PREPARATION AND CHARACTERIZATION OF H_3PO_4-MODIFIED CERIUM OXIDE CATALYSTS FOR ETHYLENE PRODUCTION FROM ETHANOL DEHYDRATION

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SUPERVISOR'S DECLARATION

I hereby declare that I have checked this thesis and in my opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Master of Science in Chemical Engineering.

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STUDENT'S DECLARATION

I hereby declare that the work in this thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at Universiti Malaysia Pahang or any other institutions.

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Thesis submitted in fulfillment of the requirements
for the award of the degree of
Master of Science

Faculty of Chemical & Natural Resources Engineering

UNIVERSITI MALAYSIA PAHANG

MARCH 2017

ACKNOWLEDGEMENTS

I would like to express my deepest gratitude to my supervisor, Assoc. Prof. Dr. Cheng Chin Kui for his guidance. In addition, I am also truly indebted to the Department of Research and Innovation, Universiti Malaysia Pahang for providing internal research grant, RDU160335 that goes directly into the financing of this project.

My sincere thanks also go to my lovely parents who support my decision to do a master degree.

Last but not least, gratitude to all my lab mates and members of the staff in the Faculty of Chemical and Natural Resources Engineering, Universiti Malaysia Pahang for the assistance that has eased my research journey.

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LIST OF SYMBOLS

θ	Angle
$Å$	Angstrom
N	Avogadro's constant
E_b	Binding energy
s	Cross-sectional area of N_2
D	Crystallite size
$X_{ethanol}$	Conversion
R	Correlation coefficient
°	Degree
C	Dimensionless constant of adsorbate
a	Effective cross-sectional area of one adsorbate molecule
v	Frequency of the exciting radiation
γ	Gamma
$\Delta G°$	Gibbs free energy
$\Delta H_f°$	Heat of formation
n	Integer for the order of reflection
d	Interplanner spacing of crystalline solid
E_k	Kinetic energy
β_d	Line broadening
g	Mass of catalyst
m	Mass of solid catalyst
F	Molar flow rate
V	Molar volume of N_2
P	Partial vapor pressure of absorbate gas
h	Planck's constant
k_{Sch}	Scherrer constant

S_i	Selectivity
vm	Volume of gas absorbed at STP to monolayer coverage
Va	Volume of gas adsorbed at standard temperature and pressure (STP)
φ	Work function of the spectrometer
Y_i	Yield

LIST OF ABBREVIATIONS

10PA-CeO_2	10wt%H_3PO_4 modified cerium oxide
20PA-CeO_2	20wt%H_3PO_4 modified cerium oxide
30PA-CeO_2	30wt%H_3PO_4 modified cerium oxide
BET	Bruneur-Emmet-Teller
BJH	Barret-Joyner-Halenda
Cf.	Confer
DEE	Diethyl ether
FBR	Fixed bed reactor
FID	Flame ionizer detector
FTIR	Fourier transform infrared unit
GC	Gas chromatography
H-FER	H-ferrierite zeolite
HM90	H-mordenites 90
HPLC	High-performance liquid chromatography
H_3PO_4/CeO_2	Phosphorus modified cerium oxide
IUPAC	International Union of Pure and Applied Chemistry
LCD	Liquid crystal display
LED	Light-emitting diode
MTO	Methanol to olefins process
OCM	Oxidation coupling of methane
OD	Outer diameter
PET	Polyethylene terephthalate
PROX	Preferential oxidation of a gas
PS	Polystyrene
PVC	Polyvinyl chloride
SAPO	Silicoaluminaphosphate

SEM	Scanning electron microscopy
STP	Standard condition for temperature and pressure
REE	Rare earth elements
REO	Rare earth oxide
TCD	Thermal conductivity detector
TGA	Thermogravimetric analysis
$TiO_2/\gamma Al_2O_3$	Titanium dioxide doped gamma alumina
TPD	Temperature programmed desorption
VCM	Vinyl chloride monomer
VOCs	Volatile organic compounds
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray diffraction
WGS	Water gas shift
WHSV	Weight hourly space velocity
ZSM-5	Zeolite socony mobil-5

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ABSTRAK

Penghasilan etena daripada dehidrasi etanol menawarkan suatu proses alternatif untuk mengurangkan kebergantungan proses semasa kepada bahan bakar minyak bumi yang terhad sumbernya. Kajian dalam bidang dehidrasi etanol sebelum ini lebih menjurus kepada masalah pembentukan karbon di dalam pemangkin. Untuk mengurangkan pembentukan karbon dan bagi mengkaji penggunaan pemangkin baru untuk dehidrasi etanol, serium oksida dan juga serium oksida yang telah diubah dengan H_3PO_4 telah diuji sebagai pemangkin dehidrasi berasaskan sifat kealkaliannya serta sifat anti-karbon. Penghasilan pemangkin yang berasaskan CeO_2 dan juga CeO_2 diubah dengan H_3PO_4 adalah melalui kaedah pengisitepuan dengan formula 10, 20 dan 30 peratus berat H_3PO_4. Tujuan penyelidikan ini adalah untuk mengkaji pengaruh muatan H_3PO_4, suhu tindakbalas kimia dan tekanan separa etanol dalam dehidrasi etanol didalam kehadiran cerium oksida dan cerium oksida yang diubah dengan H_3PO_4. Beberapa analisa seperti BET, XRD, XPS, TGA, SEM dan EDX telah dijalankan untuk mengetahui sifat fizikal dan sifat kimia pemangkin. Tindakbalas dehidrasi etanol dengan pemangkin yang telah disediakan dilakukan di dalam reaktor pada julat suhu 673 – 773 K dan tekanan separa etanol daripada 16–67 kPa. Analisis XRD menunjukkan pencirian pemangkin mengecil di atas pengaruhi muatan H_3PO_4. Kajian BET mendapati luas permukaan pemangkin dan isipadu keseluruhan liang berkurangan dengan muatan H_3PO_4. Hampir 90% pengurangan dikesan untuk 30PA-CeO_2. Di samping itu, analisis NH_3-TPD menunjukkan bahawa 30PA-CeO_2 mempunyai jumlah asid tertinggi, dimana majoritinya ialah asid jenis sederhana kuat. Kajian kinetik menunjukkan bahawa CeO_2 tulen menawarkan hasil pemangkinan yang paling rendah, manakala pemangkin H_3PO_4-cerium oksida menawarkan hasil uji pemangkinan yang tinggi (12-65.8% penukaran) dan penghasilan etena yang tinggi (37-99%). Secara keseluruhan, kedudukan dari segi hasil uji katalitik adalah: 30PA-CeO_2 > 20PA-CeO_2 > 10PA-CeO_2 > CeO_2. Penukaran etanol dan penghasilan etena yang tertinggi adalah sejumlah 65.8% dan 99% untuk pemangkin 30PA-CeO_2. Modifikasi H_3PO_4 terhadap pemangkin CeO_2 berjaya meningkatkan aktiviti pemangkin CeO_2 terhadap dehidrasi etanol.

ABSTRACT

Ethylene production from ethanol dehydration offers an alternative synthesis route to the current synthesis route that is heavily dependent on the finite fossil fuel. Previous research works on ethanol catalytic dehydration focused the issue of catalyst coke formation. To minimize carbon deposition and to search for new ethanol dehydration catalyst, cerium oxide and H_3PO_4 were employed as dehydration catalysts owing to its coke-resistance as well as acidity properties. The objectives of this study are to investigate the effects of H_3PO_4 loading, reaction temperature and partial pressure on the catalytic performance on ethanol dehydration over cerium oxide and phosphorus-modified cerium oxide catalysts. New catalysts were employed for this reaction. For the modified catalysts, the wet impregnation technique was employed to prepare phosphorus modified cerium oxides with 10, 20 and 30 wt% of H_3PO_4 loadings. Subsequently, physicochemical properties were obtained through BET, XRD, XPS, TGA, SEM dan EDX analysis. The ethanol catalytic dehydration over the as-synthesized catalysts were carried out in a fixed-bed reactor at temperatures that ranged 673 to 773 K and 16 to 67 kPa of ethanol partial pressure. The XRD profiles showed that as the phosphorus loading was increased, the crystallinity has reduced. Both the BET specific surface area and mesopore volume decreased with H_3PO_4 loading, to the tune of nearly 90% reduction for the 30wt%H_3PO_4 loading. Significantly, the acid strength from the NH_3-TPD analysis showed that 30PA-CeO_2 has the highest amount of acid site which were of predominantly moderate-strength. Activity evaluation showed that the pure CeO_2 offered little activity, while the H_3PO_4-modified ceria catalysts offered high ethanol catalytic dehydration activity (12-65.8% conversion) and high selectivity to ethylene (37-99%). Overall, the ranking in terms of activity was: 30PA-CeO_2 > 20PA-CeO_2 > 10PA-CeO_2 > CeO_2. The highest ethanol conversion and ethylene selectivity achieved were 65.8% and 99%, respectively, over the 30PA-CeO_2 catalysts. The introduction of H_3PO_4 onto CeO_2 catalyst helps in improving the catalytic performance of CeO_2 for ethylene production from ethanol dehydration. In addition there was no carbon found in the spent catalysts which showed that the phosphorus modified cerium oxide catalysts have high coke resistance.

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