

Effects of Ruthenium Loading on Carbon Monoxide Hydrogenation

Mardwita^{1*}, Selpiana², Elfidiah¹, Ani Melani¹, Netty Herawati¹

¹Chemical Engineering Department, Faculty of Engineering, Muhammadiyah University of Palembang, 30263, Indonesia,

²Chemical Engineering Department, Faculty of Engineering, Sriwijaya University, Inderalaya, Indonesia

Abstract: Ruthenium-based catalysts have been found to be the effective catalysts for the catalytic of carbon monoxide hydrogenation. In this experiment, we investigated the effects of ruthenium loading on carbon monoxide hydrogenation. A series of supported ruthenium catalysts were prepared by conventional impregnation method. The reaction was performed at an atmospheric pressure and carried out at temperature of 220 °C. The reactant gas was consisted of hydrogen-carbon monoxide-argon. The flow rate of reactant gas was closed to 23 ml/min. The products were analyzed by gas chromatograph. Carbon monoxide chemisorptions, x-ray diffractometer were used to characterize the catalysts. The experiment results showed that carbon monoxide conversion was the highest for the catalyst contain 7 wt.% ruthenium loading. CH₄ selectivity and olefin-to-paraffin ratio decreased with increasing ruthenium loading, on the other hand, C₅⁺ selectivity increased with increasing ruthenium loading. 7 wt.% ruthenium loading has a metal size 9 nm, however the ruthenium metal was not detected in x-ray diffraction result.

Keywords: Carbon monoxide hydrogenation; Ruthenium catalyst; CO chemisorptions; X-ray diffractometer; Noble metal

e-mail: wiwitdiita@gmail.com*

1. INTRODUCTION

Coal conversion process is an important reaction to generate energy due to the abundant source of coals which is estimated three times larger than oil reserve. The issue of energy crisis has been attracted due to the lack of energy source and the research on the possibility to utilize coal as the source of energy has grown faster and wide. Carbon monoxide (CO) hydrogenation is recognized as an alternative way to convert the coal gasifies gas or natural gas into higher hydrocarbon [1, 2]. The noble metal catalysts are well-known for its high performance in catalytic reactions including in CO hydrogenation [3]. Ruthenium (Ru) is one of the most active metals for CO hydrogenation and has been considered for the production of long chain hydrocarbons [4,5].

Metal dispersion in a catalyst plays an important role in catalytic reaction [6]. However, high dispersion of metal may not be obtained due to the low ability of metal to disperse onto the support, preparation method, type of support, and etc. Ali. K et al investigated the reduction effects of ruthenium-promoted alumina supported cobalt (Co/Al₂O₃) catalyst in Fischer-Tropsch synthesis, they found that the different reduction will effects the products selectivity [7]. It has been pointed out in some papers that in CO hydrogenation reaction, the increasing of Ru dispersion in a catalyst decreased the methane formation and it was also found that the CO/H increased with the decreasing Ru crystallite size [8, 9]. It is usually suggested that the metal content in supported catalysts affects the catalytic activity or behavior of the catalysts. It is assumed that a high metal loading would increase the catalytic activity automatically, however, high metal content may result low metal dispersion, and this will decrease the catalytic activity. K. Murata et al investigated Fischer-Tropsch synthesis over supported ruthenium catalysts, the reactions were carried out in a slurry phase over supported ruthenium catalysts using hexadecane as a solvent. They found that the products were dependent on the oxide support, calcinations temperature, synthesis gas composition and sulfur content [10].

In this work, we prepared a series of ruthenium supported metal catalysts by the conventional impregnation method. To investigate the effects of ruthenium on carbon monoxide hydrogenation, we conducted the reaction on the lowest temperature and at an atmospheric pressure.

2. EXPERIMENTAL DETAILS

A. Catalysts Preparation

A series of supported ruthenium catalysts (Ru/Al₂O₃ in wt.%) were prepared using conventional impregnation method. Gamma alumina powder (γ -Al₂O₃) (Aldrich Chemicals, UK) was used as the support. The appropriate amount of an aqueous solution of ruthenium chloride hydrate (RuCl₃xH₂O) was impregnated into γ -Al₂O₃. Water used as the solvent. The metal loaded powder was evaporated at 80 °C and dried overnight in an oven at 60 °C. After drying, the solid was crushed, calcined at 375 °C for 4 hours using air as the calcining gas and reduced by hydrogen and nitrogen at 375 °C for 3.5 hours. The loading amount of Ru in the catalyst was 5 wt.%, 7 wt.%, and 10 wt.%. The catalysts were denoted as 5Ru/Al₂O₃, 7Ru/Al₂O₃, and 10Ru/Al₂O₃.

B. Catalysts Characterizations

The CO chemisorptions experiment for the determination of particle size was carried out by using BEL-CAT analyzer. In this characterization, 0.04 grams of catalyst was used and placed in a U-tube quartz reactor. Before adsorption of CO, the catalysts were preheated in He for 20 min at 300 °C, reduced for 60 min at 300 °C in a H₂/Ar gas flow and in He for 5 min at 310 °C in a reaction chamber. The samples were cooled down at 50 °C under He gas flow. Finally, particle size of Ru was determined from CO pulse data. The metal surface area and dispersion of metal was characterized by the pulse technique.

X-ray diffraction (XRD) patterns were measured in a Rigaku, RINT 2000 diffractometer using Cu-K α radiation and a scintillation detector. The crystallite size was obtained from the line width of the most intense reflections using the Scherrer equation.

C. Catalytic Activity

The CO hydrogenation was carried out at atmospheric pressure. The reactor used in this experiment was made of Pyrex glass. The reactor contained quartz wool onto which 0.1 grams catalyst was added. The reactor was externally heated by a furnace connected to the temperature controller. In-situ pretreatment of catalysts at 350 °C for 1 hour was done before each experiment. The reactant gas consisted of premixed hydrogen-carbon monoxide-argon, with a volumetric composition of 60.2%:29.8%:10%, respectively. The total gas flow rate over

the catalyst was closed to 23 ml/min. The reaction was performed at a temperature 220 °C. The products were analyzed by a gas chromatograph connected online. Porapak Q was used in the thermal conductivity detector (TCD) and Unipak S was used in the flame ionization detector (FID).

3. RESULTS AND DISCUSSION

To investigate the effect of Ru loading, the catalysts were tested at atmospheric pressure and temperature at 220 °C. This temperature is the lowest temperature for the reaction. Figure 1 shows the CO conversions as a function of Ru loadings. It was found that the catalytic activity apparently dependent on the amount of Ru added in the catalyst.

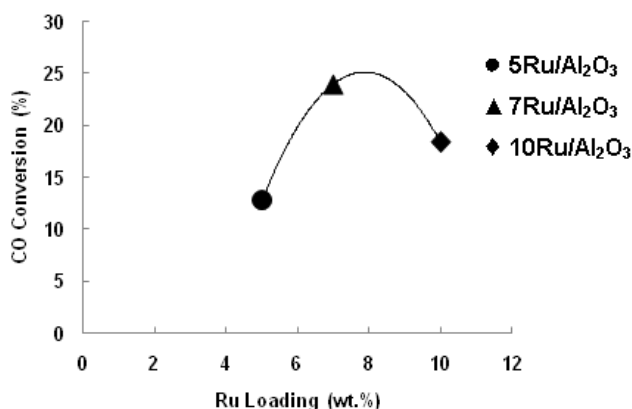


Fig.1. Effect of Ru Loading on CO Conversion

Although the CO conversion of 5Ru/Al₂O₃ catalyst was 12.8%, the value of 7Ru/Al₂O₃ catalyst was 24%, however the CO conversion of 10Ru/Al₂O₃ catalyst was only 18.4%. According to Figure 1, the activity order was 7Ru/Al₂O₃ > 10Ru/Al₂O₃ > 5Ru/Al₂O₃. The activity of supported ruthenium catalyst in CO hydrogenation depends solely on the number of active sites located on the surface of crystalline metal formed by reduction. The number of active sites is determined by the Ru particle size, loading amount, and reduction degree.

The CO chemisorptions in Figure 2 shows the Ru crystalline size of Ru/Al₂O₃ catalysts, the particle size over 5Ru/Al₂O₃ and 7Ru/Al₂O₃ catalysts were 7 and 9 nm respectively, whereas 10Ru/Al₂O₃ catalyst showed about 15 nm particle size. This result indicates that higher metal loading favorite to form large particle size of supported Ru. It was considered that 10Ru/Al₂O₃ catalyst formed large Ru particle size and it might lead to lower Ru surface area, resulting in lower catalytic activity. In this experiment, high Ru loading did not contribute directly to the catalytic activity of Ru/Al₂O₃ catalyst.

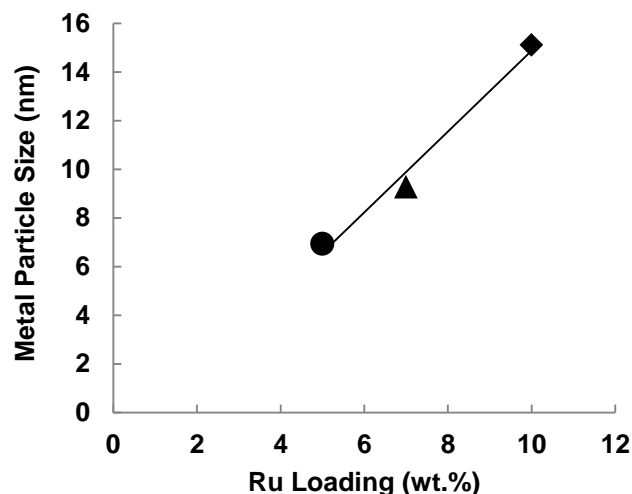


Fig.2. Metal Particle Size over Ru Loading

Figure 3 shows the effect of Ru loading over Ru/Al₂O₃ catalysts with products selectivity and olefin-to-paraffin ratio. The results showed 5Ru/Al₂O₃ catalyst exhibited lower CO conversion, C₅⁺ selectivity and higher CH₄ selectivity and olefin-to-paraffin ratio than 7Ru/Al₂O₃ and 10Ru/Al₂O₃ catalysts. The CH₄ selectivity and olefin-to-paraffin ratio decreased in the order of 5Ru/Al₂O₃ > 7Ru/Al₂O₃ > 10Ru/Al₂O₃. Olefin-to-paraffin ratio decreased with increasing Ru loading. On the other hand, C₅⁺ selectivity decreased in order of 10Ru/Al₂O₃ > 7Ru/Al₂O₃ > 5Ru/Al₂O₃.

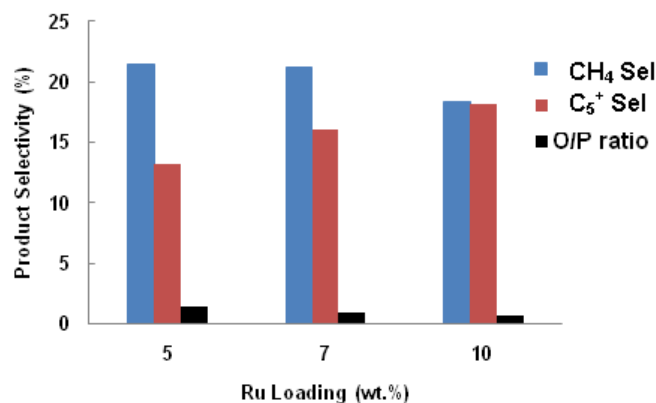


Fig.3. Product Selectivity over Ru Loading

Figure 4 represents the reaction time dependence on CO conversion of Ru/Al₂O₃ catalysts with Ru loading for CO hydrogenation. In these experiments, 5Ru/Al₂O₃ and 7Ru/Al₂O₃ catalysts showed high-steady state CO conversion with time on stream. Meanwhile, CO conversion of 10Ru/Al₂O₃ catalyst decreased gradually with time on stream. This condition corresponds to the catalyst deactivation. However, further investigation on 10Ru/Al₂O₃ catalyst deactivation was not investigated in this experiment.

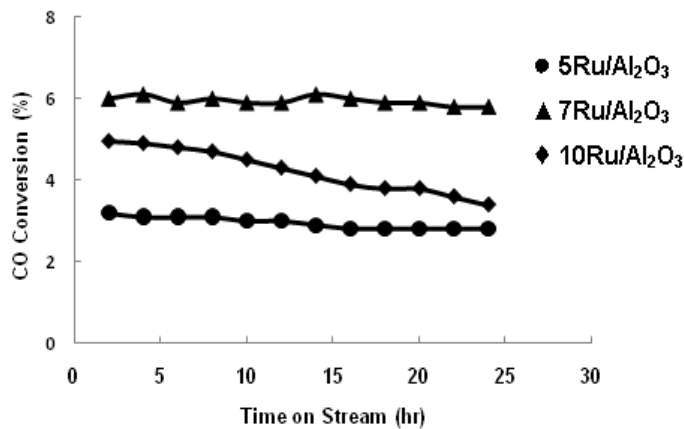


Fig.4. CO Hydrogenation Results with Time Dependence of CO Conversion over the Catalysts

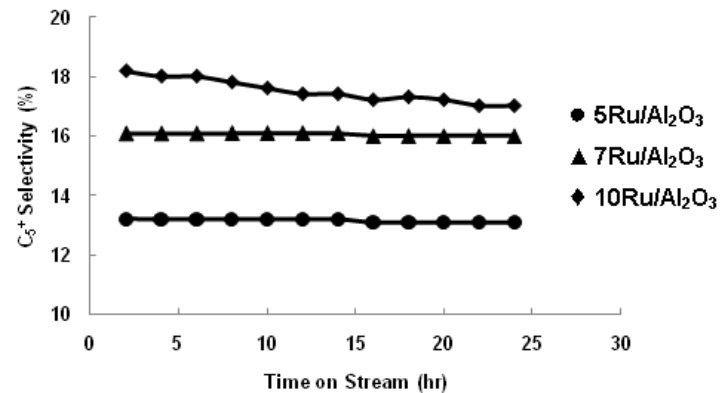


Fig.6. CO Hydrogenation Results with Time Dependence of CH₅⁺ Selectivity over the Catalysts

Figures 5 and 6 show the reaction time dependence on CH₄ and C₅⁺ selectivity over Ru/Al₂O₃ catalysts for CO hydrogenation at 220 °C. In the case of 10Ru/Al₂O₃ catalyst, it showed slightly increased in CH₄ selectivity and decreased in C₅⁺ selectivity with time on stream, but these conditions were not observed over 5Ru/Al₂O₃ and 7Ru/Al₂O₃ catalysts. Olefin-to paraffin ratio time dependence is shown in Figure 7, based on the results obtained, olefin-to-paraffin ratio was not affected by time on stream.

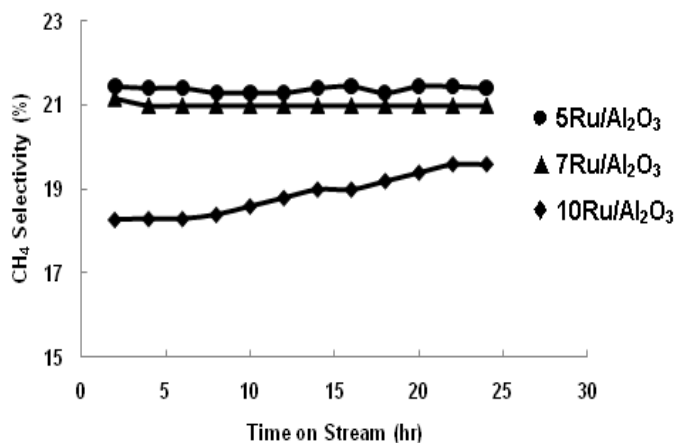


Fig.5. CO Hydrogenation Results with Time Dependence of CH₄ Selectivity over the Catalysts

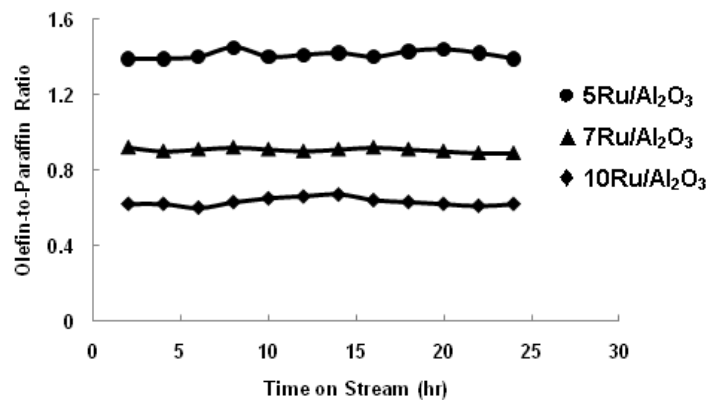


Fig.7. CO Hydrogenation Results with Time Dependence of Olefin-to-Paraffin over the Catalysts

Figure 8 shows the XRD patterns of γ -Al₂O₃, 5Ru/ Al₂O₃, 7Ru/ Al₂O₃, and 10Ru/ Al₂O₃ catalysts. γ - Al₂O₃ shows as a reference sample in this study. In this XRD patterns, all the catalysts showed similar diffraction peaks, however Ru species cannot be detected. It can be indicated that Ru species was highly dispersed on the catalyst surface [11].

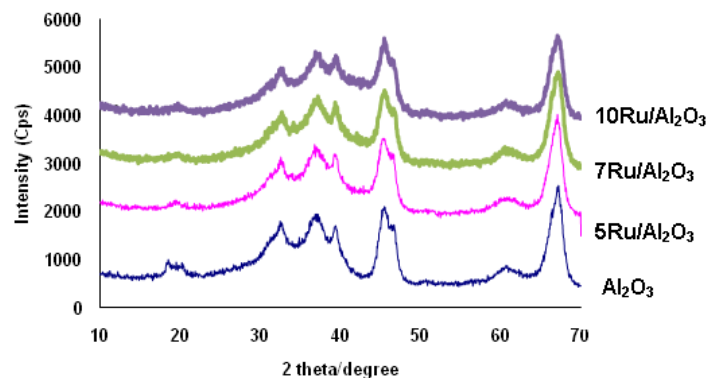


Fig.8. X-ray Diffraction of the Catalysts

4. CONCLUSIONS

In this experiment, we conclude that in a catalyst system for CO hydrogenation, an appropriate loading of Ru and moderate Ru particle size is more active than high loading of Ru. The product selectivity changed with Ru content. 7Ru/Al₂O₃ catalysts

exhibited higher CO conversion. The result indicates that higher metal loading favorite to form large particle size of supported Ru. High Ru loading did not contribute directly to the catalytic activity of Ru/Al₂O₃ catalyst.

REFERENCES

- [1] A. P. Steybergm, M. E. Dry. Fischer-Tropsch technology. *Stud. Surf. Sci. Catal.* 152 (2004)
- [2] J. Schulz. Short history and present trends of Fischer-Tropsch synthesis. *Appl. Catal. A.* 182 (1999) 3-12.
- [3] S. Ali, N. Asmawati M, Zabidi, D. Subbarao. Correlation between Fischer-Tropsch catalytic activity and composition of catalysts. *J. Chem. Central.* 5:68 (2011) 1-8.
- [4] M. A. Vannice. The Catalytic synthesis of hydrocarbons from H₂/CO mixture over the group VIII metals. *J. Catal.* 27 (1975) 449-461.
- [5] F. King, E. Shutt, A. I. Thomson. Ruthenium catalyst systems for the production of hydrocarbons from coal. *Platinum Metals Rev.* 29 (4) (1985) 146-154.
- [6] S. Bedrane, C. Descorme. An optimizes route for the preparation of well dispersed supported ruthenium catalysts. *J. Mater. Chem.* 12 (2002) 1563-1567.
- [7] A. Karimi, A. N. Pour, F. Torabi, B. Hatami, A. Tavasoli, M. R. Alaei, M. Irani. Fischer-Tropsch synthesis over ruthenium-promoted Co/Al₂O₃ catalyst with different reduction procedures. *J. of natural Gas Chemistry.* 19 No.5 (2010) 503-508.
- [8] C. H. Yang, J. G. Goodwin. Particle Size dependence for CO chemisorptions on supported Ru catalysts. *React. Kinet. Catal. Lett.* 20 (1982) 13-18.
- [9] M. Nurunnabi, K. Murata, K. Okabe, M. Inaba, I. Takahara. Performance and characterization of Ru/Al₂O₃ and Ru/SiO₂ catalysts modified with Mn for Fischer-Tropsch synthesis. *Appl. Catal. A.* 340 (2008) 203-211.
- [10] K. Murata, K. Okabe, I. Takahara, M. Inaba, M. Saito. Fischer-Tropsch synthesis over Ru/Al₂O₃ catalysts. *React. Kinet. Catal. Lett.* Vol 90. No. 2. (2007) 275-283.
- [11] P. Betancourt, A. Rives, R. Hubaut, C. E. Scott, J. Goldwasser. A study of the ruthenium-alumina system. *Appl. Catal. A.* 170 (1998) 307 – 314.