CO₂ Hydrogenation over Ru/χ-Al₂O₃ Catalyst

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Abstract. The hydrogenation of CO₂ was investigated over Ru/χ-Al₂O₃ catalyst prepared by thermal decomposition of gibbsite which was followed with impregnation using different types of ruthenium precursors. The performance of the catalysts was examined by the temperature programmed reaction of CO₂ with H₂. The Ru/χ-Al₂O₃ catalyst prepared using ruthenium (III) nitrosyl nitrate solution as the Ru source (RNN) exhibited the best performance, compared to other Ru precursors. The physiochemical properties of each catalyst were characterized using XRD diffraction, N₂ physisorption and H₂ chemisorption.

1. Introduction
In the past centuries, the amount of carbon dioxide (CO₂) in the atmosphere has increased continuously due to human activities and the combustion of fossil fuels in the industrial processes. The increase in CO₂ concentration is a key factor in the greenhouse effect, causing the rising global average temperature and climate change. Therefore, the study of potential strategies to reduce the amount of CO₂ in atmosphere such as storage of CO₂, reduction of CO₂ produced and conversion of CO₂ for usage is urgently required [1-3].

The hydrogenation of CO₂ is an interesting option to reduce greenhouse effects as, in the presence of hydrogen, it converts CO₂ with the presence of hydrogen into hydrocarbon such as methane (CH₄) accompanied by water. CO₂ can be captured from air, human activities and industrial processes by adsorption, and then CO₂ is converted into methane. Methane is a major component of synthetic natural gas (SNG) which can be utilized to produce energy through combustion. Moreover, CO₂ derived from energy production can be re-converted into methane using CO₂ hydrogenation. The reaction of CO₂ hydrogenation for methane production is shown below (equation (1)) [4,5].

\[
\text{CO}_2 + 4\text{H}_2 \leftrightarrow \text{CH}_4 + 2\text{H}_2\text{O}, \quad \Delta H = -164 \text{ kJ/mol}
\]  

As the reaction of CO₂ hydrogenation (equation (1)) is strongly exothermic, it thermodynamically favors low temperatures. Thereby, CO₂ hydrogenation reactions are highly active at low temperatures and catalysts can endure the heat of reaction. Among different types of catalyst, Ru is regarded as the most active catalyst and the most stable noble metal [6,7]. Generally, alumina is one of the most interesting catalyst supports due to its varieties of crystalline phases, which possess specific properties for particular applications. Among all Al₂O₃, χ-Al₂O₃ is one of low temperature transition alumina, which offers high surface area and thermal stability. In addition, it has high potential to be used as the catalyst and/or the support [8,9].

In this work, χ-Al₂O₃ was prepared using the thermal decomposition of microcrystalline gibbsite. The prepared χ-Al₂O₃ was used as the support for the Ru supported catalyst in the CO₂ hydrogenation reaction. The effect of Ru precursors on the physiochemical and catalytic properties of Ru/χ-Al₂O₃ was investigated.
2. Experimental

2.1 Catalyst preparation

$\chi$-Al$_2$O$_3$ support was prepared using the thermal decomposition of microcrystalline gibbsite (Sigma-Aldrich) at high temperatures. The gibbsite was calcined in a tube furnace with air flow (100 ml/min) at 600°C for 4 hours with a heating rate of 10°C/min. The 1% Ru/$\chi$-Al$_2$O$_3$ catalyst used in this study was synthesized using the incipient wetness impregnation techniques. 2 g of $\chi$-Al$_2$O$_3$ was impregnated with 3 different types of ruthenium precursors, viz., ruthenium (III) acetylacetonate (Ru(C$_5$H$_7$O$_2$)), 97%, Sigma-Aldrich), ruthenium (III) nitrosyl nitrate solution (Ru(NO)(NO$_3$)$_x$(OH)$_y$, $x + y = 3$, 1.5% Ru in nitric acid, Sigma-Aldrich) and hexaammineruthenium (III) chloride (Ru(NH$_3$)$_6$Cl$_3$, 98%, Sigma-Aldrich), respectively. The impregnated powder was kept at room temperature for 6 hours and dried at 110°C for 12 hours. After that, the dried powder was calcined in the air at 300°C for 4 hours with a heating rate of 10°C/min. The catalysts prepared using ruthenium (III) acetylacetonate, ruthenium(III) nitrosyl nitrate solution and hexaammineruthenium (III) chloride were symbolized as RAA, RNN and RCl, respectively.

2.2 Activity test

The activity test of the catalysts was performed in a continuous-flow fixed-bed reactor with the inner diameter of 7.1 mm (stainless steel) at atmospheric pressure. 0.15 ml of the catalyst powder was used in the reaction, using temperature programmed reaction method. The catalysts were reduced using H$_2$ with the flow rate of 30 ml/min at 400°C for 2 hours before the reaction start. The feed gas mixture of H$_2$/CO$_2$ = 3 with the balance helium were used in the reaction. GHSV was calculated as the volumetric flow rate versus catalyst volume. Therefore, GHSV was at 14,400 h$^{-1}$. The gaseous products were measured using a gas chromatograph (SHIMADZU GC-14B) with a TCD and FID detector.

2.3 Catalytic characterization

The specific surface area, average pore size and total pore volume of the fresh catalyst were measured by nitrogen gas adsorption at liquid nitrogen temperature (-196°C) using a BET SORP mini II. X-ray diffraction (XRD) patterns were determined using a Siemens D5000. The diffraction patterns were performed over the 2$\theta$ range between 20° and 80° using a Cu K$_\alpha$ radiation with a Ni filter. H$_2$ chemisorption was measured using a Micrometics AutoChem 2910 instrument. In each analysis, 60 mg of fresh catalyst was reduced using H$_2$ (25 ml/min) at 400°C for 2 hours. After the reduction, the sample was cooled to 100°C and then analysed at this temperature. H$_2$ uptake was determined using the pulse injection of H$_2$ into the reduced catalyst.

3. Results and Discussion

The BET surface area, pore volume and average pore diameter of the Ru/$\chi$-Al$_2$O$_3$ catalysts prepared using each ruthenium precursors are summarized in Table 1. Among the three catalysts, RAA exhibited the highest BET surface area and smallest average pore diameter, while RCl possessed the lowest BET surface area and largest average pore diameter. From XRD result, it clearly appears the peak intensity of RuO$_2$ in the three catalysts. And all catalysts exhibited the typical pattern of $\chi$-Al$_2$O$_3$.

The relative amounts of active surface Ru metal on the catalyst samples was calculated from H$_2$ chemisorption based on the assumption that one hydrogen molecule adsorbs on two ruthenium sites. The results of H$_2$ chemisorption over various ruthenium precursor catalysts are presented in Table 1. The dispersion and average particle size of Ru was calculated using the following equation (2).

$$%\text{Dispersion} = \frac{V_{STP}/22414}{S \times MW \times 100}/(\% \text{metal weight})$$

Where H$_2$ covered on Ru at STP is represented as VSTP and stoichiometric factor of H2 to atom of Ru is assigned as S = 2. The Ru metal dispersion was improved in order of RNN > RCl > RAA.
Table 1. BET surface area, pore volume, average pore diameter and H$_2$ chemisorption of Ru/χ-Al$_2$O$_3$ catalysts prepared using each ruthenium precursor.

| Catalyst | Surface area [m$^2$ g$^{-1}$] | Pore volume [cm$^3$ g$^{-1}$] | Average pore diameter [nm] | H$_2$ uptake [μmol g$^{-1}$] | Dispersion [%] |
|----------|-------------------------------|-----------------------------|-------------------------|----------------------------|----------------|
| RCl      | 155                          | 0.21                        | 5.5                     | 23.8                      | 24.10          |
| RNN      | 171                          | 0.21                        | 5.0                     | 31.0                      | 31.31          |
| RAA      | 192                          | 0.19                        | 4.0                     | 5.6                       | 5.62           |

The morphology of Ru/χ-Al$_2$O$_3$ catalysts are determined using TEM method and the results are shown in figure 1. It was found that the different RuO$_2$ particles were dispersed on the χ-Al$_2$O$_3$ surface. RNN and RCI catalyst exhibited the polyhedral shape particles of RuO$_2$, whereas, RAA catalyst appeared rod-shape particles.

Figure 1. TEM images of Ru/χ-Al$_2$O$_3$ catalysts using different ruthenium precursors:
(a) RNN, (b) RAA, (c) RCl.

The performance of the Ru/χ-Al$_2$O$_3$ catalysts was investigated using CO$_2$ hydrogenation at atmospheric pressures and different reaction temperatures between 250 and 425°C (with increasing steps of 25°C). The graph plotted between catalytic performance and reaction temperature for Ru/χ-Al$_2$O$_3$ catalysts with different ruthenium precursors is shown in figure 2. It can be seen that the increase in CO$_2$ conversion depended on the increasing reaction temperature. The RNN catalyst obtained the highest CO$_2$ conversion profile, compared to the other two catalysts. CO$_2$ conversion of the RNN catalyst started at 250°C and monotonically increased and then slowed down from 375°C onwards. For the RAA catalyst, the CO$_2$ conversion profile was slightly lower than the RNN catalyst. The RCl catalyst showed the lowest CO$_2$ conversion profile and its CO$_2$ conversion started at 275°C and slowly increased with the increasing reaction temperature.

The selectivity of the CH$_4$ profiles of the RCI catalyst was much lower than the RNN and RAA catalysts. In addition, the CH$_4$ selectivity of the RNN catalyst was indistinguishable from the RAA catalyst. The CH$_4$ yield showed that the formation rate of methane rose with the increasing reaction temperature. The RNN catalyst gave maximum CH$_4$ yield which was higher than the other catalysts. Moreover, CO formation started at the same temperature (~300°C) for all Ru precursor catalysts.

As mentioned above, the conversion of CO$_2$ into methane favored low temperatures and the maximum CO$_2$ conversion was consistent with the maximum methane formation rate. At high temperatures, the result indicated that there was the appearance of CO formation. This behaviour occurs because of the reverse water gas shift (equation (3)).


\[
\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O} \quad (3)
\]
From the catalytic performance results, RNN exhibited the best performance due to its highest Ru dispersion and also smallest Ru particle size, calculated from H₂ chemisorption. However, RCI also possessed high Ru dispersion but exhibited the lowest performance. This was probably due to the remains of residual chlorine, retarding the adsorption of feed gas on the catalyst surface [10].

**Figure 2.** The performance of Ru/γ-Al₂O₃ catalysts as a function of the reaction temperature using different ruthenium precursors: (a) CO₂ conversion, (b) CH₄ selectivity, (c) CH₄ and (d) CO yields.

### 4. Conclusion

The effect of ruthenium precursors in Ru/γ-Al₂O₃ on the catalytic performance in CO₂ hydrogenation reaction was performed using a temperature programmed reaction. The CO₂ conversion of the RNN catalyst was about 2 times higher than that of the RCI catalyst with a very small amount of byproduct at 375°C. The RCI catalyst showed low activity, probably due to the remains of residual chlorine. As the dispersion was highly effective, the Ru particle of the RNN catalyst obtained the smallest size among all the catalysts. Moreover, it gave higher CO₂ conversion and CH₄ formation than the other two ruthenium precursor catalysts. Although the RNN catalyst does not significantly differ from the RAA catalyst, it can be safely assumed that the catalytic performance is greater. As mentioned above, it is clear that the types of ruthenium precursors affect the activity and physical properties of catalysts.

### 5. Acknowledgments

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6. References

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