CO_2 hydrogenation over Ru supported on Zr-modified χ-Al_2O_3

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Abstract: Abstract is limited to 100 words.

Zr-modified χ-Al_2O_3 supports were prepared by wet impregnation of zirconium precursors on the gibbsite and following by the thermal treatment. Thus-obtained supports were impregnated with ruthenium (III) nitrosyl nitrate solution. The performance of the catalysts was examined by the temperature programmed reaction of CO_2 with H_2. Results revealed that the appropriate amounts of Zr loading improved the catalytic performance of Ru supported catalysts. The physiochemical properties of each catalyst were characterized by using XRD diffraction, N_2 physisorption and H_2 chemisorption.

Keywords: CO_2 hydrogenation, Zr modified χ-alumina, Ru catalyst

1. Introduction

In the past centuries, the amount of carbon dioxide (CO_2) in the atmosphere has increased continuously due to human activities and the combustion of fossil fuels in the industrial processes. The increasing of CO_2 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 CO_2 in atmosphere is urgently required [1]. CO_2 hydrogenation is an interesting alternative way to reduce greenhouse effects by converting CO_2 with the presence of hydrogen into value hydrocarbon products.

Among many types of catalyst, Ru is regarded as the most active catalyst and the most stable noble metal [2]. Generally, alumina is one of the most interesting supports due to its varieties of crystalline phases, which possess specific properties for particular applications. Among all Al_2O_3, χ-Al_2O_3 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 [3]. In this work, pure and Zr-modified χ-Al_2O_3 was used as the support for the Ru supported catalyst in the CO_2 hydrogenation reaction. The effect of Zr modification on the physiochemical and catalytic properties of Ru/Zr-modified χ-Al_2O_3 catalyst was investigated.

2. Experimental

2.1. Catalyst preparation

Zr-modified χ-Al_2O_3 support was prepared using the thermal decomposition of the microcrystalline gibbsite (Sigma-Aldrich) impregnating with the solution of zirconium butoxied (Sigma-Aldrich) in xylene at high temperatures. The mixture was treated 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/Zr-modified χ-Al_2O_3 catalyst was prepared using the incipient wetness impregnation techniques. 2 g of support was impregnated with ruthenium (III) nitrosyl nitrate solution ($Ru(NO)(NO_3)_x(OH)_y$, 1.5% Ru in nitric acid, Sigma-Aldrich). 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.

2.2. Activity test

The catalytic performance of the catalysts was measured in a continuous-flow fixed-bed reactor at atmospheric pressure using temperature programmed reaction method. The catalysts were prior reduced using H_2 with the flow rate of 30 ml/min at 400°C for 2 hours. The feed gas mixture of $H_2/CO_2 = 4$ with the

balance helium were used in the reaction. GHSV used in this test was fixed at 14,400 h^{-1}. The products were measured using a gas chromatograph (SHIMADZU GC-14B) with a TCD and FID detector.

3. Results and discussion

The performance of the Ru/Zr-modified χ-Al_2O_3 catalysts was investigated using temperature programmed reaction of CO_2 hydrogenation at atmospheric pressures. The graph plotted between catalytic performance and reaction temperature for Ru/χ-Al_2O_3 catalysts with different ruthenium precursors is shown in **Fig. 1**. It can be seen that the increase in CO_2 conversion depended on the increasing reaction temperature. The increasing of Zr doping contents resulted in the improvement CO_2 conversion profile. The high CH_4 selectivity (more than 90%) had been observed from all Ru supported catalysts. The physiochemical properties of all catalysts are also summarized in **Table** 1. Doping with Zr resulted in the decreasing of the BET surface area and the amounts of H_2 chemisorption. From XRD and TEM results (not shown here), the size of RuO_2 particles deposited on all catalysts did not shown much different. Therefore the drastic decreasing of the Ru metal active site could be due to the increasing of interaction between Ru metal and the Zr-modified support, which retard the adsorption of H_2.

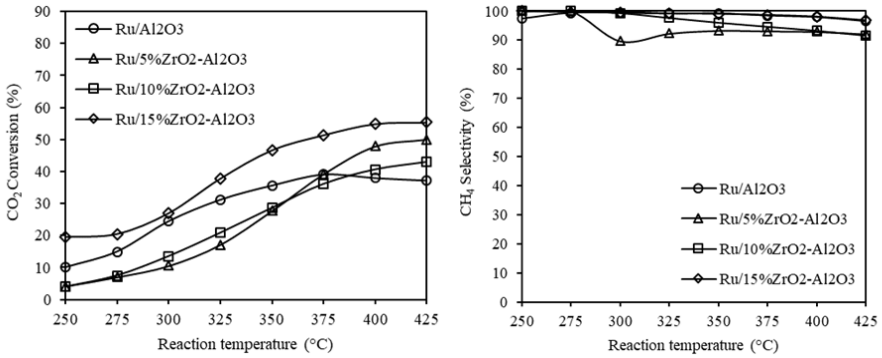

Figure 1. The performance of Ru/Zr-modified χ-Al_2O_3 catalysts as a function of the reaction temperature pattern

Table 1 Physiochemical properties of all prepared catalysts.

Catalyst	Surface area [m^2 g^{-1}]	Pore volume [cm^3 g^{-1}]	Average pore diameter [nm]	H_2 uptake [µmol g^{-1}]
Ru/Al_2O_3	171	0.21	5.0	31.0
Ru/5%ZrO_2-Al_2O_3	142	0.22	6.0	2.2
Ru/10%ZrO_2-Al_2O_3	136	0.19	5.5	6.9
Ru/15%ZrO_2-Al_2O_3	146	0.18	5.0	9.2

4. Conclusions

The addition of Zr on Ru supported χ-Al_2O_3 catalysts resulted in the improvement of catalytic performance in CO_2 hydrogenation reaction. The characterization result revealed that the addition of Zr changed the interaction between the Ru metal and the alumina support, which affected the catalytic performance of all Ru supported catalysts.

References

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