 and VS-1. Numerous synthetic factors including chemical composition and conditions were investigated to understand role of individual factors on zeolite morphology and elemental composition. Different templates produce different morphologies and growth directions of MFI crystals due to the steric effect of the template molecule. Morphology of synthesized zeolite is also altered by water content. Various factors, influencing the VS-1 zeolite properties, were investigated. Using the novel silatrane precursor, VS-1 zeolites with high vanadium loading can be prepared via hydrothermal synthesis. The influence of VS-1 zeolite synthesis parameter from silatrane precursor on the catalytic properties in oxidative dehydrogenation has been studied. Propane conversion increases as increasing vanadium content while selectivity slightly decreases. Tetrahedral vanadium within zeolite is believed to be responsible for the selectively oxidative dehydrogenation while the extrinsic vanadium or polymeric species are responsible for over oxidation, selectively giving high carbon monoxide and carbon dioxide. A shorter contact time gives higher product yield and conversion though lower in selectivity.

บทคัดย่อ

ไพรัตน์ พิริยวิรุฒม์ : การสังเคราะห์ซีโอไลต์ประเภทเอมเอฟไอโดยกระบวนการโซลเจลด้วยการใช้เทคนิคไมโครเวฟ และการประยุกต์ใช้ในปฏิกิริยาออกซิเดทีฟดีไฮโดรจีเนชัน (MFI Zeolite Synthesis via Sol-Gel Process with Microwave Technique and Application as Oxidative Dehydrogenation Catalyst) อ. ที่ปรึกษา : รองศาสตราจารย์ ดร. สุจิตรา วงศ์เกษมจิตต์, ศาสตราจารย์ ดร. อเล็กซานเดอร์ เอ็ม เจมิสัน, รองศาสตราจารย์ ดร. รัตนวรรณ มกรพันธ์ และ ผู้ช่วยศาสตราจารย์ ดร. ศิริรัตน์ จิตการคำ 133 หน้า ISBN 974-9651-78-2

สารประกอบไซลาเทรน และอลูมาเทรน ถูกสังเคราะห์ได้ด้วยกระบวนการสังเคราะห์ออกไซด์วันพอท และนำมาใช้เป็นสารตั้งต้นในการสังเคราะห์ซีโอไลต์ที่มีโครงสร้างจำพวกเอมเอฟไอ ได้แก่ ลิลิกาไลต์ แซทเอสเอ็มเอฟพี และ วีเอสวัน มีการศึกษาปัจจัยต่างๆ ทั้งทางด้านองค์ประกอบ และภาวะของการสังเคราะห์ว่าจะมีผลอย่างไรต่อลักษณะและสมบัติของผลึกทางเคมีของซีโอไลต์ที่สังเคราะห์ได้ ลักษณะที่ต่างกันของสารแม่แบบยังมีผลต่อลักษณะของผลึกซีโอไลต์ที่ได้ ซึ่งเป็นผลจากการเบียดบังกันของสารแม่แบบเมื่อปรากฏอยู่ในโครงสร้างของซีโอไลต์ และยังพบว่า การเปลี่ยนแปลงปริมาณของน้ำในการสังเคราะห์ส่งผลต่อลักษณะของผลึกซีโอไลต์เช่นกัน และได้มีการศึกษาปัจจัยต่างๆ ที่มีผลต่อการสังเคราะห์วีเอสวันซีโอไลต์เช่นกัน การใช้สารตั้งต้นประเภทไซลาเทรนนั้นพบว่า สามารถเตรียมสารวีเอสวันโดยมีวานาเดียมในโครงสร้างสูงได้ ในการทดสอบสมบัติทางด้านการทำปฏิกิริยาของวีเอสวันซีโอไลต์ด้วยปฏิกิริยาออกซิเดทีฟดีไฮโดรจีเนชันพบว่า ปฏิกิริยาของสารตั้งต้น โพรเพนเกิดเพิ่มขึ้นเมื่อมีปริมาณวานาเดียมในซีโอไลต์เพิ่มขึ้น โดยที่ความจำเพาะของปฏิกิริยาที่ให้ผลิตภัณฑ์โพรพิลลดลงเล็กน้อยพบว่าวานาเดียมในสภาวะที่มีสัญญาณของอะตอมในแบบเตตระฮีดรอลน่าจะมีความจำเพาะเจาะจงในปฏิกิริยาออกซิเดทีฟดีไฮโดรจีเนชัน ที่ให้ออกไซด์ของคาร์บอนเป็นผลิตภัณฑ์มากกว่าวานาเดียมอะตอมในแบบออกเตฮีดรอล นอกจากนี้ การทดลองยังพบว่า การปรับแต่งอัตราเร็วไหลผ่านของแก๊สมีผลต่อความจำเพาะเจาะจงของปฏิกิริยาเช่นกัน ระยะเวลาที่สั้นลงของปฏิกิริยาจะช่วยให้ผลิตภัณฑ์มีความจำเพาะเจาะจงมากขึ้น แต่จะทำให้มีการเกิดปฏิกิริยาของสารตั้งต้นลดลง

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ABBREVIATIONS

Al-TIS	Alumatrane
DR-UV	Diffuse Reflectance Ultraviolet-Visible Spectroscopy
EDX or EDS	Energy Depressive X-ray Spectroscopy
EG	Ethylene Glycol
ESR	Electron Spinning Resonance Spectroscopy
EPR	Electron Paramagnetic Resonance Spectroscopy
FAB ⁺ -MS	Fast Atomic Bombardment Mass Spectroscopy
FTIR	Fourier Transform Infrared Spectroscopy
MFI	Mobile Five (Material code refer to ZSM-5 topology)
ODH	Oxidative Dehydrogenation
OOPS	Oxide One Pot Synthesis
SEM	Scanning Electron Microscope
Si-NMR	Silicon Nuclear Magnetic Resonance Spectroscopy
Si-TEA	Silatrane
STA	Simultaneous Thermal Analysis
TBA	Tetra Butyl Ammonium
TEA	Triethanolamine
TEOS	Tetraethyl Ortho Silicate
TGA	Thermal Gravimetric Analysis
TIS	Tri-isopropanolamine
TPA	Tetra Propyl Ammonium
TPABr	Tetra Propyl Ammonium Bromide
TPAOH	Tetra Propyl Ammonium Hydroxide
TPD	Temperature Program Desorption
TPO	Temperature Program Oxidation
TPR	Temperature Program Reduction
TS-1	Titanium-silicalite
VS-1	Vanadium-silicalite
XRD	X-ray Diffraction Spectroscopy
XRF	X-ray Fluorescence Spectroscopy