UTILIZATION OF METHANE: METHYLATION OF BENZENE WITH METHANE AND GAS-TO-LIQUIDS (GTL) VIA FISCHER-TROPSCH SYNTHESIS

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ABSTRACT

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During the past decades, studies on the conversion of methane, a main component of natural gas, into more valuable fuels or chemicals have received much attention. This is because liquid-petroleum reserves are becoming scarcer, while natural gas (e.g., methane) reserves are abundant; moreover, methane can be generated by fermentation of organic materials. Previously, methane was predominantly used for heating, in both industry and in households. Once the gas-to-liguids (GTL) technology for the conversion of methane into higher valued liquid products (e.g., gasoline, diesel, and methanol) was accomplished, it has largely inspired many researchers to widen research in this area by either developing a new approach of utilizing methane or improving the performance of existing technologies. In this thesis, the work is divided into two parts. First, methylation of benzene with methane, a novel and challenging approach is aimed at directly using methane as an alkylating agent to react with the benzene ring into methylated product, especially xylenes, in a one-step process. Ag/HZSM-5 and Mo/HZSM-5 were studied as catalysts. The second study was on the heart of GTL technology, Fischer-Tropsch synthesis, a reaction to produce long chain hydrocarbons, which can be hydrocracked to produce gasoline, diesel, jet fuels, and waxes, from synthesis gas derived from methane/natural gas. The capability of some transition metals as metal promoters for Co/Al_2O_3 Fischer-Tropsch catalyst was demonstrated. Moreover, reoxidation of tiny cobalt crystallite at the onset of the reaction was explored and proposed as one of the modes of catalyst deactivation for very small nanocrystallites.

บทคัดย่อ

ธานี เจิมวงค์รัตนชัย : การใช้ประโยชน์จากก๊าซมีเทนด้วยวิธีการเติมหมู่เมทิลบนสารเบนซีนโดยใช้ก๊าซมีเทนและการเปลี่ยนก๊าซมีเทนให้เป็นสารไฮโดรคาร์บอนในสถานะของเหลวโดยใช้ปฏิกิริยาสังเคราะห์ฟิชเชอร์-โทรปช์ (Utilization of Methane: Methylation of Benzene with Methane and Gas-to-Liquids (GTL) via Fischer-Tropsch Synthesis) อาจารย์ที่ปรึกษา : ผศ. ดร. บุนยรัชต์ กิติยานันท์ ศ. ดร. เบอตัน เดวิส และ ดร. แกรี จาคอบส์ 235 หน้า

ในช่วงระยะเวลาสิบปีที่ผ่านมา มีการศึกษาการเปลี่ยนก๊าซมีเทนไปเป็นน้ำมันเชื้อเพลิงและสารเคมีชนิดอื่นที่มีมูลค่าสูงขึ้นกันอย่างกว้างขวาง เนื่องจากแหล่งน้ำมันดิบเริ่มมีปริมาณลดลง ในขณะที่แหล่งก๊าซธรรมชาติซึ่งมีก๊าซมีเทนเป็นองค์ประกอบหลักยังมีในปริมาณมากและก๊าซมีเทนยังสามารถผลิตได้จากกระบวนการหมักสารอินทรีย์ ในอดีตก๊าซมีเทนถูกใช้เป็นสารเชื้อเพลิงในภาคอุตสาหกรรมและภาคครัวเรือนเป็นหลัก นับตั้งแต่เทคโนโลยีการเปลี่ยนก๊าซเป็นของเหลว (Gas-to-Liquids (GTL) technology) ได้ถูกพัฒนาขึ้น จึงเริ่มมีการตื่นตัวในการศึกษาวิจัยการเพิ่มมูลค่าก๊าซมีเทนกันมากขึ้น ทั้งการคิดค้นเทคโนโลยีใหม่เพื่อเพิ่มมูลค่าก๊าซมีเทนและการพัฒนาปรับปรุงประสิทธิภาพเทคโนโลยีเดิม ตัวอย่างเช่น เทคโนโลยีฟิชเชอร์-โทรปช์ โดยในงานวิจัยนี้ผู้วิจัยได้ทำการศึกษาวิจัยในสองแนวทางดังกล่าว ได้แก่ 1. การคิดค้นเทคโนโลยีใหม่ โดยศึกษาปฏิกิริยาการเติมหมู่เมทิลบนวงแหวนเบนซีนโดยใช้ก๊าซมีเทน (Methylation of Benzene with Methane) เพื่อให้ได้สารเคมีที่มีมูลค่าสูงขึ้น เช่น พาราไซลีน โดยงานวิจัยนี้ได้มุ่งเน้นไปที่การใช้ตัวเร่งปฏิกิริยาและการปรับสภาวะปฏิกิริยา 2. การวิจัยเพื่อพัฒนาประสิทธิภาพของตัวเร่งปฏิกิริยาสำหรับปฏิกิริยาสังเคราะห์ฟิชเชอร์-โทรปช์ (Fischer-Tropsch synthesis) ซึ่งเป็นปฏิกิริยาการผลิตสารไฮโดรคาร์บอนโซ่ยาวจากก๊าซสังเคราะห์ (synthesis gas) ที่ได้มาจากก๊าซมีเทน ในงานวิจัยได้ศึกษาการใช้โลหะแทรนซิชันเป็นสารเพิ่มประสิทธิภาพของตัวเร่งปฏิกิริยาชนิด โคบอลต์บนตัวรองรับอะลูมินา (Co/Al_2O_3) นอกจากนี้งานวิจัยยังได้เสนอสาเหตุของการเสื่อมประสิทธิภาพของตัวเร่งปฏิกิริยา ณ ขณะเริ่มต้นปฏิกิริยาอันเนื่องมาจากปฏิกิริยาออกซิเดชันของโลหะโคบอลต์ที่มีขนาดเล็ก ซึ่งการค้นพบดังกล่าวนี้จะเป็นประโยชน์สำหรับการพัฒนาตัวเร่งปฏิกิริยาชนิดนี้ต่อไป

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ABBREVIATIONS

Ag	Silver
$Ag_n^{\delta+}$	Silver Cationic Cluster
Al_2O_3	Aluminium Oxide or Alumina
ATR	Autothermal Reforming
Au	Gold
BET	Brunauer, Emmett, and Teller
C_6H_6	Benzene
Calgon	Calgon Carbon
Car-	Carburized
CH_4	Methane
Co	Cobalt
Co_3O_4	Cobalt (II,III) oxide
$CoAl_2O_4$	Cobalt Aluminate
CoO	Cobalt (II) oxide
CPO	Catalytic Partial Oxidation
EXAFS	Extended X-ray Absorption Fine Structure
F.C.C.	Faced Center Cubic
FID	Flame Ionization Detector
FT	Fischer-Tropsch
FTS	Fischer-Tropsch Synthesis
GTL	Gas-to-Liquids
H^+	Proton
Ir	Iridium
LC	Linear Combination (fitting)
Mo	Molybdenum
Mo_2C	Molybdenum Carbide
OR	Oxidation-reduction
Oxi-	Oxidized
Pt	Platinum
Re	Rhenium

Red-	Reduced
Rh	Rhodium
Ru	Ruthenium
SiO_2	Silicon oxide or Silica
SMR	Steam Methane Reforming
TCD	Thermal Conductivity Detector
TPO	Temperature-Programmed Oxidation
TPR	Temperature-Programmed Reduction
TPR-EXAFS	Temperature Programmed Reduction- Extended X-ray Absorption Fine Structure
TPR-XANES	Temperature Programmed Reduction- X-ray Absorption Near Edge Structure
UV-Vis DRS	Ultraviolet-Visible Diffuse Reflectance Spectroscopy
WHSV	Weight Hourly Space Velocity
XANES	X-ray Absorption Near Edge Structure
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction Spectroscopy
XRF	X-ray Fluorescence Spectroscopy

LIST OF SYMBOLS

$\mathring{A}$	Angstrom
B_d	Angle width of peak
D_h	Mean crystalline diameter
$\Delta H°_0$	Standard enthalpy at reference conditions
$\Delta S°_0$	Standard entropy at reference conditions
$\Delta G°_0$	Standard Gibb free energy at reference conditions
K	Scherrer constant
λ	X-ray wavelength
θ	Bragg angle of the reflection (degree or radian)
K_a	The equilibrium constant
f_i	Fugacity of the species i
P	System pressure
T	System temperature
C_p	Heat capacity
ε	Extent of the reaction
S^2_0	The amplitude reduction factor
n_i	Fractional coordination
α	Isotropic expansion coefficient
σ^2	The Debye-Waller factor