UNIVERSITI PUTRA MALAYSIA

PREPARATION AND EVALUATION OF Ni/CeO2-SiO2 CATALYST FOR DRY REFORMING OF METHANE WITH CARBON DIOXIDE IN SYNGAS PRODUCTION

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By

SUDARNO

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirement for the Degree of Master of Science

February 2012

DEDICATIONS

To my dearest parents, Siti Lasiyah and Achmad Solichin, who always pray and encourage me sincerely.
To my beloved my brothers and family for their doa, understanding, patience and support throughout my study.

Words cannot express alone my gratitude to the people above
for their endless and boundless love, and most of all
for their ever continuous do'a for my life..

When you have come to a decision, place your trust in God alone.
He loves those who place their trust in Him.
If God is there to help you, none will overcome you, and if He forsake you,
who will help other than Him?
So only in Allah should the faithful place their trust.

Q.S. Ali Imran 159-160

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Master of Science

PREPARATION AND EVALUATION OF Ni/CeO_2-SiO_2 CATALYST FOR DRY REFORMING OF METHANE WITH CARBON DIOXIDE IN SYNGAS PRODUCTION

By

SUDARNO

February 2012

Chairman : Professor Taufiq Yap Yun Hin, PhD

Faculty : Science

Dry reforming of methane with carbon dioxide (DRMC) has received great attention, as the process can utilize the two greenhouse gases of CH_4-CO_2 and produce valuable syngas. The syngas produced from this process has H_2/CO = ~1, which is more compatible for various chemical and liquid fuel syntheses. However, carbon formation that leads to the catalyst deactivation is the main obstacle of DRMC process. This study is aimed to develop Ni-based catalysts with high activity, stability and high resistance to the carbon formation. This work studies the effects of different amount of promoter "ceria" loading and different preparation method of supports and catalysts. In the first study, a series of modified CeO_2-SiO_2 (CS) supports with different loading of ceria (CeO_2) were prepared via deposition precipitation (DP). For comparison, SiO_2 and CeO_2 were also used as supports. The Ni (5wt.%) catalysts were synthesized using impregnation method. Several characterizations of energy dispersive X-ray fluorescence (EDXRF), N_2 adsorption-desorption, X-ray diffraction (XRD), H_2 temperature-programmed reduction (H_2-TPR), CO_2 temperature programmed desorption (CO_2-TPD), scanning electron microscopy (SEM), transmission electron

microscopy (TEM) and thermal gravimetric analysis (TGA) were conducted to analyze the physico-chemical properties of the prepared samples as well as to identify the carbon formation of the used catalysts. The results showed that the properties of Ni/*x*CS catalysts were superior to the Ni/SiO_2 and Ni/CeO_2 catalysts, in terms of particle sizes, Ni dispersion, reducibility and basicity. The catalytic evaluation of DRMC showed that ceria addition on the Ni-supported catalysts influenced the catalytic performances and hindered the carbon formation significantly. Among these catalysts, Ni/9CS exhibited the best properties with high catalytic performance, high stability and low carbon deposition, thus it was considered as the best catalyst with the optimal amount of ceria. For the second study, four kinds of CeO_2-SiO_2 (CS) supports have been synthesized via different methods, *i.e.* deposition precipitation (DP), Impregnation (Imp), Sol-gel (SG) and ball milling (BM). Supported Ni (5 wt.%) catalysts were also prepared via impregnation. In addition, two other catalysts, denoted as Ni/CS-DP2 and Ni/CS-D, were prepared by impregnation of CS-DP support and co-impregnation of Ni and Ce on silica with higher temperature of catalyst calcination (700 ^{o}C). The characterization results showed that the different method gave significant different physico-chemical properties, catalytic performance and coking resistant. It was found that Ni/CS-DP1 and Ni/CS-DP2 showed the excellent activity and stability, since they have good properties (morphology, reducibility and basicity as well as Ni particle size). The order of catalyst activities is Ni/CS-DP2 $\underline{\geq}$ Ni/CS-DP1 > Ni/CS-Imp > Ni/CS-D > Ni/CS-BM and Ni/CS-SG. However, in term of carbon deposition, Ni/CS-DP1 and Ni/CS–DP2 gave higher amount of carbon deposits than those of Ni/CS-Imp, Ni/CS-D and Ni/CS-BM. Whereas, Ni/CS-SG showed the lowest activity with the worst condition of carbon formation due to the bad properties of the catalyst.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
sebagai memenuhi keperluan untuk ijazah Master Sains

PENYEDIAAN DAN PENGUJIAN PEMANGKIN Ni/CeO_2-SiO_2 TERHADAP REFORMASI KERING METANA DAN CARBON DIOKSIDA UNTUK PENGHASILAN SYNGAS

Oleh

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Februari 2012

Chairman : Profesor Taufiq Yap Yun Hin, PhD

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Reformasi kering metana dan karbon dioksida (DRMC) telah mendapat perhatian yang besar, kerana proses ini boleh memanfaatkan kedua-dua gas rumah hijau iaitu CH_4 dan CO_2 untuk menghasilkan gas berharga iaitu syngas. Syngas yang dihasilkan daripada proses ini mempunyai nisbah H_2/CO = ~ 1, yang mana lebih sesuai untuk sintesis pelbagai bahan kimia dan bahan api cecair. Bagaimanapun, pembentukan karbon yang menyebabkan kepada penyahaktifan pemangkin ialah halangan utama proses DRMC. Kajian ini bertujuan untuk membangunkan pemangkin berasaskan nickel (Ni) yang mempunyai aktiviti dan kestabilan yang tinggi serta ketahanan baik terhadap pembentukan karbon. Penyelidikan ini mengkaji kesan daripada penambahan "ceria" dengan jumlah yang berbeza dan mengkaji kesan daripada kaedah penyediaan penyokong dan pemangkin yang berlainan. Dalam kajian yang pertama, satu siri penyokong untuk pemangkin yang telah diubahsuai, CeO_2-SiO_2 (CS), dengan jumlah muatan ceria (CeO_2) berlainan telah disediakan melalui kaedah pemendakan pemendapan (DP). Sebagai perbandingan, SiO_2 dan CeO_2 juga digunakan sebagai

penyokong. Pemangkin tersokong Ni (5wt.%) telah disintesis dengan menggunakan kaedah penindihan pada penyokong tersebut. Beberapa analisis iaitu tenaga pancaran sinar-X berpendarfluor (EDXRF), penjerapan-penyahjerapan gas N_2, pembelauan sinar-X (XRD), reduksi pada suhu terprogram menggunakan aliran H_2 (H_2-TPR), penyahjerapan CO_2 pada suhu terprogram (CO_2-TPD), mikroskop imbasan elektron (SEM), mikroskop pemancaran elektron (TEM) dan analisis gravimetrik terma (TGA) telah dijalankan untuk menganalisis sifat fizikal dan kimia sampel serta untuk mengenal pasti pembentukan karbon pada pemangkin yang telah digunakan. Hasil analsis menunjukkan bahawa sifat-sifat pemangkin Ni/xCS dari segi saiz partikel, penyebaran Ni, keupayaan reduksi dan tingkat kebasaannya. Hasil uji pemangkinan untuk proses DRMC menunjukkan bahawa penambahan CeO_2 pada pemangkin Ni yang tersokong mempengaruhi aktiviti pemangkinan pemangkin tersebut dan menghalang pembentukan karbon dengan ketara. Antara pemangkin yang telah disiapkan, Ni/9CS menunjukkan sifat-sifat terbaik dengan aktiviti dan kestabilan pemangkinan yang tinggi serta pemendapan karbon yang rendah, oleh sebab itu, ia dianggap sebagai pemangkin terbaik dengan jumlah ceria yang optimum. Bagi kajian kedua, empat jenis penyokong CeO_2-SiO_2 (CS) telah disintesis dengan menggunakan kaedah yang berbeza, iaitu pemendakan pemendapan (DP), pengisitepuan (Imp), Sol-gel (SG) dan bola pengisaran (BM). Pemangkin Ni (5 wt.%) yang tersokong pada penyokong-penyokong tersebut juga disediakan melalui kaedah penindihan. Sebagai tambahan, dua pemangkin lain yang dilabelkan sebagai Ni/CS-DP2 dan Ni/CS-D, telah disediakan yang juga melalui penindihan pada penyokong CS-DP dan penindihan serentak Ni dan Ce pada SiO_2 tetapi dengan suhu pengkalsinan pemangkin yang lebih tinggi (700 ^oC). Hasil analisis menunjukkan bahawa kaedah yang berbeza untuk penyediaan sampel telah memberikan perbezaan yang signifikan terhadap sifat

fizikal dan kimia, aktiviti pemangkinan serta dan ketahanan pada pembentukan karbon. Dari hasil kajian, telah didapati bahawa Ni/CS-DP1 dan Ni/CS-DP2 menunjukkan aktiviti dan kestabilan yang sangat baik, kerana mereka mempunyai ciri-ciri yang baik dari segi morfologi, keupayaan reduksi, tingkat kebasaan serta saiz partikel nickel. Adapun urutan aktiviti pemangkinan dari pemangkin-pemangkin ialah Ni/CS-DP2 > Ni/CS-DP1 > Ni/CS-Imp > Ni/CS-D > Ni/CS-BM dan Ni/CS-SG. Walau bagaimanapun, dalam hal pembentukan karbon, Ni/CS-DP1 dan Ni/CS-DP2 memberi jumlah deposit karbon yang lebih tinggi dibandingkan yang Ni/CS-Imp, Ni/CS-D dan Ni/CS-BM. Manakala Ni/CS-SG menunjukkan aktiviti terendah dengan jumlah deposit karbon paling teruk akibat sifat-sifat yang tidak baik pada pemangkin tersebut.

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I certify that a Thesis Examination Committee has met on 1st February 2012 to conduct the final examination of Sudarno on his thesis entitled "**Preparation and Evaluation of Ni/CeO_2-SiO_2 Catalyst for Dry Reforming of Methane with Carbon Dioxide in Syngas Production**" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science.

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DECLARATION

I declare that the thesis is my original work except for quotations and citations, which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.

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SUDARNO

Date: 1 February 2012

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