GAS PHASE GLYCEROL DEHYDRATION TO ACROLEIN OVER SUPPORTED SILICOTUNGSTIC ACID CATALYST

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A thesis submitted in fulfilment of the
requirements for the award of the degree of
Doctor of Philosophy (Chemical Engineering)

Faculty of Chemical Engineering
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OCTOBER 2015

TO MY BELOVED WIFE AND MOTHER

ACKNOWLEDGEMENT

First of all, I would like to thank Allah for giving me the strength, perseverance and intention to go through and complete my study.

I would like to express my sincere gratitude to my respected supervisor Prof. Dr. Nor Aishah Saidina Amin for her help, support, and guidance. I owe her a lot for what she taught me during these years. Without her valuable guidance this study could never have reached its completion.

Last but not least, I wish to express my deepest gratitude and love for my beloved family members especially my wife, mother, father and mother-in-law, and brother for their utmost support, patience and understanding throughout my PhD study.

ABSTRACT

Due to the various environmental concerns, a steep hike in fossil fuel price and an increasing demand of non-renewable fossil fuels consumption, the bio-based gas-phase dehydration of glycerol to acrolein has attracted much attention recently. Thus, the gas phase dehydration of glycerol to acrolein over two groups of supported silicotungstic acid on aluminum oxide (Al_2O_3) nanoparticle and zirconium dioxide catalyst is being investigated in this study. The catalysts were characterized by, X-ray diffraction, Fourier transform infrared spectroscopy, field-emission scanning electron microscopy and energy dispersive X-ray techniques, temperature programmed desorption, thermogravimetric analysis, and elemental analyzer. The characterization results revealed that Al_2O_3 nanoparticle loading increased thermal stability, pore diameter, and specific surface area of the synthesized catalysts. Optimization by response surface methodology revealed the highest acrolein selectivity of 88.5% at 97% glycerol conversion was obtained over 30HZ-20A catalyst with turnover frequency being 136 h^{-1} in 3 h for glycerol feed concentration of 10.3 wt% and 0.5 g catalyst at 300 ˚C. Coke deposition has no significant effect on the catalyst activity due to the large catalyst pore diameter (> 27 nm). The prepared catalysts were highly active and selective for acrolein production even after 40 h without any needs for gas co-feeding or application of noble metals. In addition, the kinetic study results demonstrated that glycerol dehydration to acrolein followed first-order rate with the activation energy (Ea) of 27.5 kJ/mol and frequency factor (A) of 5.35×10^5 s^{-1}. Finally, the theoretical and experimental approaches confirmed no internal mass transfer limitation in glycerol dehydration reaction with catalyst pellet sizes of d_p= 2-4 and 5-7 µm due to effectiveness factor equal to 1 (η=1). Calculation of the overall effectiveness factor (Ω) also confirmed the absence of external diffusion in presence of catalysts with pellet size of d_p< 7 µm.

ABSTRAK

Disebabkan oleh pelbagai kebimbangan terhadap alam sekitar, peningkatan mendadak harga bahan api fosil dan peningkatan permintaan penggunaan bahan api fosil tidak boleh diperbaharui, penyahhidratan fasa gas gliserol kepada akrolein berdasarkan bahan bio telah menarik perhatian ramai baru-baru ini. Oleh itu, penyahhidratan fasa gas gliserol kepada akrolein menggunakan dua kumpulan asid silikotungstik yang disokong oleh partikel nano aluminum oksida (Al_2O_3) dan pemangkin zirkonium dioksida telah dikaji dalam kajian ini. Pemangkin-pemangkin dicirikan dengan menggunakan teknik pembelauan sinar-X, spektroskopi inframerah transfromasi Fourier, mikroskop elektron imbasan pemancaran medan dan sebaran tenaga sinar-X, penyaherapan suhu berprogram, analisis termogravimetrik, dan penganalisis unsur. Keputusan pencirian menunjukkan bahawa muatan partikel nano Al_2O_3 menunjukkan kestabilan terma, diameter liang, dan luas permukaan spesifik bagi pemangkin yang disintesis. Pengoptimuman oleh kaedah tindak balas permukaan menunjukkan kepilihan akrolein tertinggi iaitu 88.5% pada penukaran gliserol 97% telah diperoleh menggunakan pemangkin 30HZ-20A dengan frekuensi pusingan balik 136 h^{-1} dalam tempoh 3 jam bagi kepekatan suapan gliserol 10.3 wt% dan pemangkin 0.5 g pada 300 °C. Pengenapan kok tidak mempunyai kesan signifikan terhadap aktiviti pemangkin disebabkan oleh diameter liang pemangkin yang besar (> 27 nm). Pemangkin yang disediakan adalah sangat aktif dan selektif bagi penghasilan akrolein walaupun setelah 40 jam tanpa sebarang keperluan untuk penyuapan bersama gas atau aplikasi logam adi. Di samping itu, keputusan kajian kinetik menunjukkan penyahhidratan gliserol kepada akrolein mengikut kadar tertib pertama dengan tenaga pengaktifan (Ea) 27.5 kJ/mol dan faktor kekerapan (A) 5.35×10^5 s^{-1}. Akhir sekali, pendekatan teori dan eksperimen mengesahkan tiada pengehadan pemindahan jisim dalaman bagi tindak balas penyahhidratan gliserol dengan saiz pelet pemangkin d_p= 2-4 dan 5-7 µm disebabkan oleh faktor keberkesanan adalah bersamaan dengan 1 (η=1). Pengiraan faktor keberkesanan keseluruhan (Ω) juga mengesahkan ketiadaan peresapan luaran dalam kehadiran pemangkin dengan saiz pelet d_p< 7 µm.