

DESIGN AND OPTIMIZATION OF LANTHANIDE OXIDES BASED  
CATALYSTS FOR CARBON DIOXIDE METHANATION

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## ABSTRACT

The Malaysian crude natural gas contains toxic and acidic gases such as carbon dioxide, CO<sub>2</sub> (20-30%), and hydrogen sulfide, H<sub>2</sub>S (0-1%), therefore it should be treated. The current gases treatment process including chemical solvents, adsorption process using hybrid solvents and membrane failed to meet the processing requirement. Instead, catalysts used for the CO<sub>2</sub> methanation have been extensively studied and high potential towards converting CO<sub>2</sub> gas to methane. In this research, a series of lanthanide oxide based catalysts supported on alumina and doped with manganese and ruthenium were prepared by wetness impregnation method. The lower performance of monometallic and bimetallic oxide catalysts have steered the exploration of trimetallic oxide catalyst. The potential trimetallic oxide catalysts were calcined at 400°C, 700°C, and 1000°C for 5 hours separately. In-home-built micro reactor, Fourier transform infrared (FTIR) spectroscopy and gas chromatography analysis (GC) were used to study the catalytic performance by determining the percentage of CO<sub>2</sub> conversion and also the percentage of CH<sub>4</sub> formation. From the catalytic screening, it was found that the catalysts with Ru/Mn/Ce (5:35:60)/Al<sub>2</sub>O<sub>3</sub> calcined at 700°C, and Ru/Mn/Sm (5:35:60)/Al<sub>2</sub>O<sub>3</sub> calcined at 1000°C achieved 100% CO<sub>2</sub> conversion, Ru/Mn/Pr (5:30:65)/Al<sub>2</sub>O<sub>3</sub> calcined at 800°C achieved 96% CO<sub>2</sub> conversion were potential catalysts. The active species in the methanation reaction for each catalyst were MnO<sub>2</sub>, and RuO<sub>2</sub> and CeO<sub>2</sub> or Sm<sub>2</sub>O<sub>3</sub> or Pr<sub>2</sub>O<sub>3</sub> respectively. Using two series furnace reactors, all three potential catalysts showed the increasing of CH<sub>4</sub> formation. For optimization, the parameters studied were calcination temperatures, based loadings, and catalyst dosage. The optimization was done by using response surface methodology (RSM) with Box-Behnken design which showed the significant parameters and optimum result of cerium with calcination temperature of 697.47°C, based metal ratio of 60.38% and catalyst dosage 6.94 g as suggested by RSM. This result was tested and verified experimentally with difference of only 1%. X-rays diffraction analysis showed that the catalysts imposed an amorphous phase, while field emission scanning electron microscopy illustrated the catalyst surface was covered with small and dispersed particles with undefined shape. From electron dispersive X-rays analysis revealed that there were a reduction of Ru in the used catalyst compared to the fresh catalyst for each potential catalysts. Nitrogen gas adsorption showed that the catalysts were mesoporous structure with type H3 hysteresis loop and Type IV isotherm. Electron spin resonance spectrum showed a free electron interaction due to the presence of the peak for each potential catalyst. Temperature programmed reduction analysis of Ru/Mn/Ce (5:35:60)/Al<sub>2</sub>O<sub>3</sub> catalyst showed more reducible species compared to catalysts containing Sm and Pr due to the presences of more reduce species at lower reduction temperature. The postulated methanation reaction follows the Langmuir Hinselwood mechanism which initially involves adsorption of CO<sub>2</sub> and H<sub>2</sub> gases on the catalyst surface. For Ru/Mn/Ce (5:35:60)/Al<sub>2</sub>O<sub>3</sub> and Ru/Mn/Sm (5:35:60)/Al<sub>2</sub>O<sub>3</sub> catalysts the product obtained were CH<sub>4</sub>, CH<sub>3</sub>OH and H<sub>2</sub>O. Meanwhile, for Ru/Mn/Pr (5:30:65)/Al<sub>2</sub>O<sub>3</sub> catalyst only CH<sub>4</sub> and H<sub>2</sub>O were observed as a products of the reaction. Lastly, the spent catalysts were successfully regenerated by running under O<sub>2</sub> flow at 100°C for 1 hour.

## ABSTRAK

Gas asli mentah Malaysia mengandungi gas toksik dan berasid seperti dioksida, CO<sub>2</sub> (20-30%), dan hidrogen sulfida, H<sub>2</sub>S (0-1%). Oleh itu, ia perlu dirawat. Pada masa kini, proses rawatan gas termasuk pelarut kimia, proses penjerapan menggunakan pelarut hibrid dan membran gagal memenuhi keperluan pemprosesan. Sebaliknya, mangkin yang digunakan untuk metanasi CO<sub>2</sub> telah dikaji secara meluas dan mempunyai potensi yang tinggi untuk menukarkan gas CO<sub>2</sub> kepada metana. Dalam kajian ini, satu siri mangkin berasaskan lantanida oksida disokong pada alumina dan didopkan dengan mangan dan rutenium telah disediakan dengan kaedah pengisitepuan basah. Prestasi mangkin mono logam dan dwilogam oksida yang lebih rendah telah mendorong kepada penerokaan mangkin trilogram oksida. Mangkin trilogram oksida yang berpotensi telah dikalsin pada suhu 400°C, 700°C, dan 1000°C selama 5 jam secara berasingan. Reaktor mikro buatan tempatan dengan spektroskopi infra-merah transformasi Fourier (FTIR) dan gas kromatografi (GC) telah digunakan untuk mengkaji prestasi mangkin dengan menentukan peratusan penukaran CO<sub>2</sub> dan juga peratusan pembentukan CH<sub>4</sub>. Daripada penyaringan mangkin didapati bahawa mangkin Ru/Mn/Ce (5:35:60)/Al<sub>2</sub>O<sub>3</sub> pada suhu 700°C, dan Ru/Mn/Sm (5:35:60)/Al<sub>2</sub>O<sub>3</sub> pada suhu 1000°C mencapai 100% penukaran CO<sub>2</sub>, Ru/Mn/Pr (5:30:65)/Al<sub>2</sub>O<sub>3</sub> pada suhu 800°C mencapai 96% penukaran CO<sub>2</sub> adalah mangkin-mangkin berpotensi. Dalam tindak balas metanasi, spesies aktif untuk setiap mangkin adalah MnO<sub>2</sub> dan RuO<sub>2</sub> dan CeO<sub>2</sub> atau Sm<sub>2</sub>O<sub>3</sub> atau Pr<sub>2</sub>O<sub>3</sub>. Dengan menggunakan reaktor relau dua siri, ketiga-tiga mangkin berpotensi menunjukkan peningkatan pembentukan CH<sub>4</sub>. Untuk pengoptimuman, parameter yang dikaji ialah suhu pengkalsinan, nisbah asas, dan dos pemangkin. Proses pengoptimum ini telah dilakukan dengan menggunakan kaedah respon permukaan (RSM) dengan reka bentuk Box-Behnken yang menunjukkan parameter penting dan keputusan yang optimum untuk cerium dengan suhu pengkalsinan 697.47°C, nisbah asas 60.38% dan dos pemangkin 6.94 g seperti yang dicadangkan oleh RSM. Keputusan ini telah diuji dan disahkan secara eksperimen dengan perbezaan hanya 1%. Analisis belauan sinar X menunjukkan bahawa mangkin membentuk fasa amorfus, manakala pelepasan medan mikroskopi pengimbasan elektron menggambarkan permukaan mangkin itu dipenuhi dengan zarah kecil dan tersebar dengan bentuk yang tidak sekata. Dari tenaga serakan sinar-X analisis pula menunjukkan terdapat pengurangan Ru pada mangkin yang telah digunakan berbanding dengan mangkin yang belum digunakan bagi setiap mangkin berpotensi. Penjerapan gas nitrogen menunjukkan mangkin berstruktur liang meso dengan keluk jenis histerisis H3 dan isoterma Jenis IV. Spektrum resonan putaran elektron menunjukkan interaksi elektron bebas yang disebabkan oleh kehadiran puncak bagi setiap mangkin berpotensi. Analisis penyahjerapan pengaturcaraan suhu dari mangkin Ru/Mn/Ce (5:35:60)/Al<sub>2</sub>O<sub>3</sub> menunjukkan banyak spesies terturun berbanding mangkin yang mengandungi Sm dan Pr kerana kehadiran banyak spesies terturun pada suhu yang lebih rendah. Tindak balas metanasi diramal mengikut mekanisme Langmuir Hinselwood yang pada mulanya melibatkan penjerapan gas CO<sub>2</sub> dan H<sub>2</sub> pada permukaan mangkin. Untuk mangkin Ru/Mn/Ce (5:35:60)/Al<sub>2</sub>O<sub>3</sub> dan Ru/Mn/Sm (5:35:60)/Al<sub>2</sub>O<sub>3</sub>, produk yang dapat adalah CH<sub>4</sub>, CH<sub>3</sub>OH, dan H<sub>2</sub>O. Manakala, untuk mangkin Ru/Mn/Pr (5:30:65)/Al<sub>2</sub>O<sub>3</sub> hanya CH<sub>4</sub> dan H<sub>2</sub>O dihasilkan sebagai produk tindak balas. Akhir sekali, pemangkin yang telah digunakan dan tidak aktif dijana semula di bawah keadaan aliran O<sub>2</sub> pada 100°C selama 1 jam.