CO_2 / H_2 METHANATION ON NICKEL OXIDE BASED CATALYST DOPED WITH VARIOUS ELEMENTS FOR THE PURIFICATION OF NATURAL GAS

Nor Aziah Buang*, Wan Azelee Wan Abu Bakar, Faridah Mohd Marsin, Mohd Hasmizam Razali

Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310, Skudai, Johor.

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Abstract

Nickel possess characteristics similar to noble metals, apart from being easily deactivated by carbon deposition and poisoning. In this study, the activity of prepared nickel based catalysts doped with selected elements (Mg, Zr, Mo, Mn, Co, Fe, and Cu) that were presumed to help nickel active sites has been investigated for the CO_2 elimination in the presence of H_2 in the hopes for a methanation reaction. With the addition of lanthanide series as co-dopant in the catalyst, the synthesized catalysts were tested for its catalytic activity and reproducibility by FTIR spectroscopy. It was found that only several elements can boost CO_2 elimination, namely magnesium, cobalt and ferum, with cobalt showing the highest conversion for both ratios, Ni/Co/Pr 60:30:10 and 60:10:30. Furthermore, Ni/Co/Pr with the ratio of 60:30:10 was proven superior as it yielded highest CH_4 in the lowest conversion temperature of approximately 350 °C. Further characterization on Ni/Co/Pr with the ratio of 60:30:10 showed the supremacy towards the conversion of CO_2 to CH_4. Single point BET analysis showed that Ni/Co/Pr did not have any changes in the surface area, as it did not adsorb CO_2. This statement is in agreement with the XRD and EDX results obtained whereby there are no traces of carbon deposition. From TPD results showed CO_2 desorption peaks at low and high temperature indicated intermediate bonding of CO_2 on the surface of the catalyst. This shows the presence of dopant will result in the enhancement of CO_2 elimination to a 100%.

Abstrak

Nikel mempunyai ciri-ciri yang menyamai logam yang mahal (paladium, platinum). Walau bagaimanapun ia mudah terencat dengan kehadiran karbon dan keracunan mangkin. Dalam kajian ini, aktiviti pemangkinan bagi mangkin Ni yang didop dengan bahan pendop terpilih (Mg, Zr, Mo, Mn, Co, Fe, and Cu) untuk meningkatkan keupayaan pemangkinan disamping memberi ketahanan kepada keracunan mangkin dalam proses menukarkan CO_2 kepada gas metana. Dengan penambahan praseodymium daripada kumpulan lantanida, mangkin tersebut telah di uji dari segi keupayaan pemangkinan dan ketahanan menggunakan analisis FTIR. Kajian telah mendapati bahawa hanya beberapa elemen sahaja yang boleh menyingkirkan CO_2, iaitu magnesium, ferum dan cobalt. Cobalt menunjukkan keupayaan pemangkinan yang tinggi dalam kedua-dua nisbah Ni/Co/Pr 60:30:10 dan 60:10:30. Selain itu, Ni/Co/Pr dengan nisbah 60:30:10 merupakan mangkin yang paling efektif untuk menyingkirkan CO_2 disamping menukarkannya kepada CH_4 pada suhu lebih kurang 350ºC. Kajian pencirian mangkiin menunjukkan bahawa Ni/Co/Pr dengan nisbah 60:30:10 lebih berkesan menukarkan CO_2 kepada CH_4. Kajian luas permukaan BET menunjukkan bahawa Ni/Co/Pr tidak menunjukkan sebarang perubahan dalam luas permukaan, bermakna ia tidak menyerap CO_2. Analisis XRD and EDX menunjukkan tiada perubahan struktur dan tiada karbon terbentuk di atas permukaan mangkin. Analisis TPD menunjukkan puncak penyahjerapan CO_2 berada pada kedua-dua suhu yang rendah dan tinggi. Ini menunjukkan terdapat penjerapan CO_2 di atas permukaan mangkin. Ini semua menunjukkan peningkatan kepada keupayaan mangkin untuk menyingkirkan CO_2 100%.

Introduction

The necessity of natural gas purification into high quality products boosted both the applied and academic research activity. In recent years, renewed interest in CO_2 elimination process has arisen. Noble metals such as Rh, Ru and Ir exhibit high stability and less sensitivity in catalytic process [1-2], cost and limited avaibility of these metals discourage their widespread industrial applications. Nickel oxide exhibited high activity and selectivity of methane due to the ability of NiO to undergo reduction process owing to the presence of defect sites of the surface [3]. Despite of the fast catalyst deactivation and carbon deposition, NiO catalyst was still favored for its high thermal stability [4], and its low price [5]. Therefore, it is very important to develop stable and effective nickel oxide catalyst with improved resistance to deactivation caused by coking and poisoning. A study by Valentini *et al.* [6] found that the catalytic properties, metal dispersion and the structural features of species depend on the method to process these materials and on the support used. The addition of dopant into nickel oxide base catalyst was found to enhance the capability of the catalyst. The usage of catalyst will depend on the dopant used in order to form a durable, sulfur tolerant, high catalytic activity catalysts. The selected dopants studied were magnesium (Mg), zirconium (Zr), molybdenum (Mo), manganese (Mn), ferum (Fe), cobalt (Co), and copper (Cu).

Cobalt was mainly used for Fisher-Troposh Synthesis (FTS) and was chosen due to its reducibility of CO. Jacobs *et al*. [7] found that addition of Ru and Pt exhibited a similar catalytic effect on decreasing both the reduction temperatures of cobalt oxides. The hydrogenation of CO and CO_2 were found to catalyze by the larger cobalt clusters formed by three incipient wetness impregnations [8]. Other research by Guczi *et al.* [9] found that Co–Pd samples are fully reducible and form bimetallic particles which can be reversibly oxidized/ reduced. CO hydrogenation takes place in the range of 200–300^{o}C producing mainly alkenes on pure cobalt catalyst with short chains. Synergism on the addition of small amount of palladium to cobalt is observed and the rate of the CO hydrogenation significantly increases.

In this research, Nickel based catalyst was doped with selected metal elements and praseodymium, to alter the surface and bulk structure of the catalyst so it will become polycrystalline. Different ratios of dopant was introduced into the catalyst matrices and was then used to eliminate CO_2 with the presence of H_2 with the hopes for CO_2 hydrogenation to occur. The reducibility and characteristics of the doped Nickel based catalysts were tested by means of FTIR for catalytic activity of the CO_2 removal and methane production, X-Ray Diffraction for phase or structural changes, Temperature Programmed Desorption(TPD) for the determination of active site, and BET Surface Area of the catalyst.

Experimental

Catalyst preparation

Ni/M*/Pr (M*= Mg, Zr, Mo, Mn, Fe, Co, and Cu) in both higher and lower atomic ratios of selected dopant, 60:30:10 and 60:10:30, were prepared via optimized sol gel method. This method includes the addition of its specific metal salts with its base metal, $Ni(NO_3)_2.6H_2O$, and second dopant, $Pr(NO_3)_3.6H_2O$. it was then aged at 75°C for 48 hours before it was calcined at 400°C for 17 hours.

Catalytic activity measurement

The prepared samples were tested for its activity towards CO_2 removal via methanation reaction. This was done using a flow bed reactor of 10 mm inner diameter under atmospheric pressure. The reaction gas mixture of CO_2 and H_2 was passed continuously through the catalyst which flows through the FTIR whereby the CO_2 peaks elimination and CH_4 formation will be detected and monitored.

Characterization

X-ray Diffraction Analysis : The catalyst samples were characterized by using a Philips D5000 X-Ray Diffractometer (Cu-K_α radiation) with 2θ values ranging from 10-80°,

Single Point BET Surface Area: the surface area of samples before and after exposure to CO_2/H_2 were measured using Micromeritics ASAP, whereby it uses nitrogen as the adsorption gas for the physical characterization of the catalyst.

Temperature Proggrammed Desorption Analysis: the H_2 and CO_2 desorption from the catalyst were taken into account using the Thermofinnigan TPD/R/O 1100.

Results and disscussion

Catalytic activity

For the lower ratio of the selected dopant, Ni/M*/Pr (M =Mg, Zr, Mo, Mn, Co, Fe, and Cu) with the ratio of 60:10:30, from the results it indicated that for the lower addition of various metals as dopants, most of the catalyst exhibit CO_2 elimination properties. The three highest CO_2 elimination catalysts were Ni/Mg/Pr, Ni/Fe/Pr, and Ni/Co/Pr. Starting from 300°C, Ni/Mg/Pr has already eliminated over 80% of the CO_2. The highest CO_2 elimination is at 330°C with 93.26%. For Ni/Fe/Pr and Ni/Co/Pr, the light off temperature (T_{LO}) were both at 250°C, while complete elimination of CO_2 was also both at around 427°C. Ni/Mo/Pr and Ni/Cu/Pr also showed response in the CO_2 elimination whereby at 300°C, the catalyst eliminated 17.69% and 40% respectively. Hence the CO_2 elimination for Ni/Cu/Pr terminated at 430°C with a maximum elimination of 67%, while after 50% of elimination, the performance of Ni/Mo/Pr declined at 450°C. Ni/Mn/Pr, and Ni/Zr/Pr did not show any significant CO_2 elimination throughout the catalytic measurement.

Figure 1 showed the catalytic activity of Ni/M*/Pr (M =Mg, Zr, Mo, Mn, Co, Fe, and Cu) with catalyst ratio 60:30:10 for CO_2 elimination that were calcined at 400°C for 17 hours and tested under stoichiometric conditions, consisting of CO_2 and H_2, from 300-500°C.

Results indicated that for the higher loading of various metals as dopants, most of the catalysts performances have been suppressed in eliminating CO_2 in the system. Most of the catalyst eliminated less than 20% of CO_2, except for the Ni/Co/Pr catalyst. The later maintained its performance in eliminating CO_2 at T_{LO} of 300°C with 20% elimination, and further elimination at 400°C with highest percentage of 97.42%.

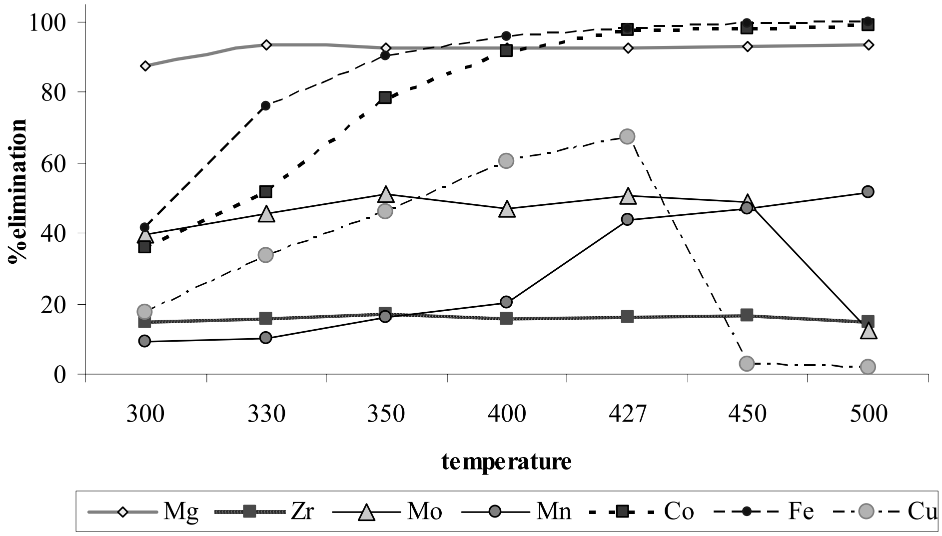

Figure 1: Catalytic activities of Ni/M*/Pr (M =Mg, Zr, Mo, Mn, Co, Fe, and Cu) ratio 60:10:30 for CO_2 elimination versus temperature

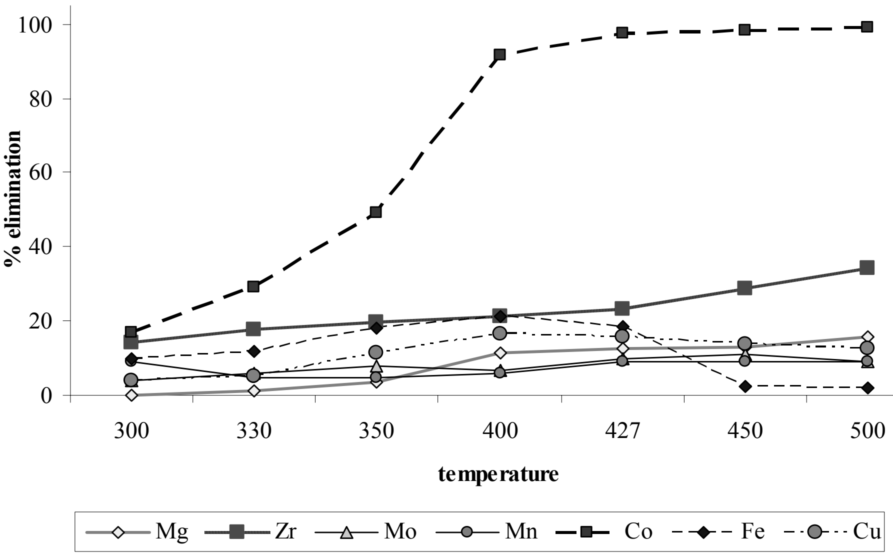

Figure 2: Catalytic activities of Ni/M*/Pr (M =Mg, Zr, Mo, Mn, Co, Fe, Cu, and Zn) ratio 60:30:10 for CO_2 elimination versus temperature

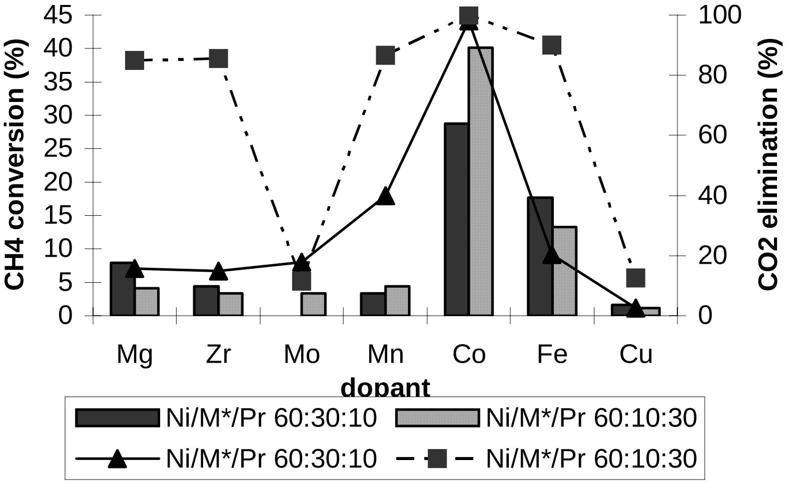

Figure 3: Catalytic activities of Ni/M*/Pr (M =Mg, Zr, Mo, Mn, Co, Fe, Cu, and Zn) ratio 60:30:10 and 60:10:30 for CO_2 elimination and CH_4 conversion at 400ºC

As we compare the dopants according to ratios shown in Figure 2 and Figure 3, we can see significant difference in each ratio for each dopant. The line chart in Figure 3 showed the CO_2 elimination for the catalyst indicated that the catalyst doped with cobalt for both higher and lower amount of dopant, were superior from the rest. It was observed in the Ni/Co/Pr catalyst, which has special features itself, showed that, it still does the function of eliminating CO_2 and forming CH_4 as the product. Further study on the cobalt doped catalyst shows that the optimum ratio of the dopant added to Ni/Co/Pr are with the ratio of 60:35:5. with only low addition of praseodymium, the catalyst structure was altered to a suitable structure for methanation catalyst.

Characterization

In order to further understand the performance of the catalyst and role of dopant in the enhancement of the catalytic performance material, the best catalyst was characterized by various techniques.

X-Ray Diffraction(XRD)

XRD analysis was carried out on Ni/Co/Pr with the ratio of 60:35:5 prepared by calcination at 400^{o}C for 17 hours. From Figure 4, it was found out that the catalyst formed a polycrystalline phase, a form of mixture of amorphous and crystalline phases, which indicates a good catalyst. We can clearly see formation of spinel compound of Co_3O_4 on the surface of catalyst. This was preferred because the spinel compound is a combination of two oxidation state that is CoO and Co_2O_3 which served as an active site on the surface. The particle size calculated from Scherrer's equation is 17.65nm. From the XRD analytical data, we presumed that spinel compound that formed in the catalyst plays a major role in enhancing the performance of the catalyst. Meanwhile, the addition of Pr has also played a part in the enhancement of physical properties of the catalyst which probably affected the physical structure by making it more amorphous and also contributes in the CO_2 conversion mechanism to form methane.

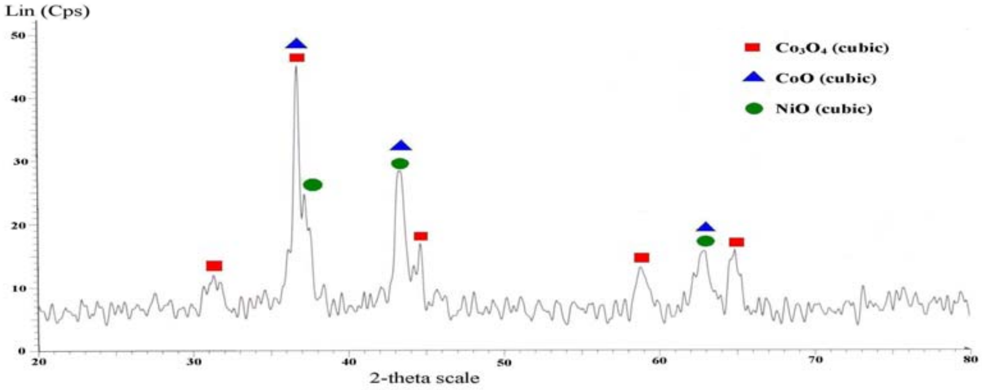

Figure 4: X-Ray Diffraction pattern for Ni/Co/Pr with the ratio of 60:35:5 calcined 400°C for 17 hours

BET surface area

Ni/Co/Pr 60:35:5 catalysts was sent for the surface area analysis. Table 1 showed the comparison between the previous studied catalyst Ni/Pr with the ratio of 60: 40 and Ni/Co/Pr 60: 35: 5. It seems that the surface areas for Ni/Pr 60:40 and Ni/Co/Pr 60:35:5 catalysts have only had a slight difference in the surface area. While Ni/Co is about half of Ni/Co/Pr, which means that, the surface area of the new modified catalyst have similarity of the previous catalyst and we can presume that the catalytic activity should be the same. This also showed that the addition of Pr change the physical properties by increasing the surface area of the catalyst

Table 1: BET surface area of catalysts

Catalyst	BETsurface area (m^2 /g)
Ni/Pr [11]	75.58
Ni/Co/Pr	59.86
Ni/Co	38.49

Temperature Programmed Desorption

To determine the sorption profile of CO_2 and H_2 on the surface of catalyst, TPD was used whereby the ability of Ni/Co/Pr with the ratio of 60: 35: 5 to absorb CO_2 and H_2 was studied. The TPD profile of CO_2 by the catalyst is shown in Figure 5. Three desorption peaks at 270°C, 600°C and 750°C can be distinguished. Peak evolve at a lower temperature and two remain peaks are at a higher temperature. This was probably due to the different bonding modes of CO_2 with the active sites, during the adsorption on the surface.

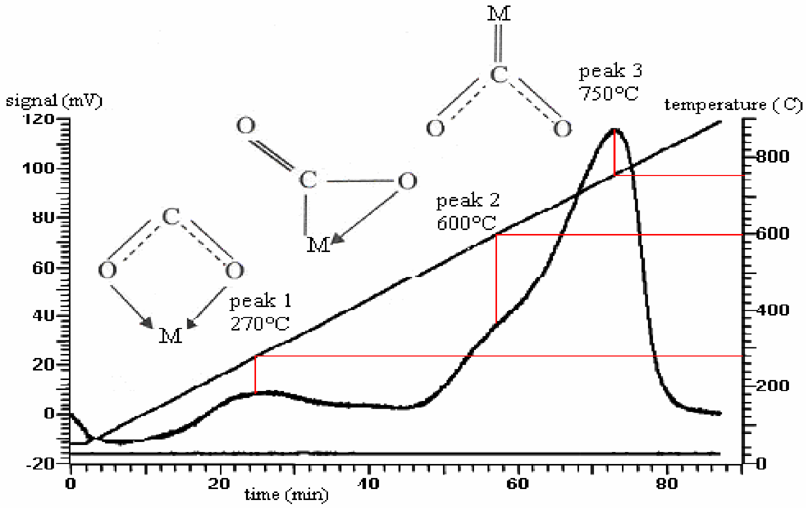

Figure 5: TPD profile of $CO_2$for Ni/Co/Pr with the ratio of 60:35:5

A study by Cox [11], mentioned that the coordination of CO_2 onto metal oxide has different energies, which will cause different desorptions profile. The peak at lowest temperature of 270°C is due to desorption of the weakest bonding mode of CO_2 onto the catalyst surface. It was proposed that three bonding modes occurred. The peak area showed the amount of CO_2 sorption of the species. It was clearly seen that the metal carbene ($M=CO_2$) primarily dominated the bonding mode on the surface of the catalyst. This means that the catalyst that formed strong bonds with CO_2, and needed high temperature to produce more energy for desorption the CO_2. The sorption sites of H_2 on the surface of the catalyst were also being studied. Two significant peaks were detected at 350°C and 780°C. It was probably due to the sorption of hydrogen between the NiO or CoO lattices to form metal hydrates (M-H). Nevertheless, H_2 sorption correlates with the CO_2 sorption at the higher temperature of 780°C. It can be concluded that the chance for formation of methane at lower temperature is less compared to catalyst at higher temperature. But the lower desorption peaks can still be accounted because it still can convert to methane

Conclusion

The catalytic testing of all the catalyst with higher and lower loading of dopants (ratio 60:30:10 and 60:10:30 respectively), the testing showed that addition of specific dopants resulting in a high catalytic activity, and some suppress the catalytic activity of the catalyst. For the ability of the catalyst to eliminate CO_2 as well as to converted to methane simultanously, the Ni/Co/Pr with an optimum ratio of 60:35:5 was identified to be able to do almost 100% of CO_2 elimination.

Characterization of the best performance catalyst was studied in depth. XRD analysis found that the catalyst consists of a cubic NiO, and a spinel compound of Co_3O_4 which consist of mixture of cubic CoO and Co_2O_3. The present of Co_3O_4 was identified to be the major contribution to the catalytic activity enhancement of the Ni/Co/Pr catalyst. The single point BET analysis, obtained for the Ni/Co/Pr (60:35:5) showed high surface area of 59.86m^2/g when compared to the Ni/Co 60:40 (38.50m^2/g). It was predicted that the incorporation of Pr attributed to the surface area and thus making it superior. Commencing the TPD analysis of the catalyst, three major peaks for the sorption of CO_2 and two major peaks for the sorption of H_2 were depicted. As the lower peaks contributed to the elimination of CO_2 at lower temperature (270°C) with the high formation of methane (350°C), the actual desorption of both CO_2 and H_2 occured at higher temperature. This means that the Ni/Co/Pr catalyst full potential towards methanation reaction lies in the temperature ranging from 600-800°C.

From the characterization, we can conclude that the addition of Co as dopant enhanced the catalytic activity of the Ni/Co/Pr catalyst as it contributed to the formation of additional active sites and change the chemical properties of the catalyst. Hence,the incorporation of Pr cause changes in the physical properties of the Ni/Co/Pr catalyst.

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References

1. Kudo, K., and Komatsu, K. (1999). Reduction of alkali metal carbonate to methane with water in the presence of Raney alloy. *J. of Molec. Catalysis. A: Chemical.* 145: 159–167
2. Cattenot, M., Geantet, C., Glasson, C., and Breysse, M. (2001). Promoting effect of ruthenium on NiMo/Al_2O_3 hydrotreating catalysts". *Appl. Catalysi. A: General*. 213: 217–224.
3. Jose, A., R., Jonathan, C., H., Anatoly, I., F., Jae, Y., K. and Manuel, P. (2001). Experimental and Theoretical Studies on the Reaction of H_2 with NiO. Role of O Vacancies and Mechanism for Oixde Reduction*. J. Am. Chem.Soc.* 124, 346-354
4. Wang, L., Murata, K., and Inaba, M. (2004). Control of the Product Ratio of CO_2/ ($CO+CO_2$) and Inhibition of Catalyst Deactivation for Steam Reforming of Gasoline to Produce Hydrogen. *Appl. Catalysis B: Environmental*. 48: 243-248
5. Hou, Z., Yokota,O., Tanaka, T., and Yashima, T. (2004). Surface Properties of a Coke-free Sn Doped Nickel Catalyst for the CO_2 Reforming of Methane. *Appl. Surf. Sci.*. 233: 58-68.
6. Valentini, A., Carreno, N.L.V., Probst, L.F.D., Lisboa-Filho, P.N., Schreiner, W.H., Leite, E.R., and Longo, E. (2003). Role of vanadium in Ni:Al_2O_3 catalysts for carbon dioxide reforming of methane. *Appl. Catalysis A:General* 255: 211-220
7. Jacobs, G., Das, T.K., Zhang, Y., Li, J., Racoillet, G., and Davis, B.H. (2002). Fisher-Troposh synthesis: support, loading, and promoter effects on the reducibility of cobalt catalyst. *Appl. Catalysis A: General* 233: 263-281.
8. Zhang, Y., Jacobs, G., Sparks, D.E., Dry, M.E., and Davis, B.H. (2002). CO and CO2 hydrogenation study on supported cobalt Fisher-Troposh synthesis catalysts. *Catalysis Today* 71: 411-418
9. Guczi, L., Schay, Z., Stefler, G., and Mizukami, F. (1999). Bimetallic catalysis: CO hydrogenation over palladium–cobalt catalysts prepared by sol gel method. *J. of Molec. Catalysis A: Chemical*. 141: 177–185.
10. Mohd Hasmizam, R. (2005). CO_2 Methanation on Nickel-Based Catalysts. MSc thesis, UTM.
11. Cox, P., A. (1995). *The Elements on Earth-Inorganic Chemistry in the Environment*. Oxford. Oxford University Press. 147-158.