GLYCEROL DRY REFORMING FOR SYNGAS PRODUCTION OVER Ag-PROMOTED ON Ni-BASED CATALYSTS

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Master of Engineering

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SUPERVISOR'S DECLARATION

We hereby declare that we have checked this thesis and in our opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Master of Engineering in Chemical

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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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for the award of the degree of
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LIST OF SYMBOLS

F	Flow rate
X_G	Glycerol conversion
Y_{H2}	Hydrogen yield
Yi	Yield of Carbon containing species
λ	Wavelength
θ	Bragg angle

LIST OF ABBREVIATIONS

BET	Brunauer-Emmett-Teller
CGR	Carbon to glycerol feed ratio
FESEM-EDX	Field emission scanning microscopy/Energy dispersive X-ray
IUPAC	International Union of Pure and Applied Chemistry
OPEC	Organisation of the Petroleum Exporting Countries
SEM	Scanning electron microscopy
TGA	Thermogravimetric analysis
TPC	Temperature programmed calcination
TPD	Temperature programmed desorption
TPO	Temperature programmed oxidation
TPR	Temperature programmed reduction
WHSV	Weight hourly space velocity
XRD	X-ray diffraction

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ABSTRAK

Penggunaan gliserol telah dikaji secara meluas dan merupakan salah satu bahan mentah alternatif dalam pengeluaran gas sintetik (*syngas*). Proses tindakbalas gliserol dan CO_2 adalah satu proses yang menarik kerana ia menukarkan karbon dioksida, gas rumah hijau kepada gas sintetik dan pada masa yang sama dikeluarkan daripada kitaran karbon. Objektif utama penyelidikan ini adalah untuk mengkaji tindakbalas gliserol dan CO_2 dengan menggunakan mangkin berasaskan nikel yang ditambah logam (perak) dan logam oksida (aluminium oksida dan silikon oksida). Logam perak jarang digunakan sebagai mangkin dalam kajian pembaharuan (*reforming*). Namun, ia telah dibuktikan bahawa logam perak mempunyai kebolehan untuk mengurangkan pengumpulan karbon di permukaan mangkin dan meningkatkan hasil gas hydrogen di samping ianya lebih rendah dari segi kos berbanding logam di dalam kumpulan logam *noble* yang lain. Mangkin telah disediakan melalui kaedah pengisitepuan (*wet impregnation*) menggunakan kombinasi logam-oksida yang berbeza. Pencirian terhadap sifat mangkin telah dinilai menggunakan kaedah penjerapan fizikal N_2 (kaedah *Brunauer-Emmet-Teller* (BET)), analisis pembelauan sinar-X (XRD), mikroskop elektron pengimbasan (SEM), pengkalsinan suhu berprogram (TPC), penurunan suhu berprogram (TPR), pengoksidaan suhu berprogram (TPO), dan penyahjerapan suhu berprogram (TPD). Kajian saringan pada peringkat awal telah dijalankan untuk menilai prestasi jenis-jenis oksida yang digunakan dan didapati bahawa Ni/Al_2O_3 memberikan tindakbalas gliserol dan hasil hidrogen yang lebih tinggi berbanding Ni/SiO_2 kerana saiz kristal yang lebih kecil di atas permukaan luar mangkin dan luas permukaan yang tinggi. Selain itu, alumina boleh meningkatkan kesebatian logam serta mengelakkan pemendapan karbon dan pada masa yang sama meningkatkan aktiviti dan kestabilan mangkin. Selain itu, apabila campuran Ag yang berbeza telah ditambah kepada mangkin ini, 3wt% Ag dalam Ni/Al_2O_3 memberikan prestasi mangkin yang terbaik kerana kewujudan zarah aktif yang menyebabkan luas permukaan yang tinggi. Campuran Ag (> 3wt%) menyebabkan pembentukan zarah kecil yang menyelaputi tapak aktif mangkin dan menjejaskan prestasi mangkin. Siasatan lanjut mengenai kesan-kesan faktor lain dalam sesebuah tindak balas (iaitu suhu tindak balas, berat mangkin yang digunakan dan nisbah CO_2 kepada gliserol (CGR)) kepada pengeluaran gas sintetik telah dijalankan mengunakan mangkin yg terbaik yang diperolehi melalui ujian saringan mangkin, iaitu $Ag(3)\text{-}Ni/Al_2O_3$. Peratusan tindakbalas gliserol dan penghasilan produk yang terbaik ditemui pada suhu 1073 K, CGR 1 dan WHSV 36 L g_{cat}^{-1} h^{-1} yang memberikan 41.09% tindakbalas gliserol dan 32.31% hasil hidrogen. Tindakbalas selama 72 jam mendedahkan bahawa mangkin tersebut stabil sepanjang tempoh tersebut selepas mengalami penurunan pada jam yang kesepuluh. Selain itu, kajian terhadap mangkin yang telah digunakan dalam proses tindakbalas tersebut menunjukkan kehadiran karbon jenis yang berserabut pada permukaan mangkin, yang boleh disingkirkan melalui proses pengoksidaan.

ABSTRACT

The use of glycerol has been widely investigated and one of the possible alternatives is as a feedstock in the production of synthesis gas (syngas). The glycerol CO_2 dry reforming process is an attractive process as it converts carbon dioxide, a greenhouse gas, into a synthesis gas and simultaneously removed from the carbon biosphere cycle. The main objective of this research work is to study the process of CO_2 dry reforming of glycerol over noble catalyst i.e. a noble metal (silver) promoted on nickel-based catalyst supported on oxides (aluminium oxide and silicon oxide). Silver is rarely used as catalyst in reforming studies. However, it is proven that silver has the ability to reduce the carbon deposition and increase selectivity of hydrogen production besides lower in cost compared to other noble metal. The catalysts were formulated through wet impregnation method using different combinations of noble metal-oxides support. Their physicochemical characteristics were evaluated using nitrogen physisorption (Brunauer-Emmet-Teller (BET) method), X-ray diffraction (XRD), Scanning electron microscopy (SEM), Temperature programmed calcination (TPC), Temperature programmed reduction (H_2-TPR) and Temperature programmed desorption (TPD). The screening study was conducted to evaluate the performance of different types of supports, and it was found that Ni/Al_2O_3 catalyst series gave higher glycerol conversion and hydrogen yield compared to Ni/SiO_2 catalyst series due to their small crystallites size and high surface area. Moreover, alumina support could increase metal dispersion as well as avoiding the carbon deposition, which simultaneously improved the activity and stability of the catalyst. Apart from that, when different Ag loadings were introduced to these catalysts, 3wt% of Ag in Ni/Al_2O_3 was found to give the best catalyst performance due to the well-dispersion of active sites on the catalyst surface, which created high surface area. Higher Ag loading (>3wt%) resulted in formation of small particles, which covered the active sites of the catalyst thus impaired the catalyst performance. Further investigation on the effect of reaction variables (i.e. reaction temperature, weight hourly space velocity (WHSV) and CO_2-to-glycerol ratio (CGR)) to the production of syngas were conducted using the best catalyst obtained from the screening study. The best reaction condition was found at temperature of 1073 K, CGR of 1 and WHSV of 36 L g_{cat}^{-1} h^{-1} (catalyst loading of 0.2 g) which gave 41.09% glycerol conversion and 32.31% hydrogen yield. During the catalyst longevity study, Ag(3)-Ni/Al_2O_3 was found to stabilise along the 72 hours reaction after experiencing a reduction at tenth hour. Apart from that, the study on the catalyst deactivation of the used catalyst shows the presence of filamentous and encapsulated carbon types on the catalyst surface, which can be removed through oxidation.

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