

Effects of Ni and Pd metals catalyst on Gamma Alumina support

Z. Yaakob*, M. R. Yosfiah, L.J. Minggu, M.A.Ibrahim.W.R.W.Daud

*Department of Chemical and Process Engineering, Faculty of Engineering, Universiti Kebangsaan Malaysia,
43000 Bangi, Selangor Darul Ehsan, Malaysia.*

Abstract

Catalysts containing Ni or combinations of Pd, Cu and Zn on gamma alumina support have been developed for testing in autothermal methanol reforming reaction. The hydrogen produced by the catalytic reforming of methanol is targeted to be used as a feed for fuel cell. The reaction for reforming of methanol can be performed at low temperature and pressure in the presence of catalysts with high yield and low CO. The calcined catalysts has been characterized by Brunauer, Emmett and Teller (BET) for surface area, Scanning Electron Microscopy (SEM) for shape and dispersion of metals, Powder X-ray diffraction (XRD) for species present and degree of crystallinity and Temperature Programmed Reduction (TPR) for reducible species presence, their interaction and degree of reducibility. The catalyst has specific characteristic in physical and chemical properties due to the location of Ni metal on the surface of the γ -Al₂O₃. The effects could be observed in colour, SEM, and the total number of pores of the catalyst. The amount of metal in the supporting material γ -Al₂O₃ also influenced the physical properties of the catalysts. From the catalyst produced with various concentration, it is found that the content of Ni metal with specific amount, fill the channels on the surface of supporting material γ -Al₂O₃. Based on the catalyst activities data, suitable catalyst to produced hydrogen can be formulated.

Keywords : Nickel, Pd, Cu catalyst, Gamma alumina, Hydrogen production

1.0 Introduction

Catalyst used for each reaction has very specific characteristics depending on the type of process. When products are to be obtained from catalytic reaction, the suitable catalyst must be identified and compounds that can poison the catalysts should be eliminated or reduced considerably. The selection of catalysts that have long life span will reduce the cost of buying fresh catalysts and decrease the time for replacing the catalyst [1,2].

Catalyst that has high resistance toward poisoning substance indicates the catalyst has long life span and high activation energy. The catalyst should be able to be regenerated with ease without affecting its activity. Large scale production is possible, as basically every industry require catalyst in huge amount [3]. The objective of this work is to synthesize an active catalyst for better reforming of methanol to produce hydrogen.

* Corresponding author: Tel : 603-89216420 Fax : 603-89216148 email : zahira@eng.ukm.my

2.0 Methodology

The Ni based catalysts were prepared by wet impregnation, where Nickel (II) Nitrate solution was added with 50 g of γ -Al₂O₃ as a support. The mixture is then heated to 90°C and continuously stirred for one to two hours (until all the water in the mixture has evaporated). The catalysts were then dried in an oven for 24 hours at temperature 110 – 115°C. The resulting catalysts were calcined in the flow of nitrogen at 500°C for 3 hours before it is reduced in hydrogen at 400°C for 2 hours. The Cu based catalysts promoted by Pd were prepared by impregnation method using the incipient wetness technique. The Pd/Al₂O₃, Cu/Al₂O₃ and Zn/Al₂O₃ catalysts were each prepared by impregnation of γ -Al₂O₃ with their respective precursor solution. The CuZn/Al₂O₃ catalyst was prepared by co-impregnation of γ -Al₂O₃ with mixture of the Cu and Zn precursor solution. The PdCu/Al₂O₃ and PdZn/Al₂O₃ catalysts were prepared by sequential-impregnation where the γ -Al₂O₃ was first impregnated with Cu or Zn precursor solution, dried and calcined. Then each catalyst was impregnated with Pd precursor solution. The PdCuZn/Al₂O₃ catalyst was prepared by co-impregnation of γ -Al₂O₃ with mixture of Cu and Zn precursor solution which was dried and calcined and then followed by sequential-impregnation with Pd precursor solution. The resulting catalysts were then dried at 65°C with occasional stirring for one hour and then leave overnight at 110°C. The dried catalysts were calcined in the flow of nitrogen at 500°C for 3 hours to decompose the nitrate. The catalysts were characterized by SEM to examine the catalyst surface and EDX mapping to determine the metal distribution. BET is used for the study of surface area and pore volume.

3.0 Results and Discussion

Figure 3.1 shows the support γ -Al₂O₃ before impregnation, where the color is still white. This indicates there is still no Nickel metal adsorbed onto the surface of the γ -Al₂O₃ support. After the support is impregnated with Nickel, the color changed to blue as shown by a darker color in Figure 3.2. When the γ -Al₂O₃ support had not been impregnated with Nickel metal or calcined, the number of pores were relatively small as shown in Figure 3.3 [4].

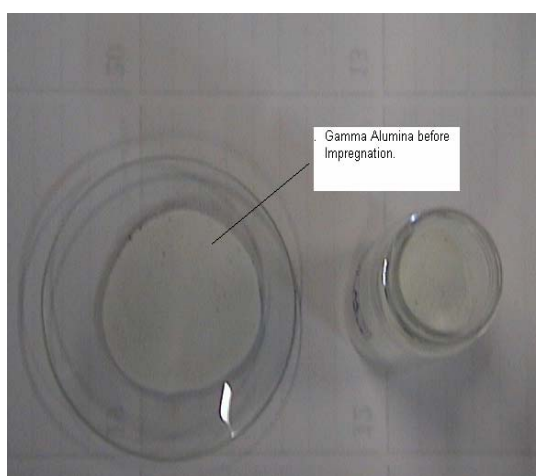


Figure 3.1 γ -Al₂O₃ before impregnation.

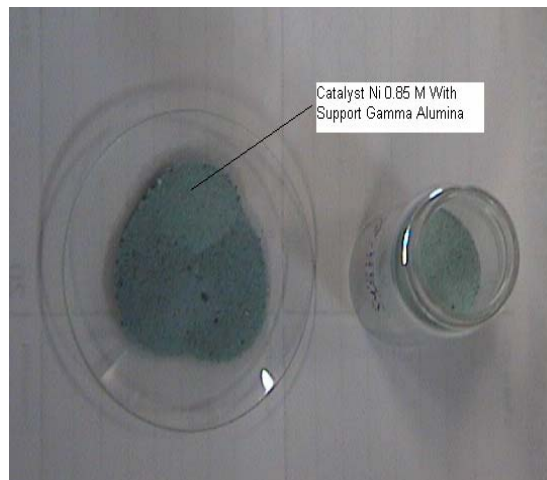


Figure 3.2 γ -Al₂O₃ after impregnation with Ni.

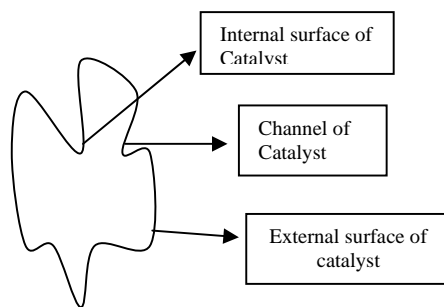


Figure 3.3 Surface area of γ -Al₂O₃ before impregnation and calcinations process.

Before the impregnation, γ -Al₂O₃ support alone is not very reactive. This is due to the active metal that is absorbed into the support pore after impregnation will influence a reaction to take place. Before calcinations, there were few channels observed on the support particle as shown in Figure 3.3. The small number of channels will influence the size of the catalysts surface area.

As shown in Figure 3.4, the catalysts after calcinations shows more channels are formed. This condition assists the complete reaction to occur. The illustration shows metal particles, represented by dark spots, adsorbed (impregnated) on the catalyst surface. The metal particles can be adsorbed on several different positions such as on the external surface area (a), internal surface area (c) and metal particles that were adsorbed deeper in the pore that has larger surface area (d). Positions a, c and d are good for the impregnated metal particles which prevent the particles dislodging from the support as compared to position (b), where the particle can easily be displaced. When the adsorbed metal particles could not adhere to or adsorbed correctly on the support surface, the resulting catalyst will have reduced reactivity. If the mixing process during catalyst preparation is not thorough, the metal particles will form clusters on the catalyst surface.

This condition will cause the reactivity on the catalysts surface to be uneven. This will also affect the proper impregnation of metal particles into the support pores.

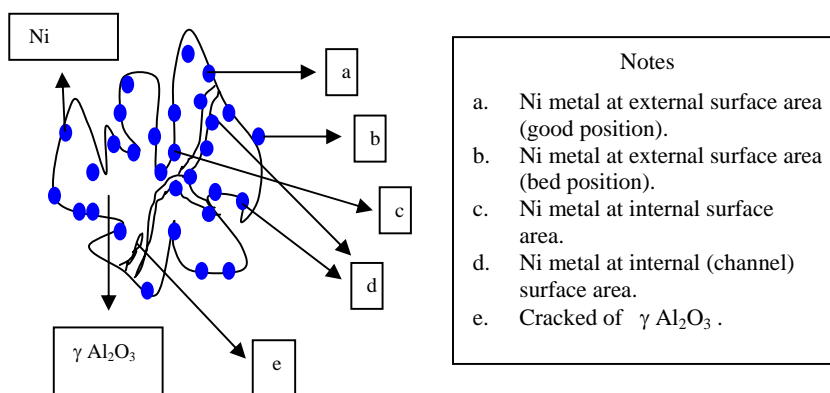


Figure 3.4 Surface area of γ - Al_2O_3 after impregnation with Ni and calcined.

SEM studies were used to observe the three dimensional shape on the catalyst surface. The reactivity of catalyst can be inferred from its surface phenomenon [5]. Uneven surface morphology and the formation of cavities or pores on each catalyst particle will ensure the catalyst is adequate for its process. Beside this, the materials used will also influence the catalyst performance.

From the SEM analysis of Ni/ γ - Al_2O_3 catalyst shown in Figure 3.5, the catalysts produced were in crystalline form. The crystalline shape enables the formation of crevices on the catalysts. In Figure 3.6, channels can be seen between cracks on the catalyst surface.

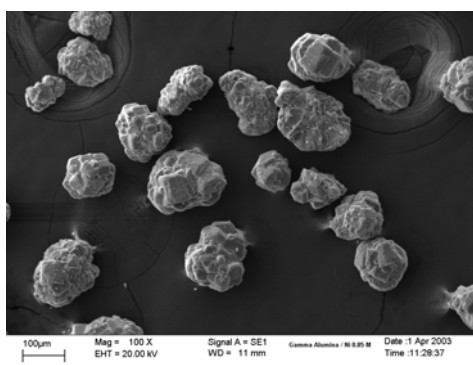


Figure 3.5 SEM image of Ni/ γ - Al_2O_3 catalyst at 100x magnifications.

The large number of pores on each catalyst particle will provide vast surface area for the particle. The larger the surface area of the catalyst, the potential for reaction on the surface increases. This is so because one of the factors affecting reaction on the surface is the surface area of the catalyst.

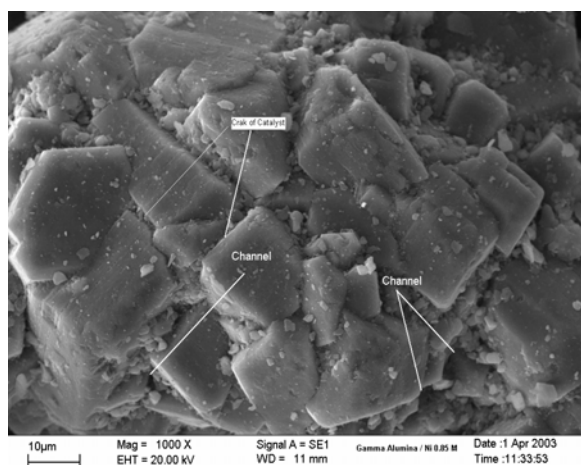


Figure 3.6 SEM image of Ni/ γ -Al₂O₃ at 1000x magnifications.

The SEM with EDX mapping for PdCuZn/ γ -Al₂O₃ catalyst indicates Pd, Cu and Zn were well distributed on the Alumina support as shown in Figure 3.7.

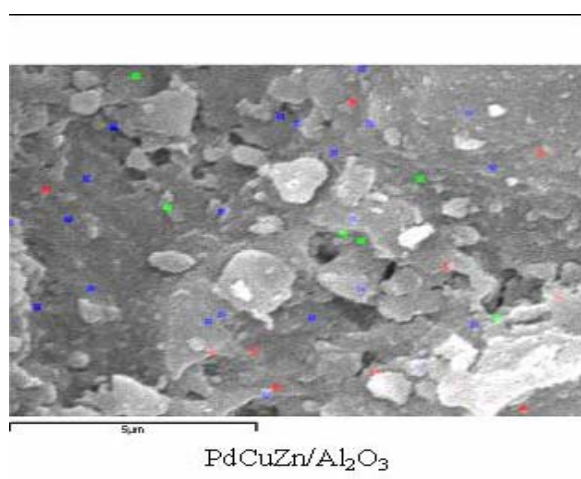


Figure 3.7 SEM image of PdCuZn/ γ -Al₂O₃ catalyst with EDX mapping, 10kx magnifications. (● -Pd ■ -Cu ▲ -Zinc)

The active metals distribution and placement in the channels in an even manner is expected to contribute to a successful reaction. TPR characterization was performed on PdCu/ γ -Al₂O₃ catalyst with the profile as shown in Figure 3 8.

The TPR profile showed that there are two distinct peaks at 62°C and 87 °C and a broad low intensity peak at 227°C. The broad low intensity peak is attributed to the CuO species which had not interacted with palladium. Although PdO is readily reduced below room temperature, only the residual CuO or PdO species from the mixed oxide Pd-Cu-O is reduced in the first peak but the first peak obtained in this study is intense and higher than the second peak. Therefore the first

peak is attributed to the palladium reduction from the mixed oxide of Pd-Cu-O and the second peak is assigned to the copper reduction from the mixed oxide. The PdCu combination has strong interaction as shown in the presence of a mixed oxide of Pd-Cu-O in the TPR.

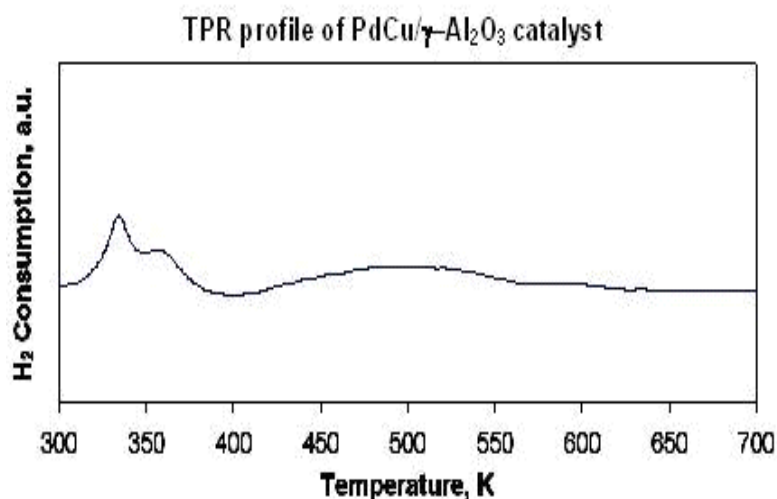


Figure 3.8. TPR profile of PdCu/γ-Al₂O₃ catalyst.

The XRD spectrum for the above PdCu/γ-Al₂O₃ catalyst is shown in Figure 3.9. Only the peak for PdO and the support (γ-Al₂O₃) can be detected in PdO-CuO/γ-Al₂O₃ precursor, but the TPR profile in Figure 3.8 indicates the presence of mixed oxide Pd-Cu-O and also CuO. The catalyst has poorly crystalline structure as indicated by the low intensity and diffuse peaks.

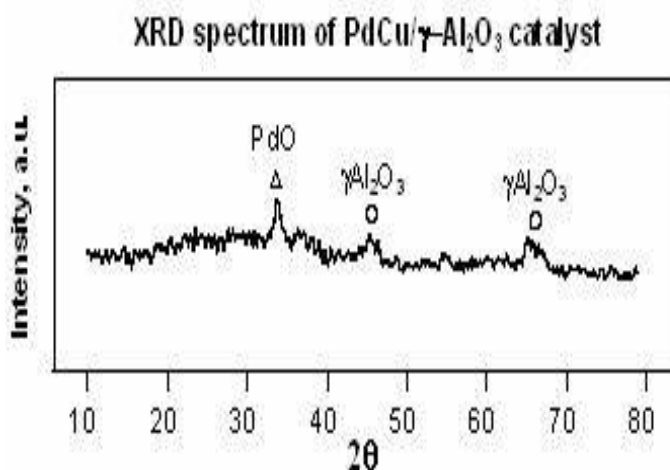


Figure 3.9 XRD spectrum of PdCu/γ-Al₂O₃ catalyst.

4.0 Conclusion

Thorough mixing and excellent solubility of Nickel (II) Nitrate produce an even distribution of Ni on the surface and into the pores. The good distribution of Pd, Cu and Zn affects the physical properties of the catalyst positively. The ease of reducibility implies that PdCu/ γ -Al₂O₃ catalyst has high activity.

Acknowledgements

The author would like to express sincere appreciation and gratitude to the financial support provided by the Ministry of Science, Technology and Innovation, through the project IRPA 02-02-02-0004-PR0023/11-09, without which this research would not be possible.

References

- [1] Agrell, J., K. Hasselbo, K. Jansson, S.G. Jaras, S.G. M. Boutonnet, M. 2001. Production of Hydrogen by Partial Oxidation of Methanol over Cu/Zn Catalysts Prepared By Microemulsion Technique. *Applied Catalysis A: General*. 211: 239-250
- [2] Anderson J. R., and K. C Pratt., 1985. "Introduction to Characterization and Testing Catalysts", CSIRO Division of Material Science, University of Melbourne, Australia.
- [3] Lindstrom, B. And L.J. Pettersson,. 2001. Hydrogen Generation by Steam Reforming Of Methanol Over Copper-Based Catalysts For Fuel Cell Applications. *International Journal of Hydrogen Energy* 26: 923-933
- [4] Rusli, M. Y., Z. Yaakob, W.R.W. Daud, and J. Jahim, 2003, "The Effect of Metal Compound Particle In Surface Area Of Support γ Al₂O₃", "Asian Particle Technology 2nd", 449-453, Pinang, Malaysia.
- [5] Velu, S., K. Suzuki, M.P Kapoor, F.Ohashi, and T. Osaki, 2001. Selective Production Of Hydrogen For Fuel Cells Via Oxidative Steam Reforming Of Methanol Over CuZnAl(Zr)-Oxide Catalysts. *Applied Catalysis A: general*, 213: 47-63.