



Effect of magnesium in the mixed magnesia-zirconia supported Co catalyst on the Fischer-Tropsch synthesis

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Abstract

The Fischer-Tropsch synthesis (FTS) over mixed magnesia-zirconia supported Co catalyst was investigated. The supports of binary mixed oxides were prepared by flame spray pyrolysis (FSP). The magnesium loading was adjusted as 10, 30 and 50 wt%. The 10 wt% Co was impregnated on these supports. Three phases of monoclinic, tetragonal and orthorhombic zirconia were found in the catalyst without magnesium confirmed by the XRD results. The presence of magnesium in the support accelerated phase transformation from monoclinic to tetragonal. The adsorption-desorption isotherms of both catalysts with and without magnesium indicated a similarity of the slit-shaped pores but only 10 and 30 wt% Mg loadings showed lower BET surface area. The TPR results for three catalysts with magnesium showed the reduction peaks at high temperature. This implied to strong metal-support interaction resulting in a dramatic decrease of hydrogen chemisorption ability. All three catalysts supported on the mixed magnesia-zirconia promoted significantly the FTS product selectivity to heavy hydrocarbon. However, only 10 and 30 wt% Mg loadings showed higher rate of reaction.

Keywords: Fischer-Tropsch synthesis, Cobalt catalyst, FSP-made magnesia-zirconia support

Introduction

Currently, liquid hydrocarbon is a high demand energy source in the world, which is future predicted to increase continuously. Concerns about a decrease of source of liquid hydrocarbon result in development of alternative technology to produce synthetic fuel. Fischer-Tropsch synthesis (FTS) is interesting because it can convert syngas, the mixture of hydrogen (H₂) and carbon monoxide (CO), to clean hydrocarbon product [1]. Cobalt (Co), iron (Fe), nickel (Ni), ruthenium (Ru) and osmium (Os) are commonly accepted to be the best catalytic materials for use to FTS [2]. Cobalt based catalyst is interesting because it can be operated at low temperature, high stability, low water gas shift (WGS), high selectivity to heavy hydrocarbon and high resistance to deactivation [3-5]. Performance of catalyst is dependent on preparation, active sites, support and promoter.

Among many supports, zirconia (ZrO₂) and magnesia (MgO) are interesting. Zirconia is multifunctional transition metal oxide with bifunctional surface properties of base and acid and unique redox property [6]. Zirconia and cobalt species can lead to moderate surface area, high reducibility, high C₅₊ selectivity and high CO conversion under low pressure [7]. Magnesia has low surface area but it can improve catalyst to high activity, high stability, and high C₅₊ hydrocarbon selectivity [8-9]. In this work, binary mixed oxide support consisting of ZrO₂ and MgO was focused. This support was synthesized by flame spray pyrolysis (FSP), which is the technique to prepare the material from the metal precursor dissolved in a solvent and sprayed into the flame zone. The metal oxide nanoparticles are sufficiently formed and therefore the surface area increase to improve catalyst performance [10]. The effect of oxide compositions in the mixed support on the catalytic properties of Co based catalyst was studied.

Materials and methods

Catalyst preparation

The support was synthesized by flame spray pyrolysis. The Mg loadings were varied as 0, 10, 30 and 50 wt %. The precursors were 80 wt % zirconium (IV) butoxide ($Zr(OC_4H_9)_4$) solution in 1-butanol and magnesium acetate tetrahydrate ($(CH_3COO)_2Mg \cdot 4H_2O$). They were diluted by 1-butanol to obtain 0.5 M concentration. A 5 ml/min of liquid solution was injected into the flame. The powder was formed and collected by the filter connected with vacuum pump. The cobalt (II) nitrate hexahydrate precursor ($Co(NO_3)_2 \cdot 6H_2O$) was loaded on the support using wet impregnation. The cobalt loading was fixed as 10 wt %. The mixture was stirred at 70 °C for 6 h and then dried at 110 °C for 12 h. After impregnation, the catalyst was calcined at 500 °C for 4 h under air flow.

Catalyst characterization

The bulk crystalline phases of the catalysts were evaluated by X-ray diffraction (XRD). It was operated in the range of 2θ from 20° to 80° with Cu $K\alpha$. The crystallite sizes were calculated from XRD data using the Scherrer equation. The specific surface area and the pore characteristics of the catalysts were measured by N_2 physisorption. Before measurement, the catalyst was pretreated at 150 °C for 3 h under helium flow. Temperature programmed reduction (TPR) presented bulk reduction behavior and the reducibility of catalyst. A 0.15 g of the catalyst was added in a quartz tubular reactor. Before measurement, the catalyst was pretreated at 150 °C for 1 h under nitrogen flow to remove the adsorbed water on the catalyst surface. The reduction step was proceeded under 10 % H_2 in N_2 from room temperature to 800 °C with a heating rate of 10 °C/min. The active sites of the catalysts were determined by hydrogen chemisorption. A 0.15 g of the catalyst was added in a glass tubular reactor. Before measurement, the catalyst was reduced by hydrogen at 350 °C for 2 h. The metal active sites were measured at 100°C. The purified hydrogen gas (50 μ l) was repeatedly injected on the catalyst surface until the saturation. The data was calculated using the method described by Reuel and Bartholome.

Catalyst evaluation

The catalytic property was tested by FTS reaction, which was occurred in a fixed-bed reactor at 230 °C and 1 atm. The feed stream was 30 mol % CO in H_2 . The gas hourly space velocity (GHSV) was about 6000 h^{-1} . Before the catalytic test, the catalyst was reduced by H_2 at 350 °C for 2 h. During the catalytic test, the outlet stream was analyzed by two gas chromatographs (GC) with connected with a thermal conductivity detector (TCD) and a flame ionization detector (FID). The reaction was proceeded until steady state. A flow diagram of the system for testing the catalyst activity is shown in Figure 1.

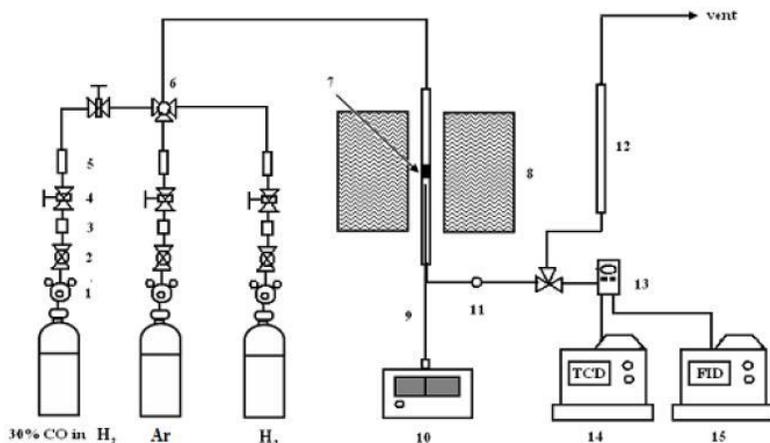


Figure 1 Schematic diagram of the reaction line for testing the FTS

Results and discussion

The XRD patterns of the Co/MgO-ZrO₂ catalyst are shown in Figure 2. The symbol of Co/*x*MgO-*y*ZrO₂ meant 10 wt % Co impregnated on the mixed support with *x* wt % MgO and *y* wt % ZrO₂ (The percentage of Co was based on the catalyst weight but *x* and *y* were based on the support weight. The main peak of Co₃O₄ indicated at 37° [1] was observed for all four catalysts. The Co/ZrO₂ indicated three phases of zirconia, i.e., monoclinic, tetragonal and orthorhombic. The presence of MgO in the support accelerated the phase transformation of monoclinic to tetragonal phase. The maximum crystalline size of both tetragonal and orthorhombic zirconia was found at 30 wt % Mg loading. They were 52 and 67 nm, respectively. Only 50 wt % Mg loading showed the XRD pattern of MgO phase at 43° and 62°. This was indicated that at 10 and 30 wt % Mg loading the magnesium oxide was well dispersed in the mixed oxide matrix.

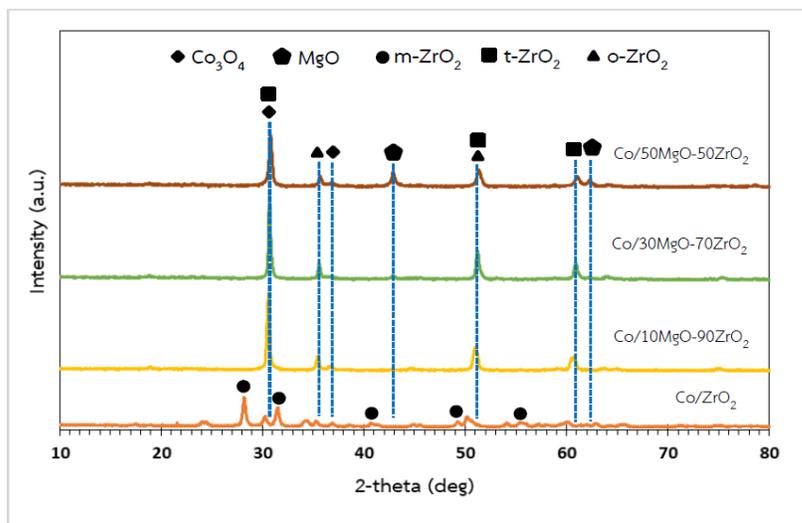


Figure 2 The XRD pattern of the Co/MgO-ZrO₂ catalyst with various Mg loadings

The BET surface area of the catalysts measured by N₂ physisorption is shown in table 1. At below 30 wt % Mg loading, the BET surface area was low compared to the catalyst without magnesium. Considering only the Mg-loaded catalysts, the BET surface area was increased with increasing magnesium content. The adsorption-desorption isotherms of all catalysts, not shown here, indicated a similarity of the slit-shaped pores.

Table 1 The specific surface area of the Co/MgO-ZrO₂ catalyst with various Mg loadings

Catalyst	BET Surface area (m ² ·g ⁻¹)
Co/ZrO ₂	28.7
Co/10MgO-90ZrO ₂	13.5
Co/30MgO-70ZrO ₂	19.2
Co/50MgO-50ZrO ₂	32.0

TPR profiles were shown in Figure 3. For the Co/ZrO₂ catalyst, the reduction was occurred in a broad range of 150-500 °C. This was implied to non-uniform Co₃O₄ particle sizes. In general, Co₃O₄ bulk was reduced by two steps. The first step assigned to the reduction of Co₃O₄ to CoO and the second step represented the reduction of CoO to Co⁰. The addition of Mg showed sharp peak at low temperature and broad peak at temperature above 500 °C. More than 30 wt % Mg loading, the peak at moderate temperature was also observed. The peaks at low and moderate temperature indicated two reduction steps of Co₃O₄ to Co⁰ while the broad peak at high temperature was assigned as the cobalt strongly interacted with the support.

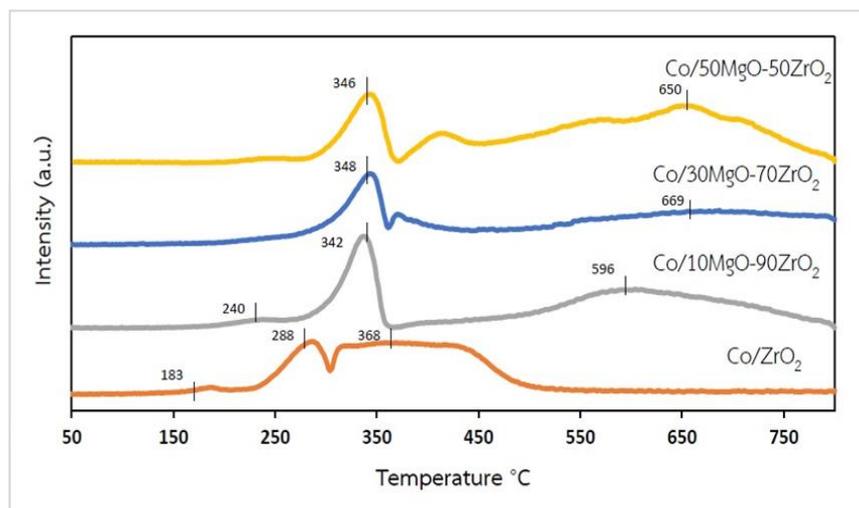


Figure 3 TPR profiles of the Co/MgO-ZrO₂ catalyst with various Mg loadings

The amount of cobalt active sites on the catalyst surface was determined by H₂ chemisorption at 100 °C. The result is shown in Figure 4. The active sites were significantly decreased when the support was binary mixed oxides. Before the measurement, the catalyst was reduced at 350 °C for 2 h and therefore from the TPR result the cobalt strongly interacted with the support was partially reduced. This was a reason for a decrease of H₂ adsorbed on the catalyst surface. However, a strong interaction between the cobalt and the support resulted in loss of ability to adsorb H₂ as well [11].

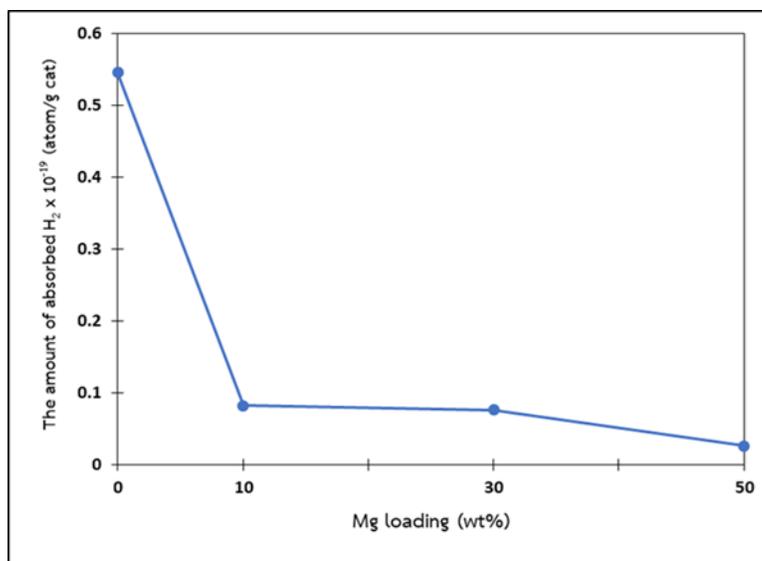


Figure 4 The metal active sites of the Co/MgO-ZrO₂ catalyst with various Mg loadings

The reaction rate, turnover frequency (TOF) and product selectivity of the Co/MgO-ZrO₂ catalysts with various Mg loadings are shown in Figures 5 and 6. When the Mg was added, the reaction rate, TOF and kerosene selectivity were enhanced, except 50 wt % Mg loading. All Mg-loaded catalysts showed high selectivity to kerosene. It was possible that Mg promoted strong cobalt-support interaction and accelerated long chain propagation. This was agreement with the strong interaction of cobalt and support by which the catalyst was able to selectively cleave C---O bond in furan ring [11].

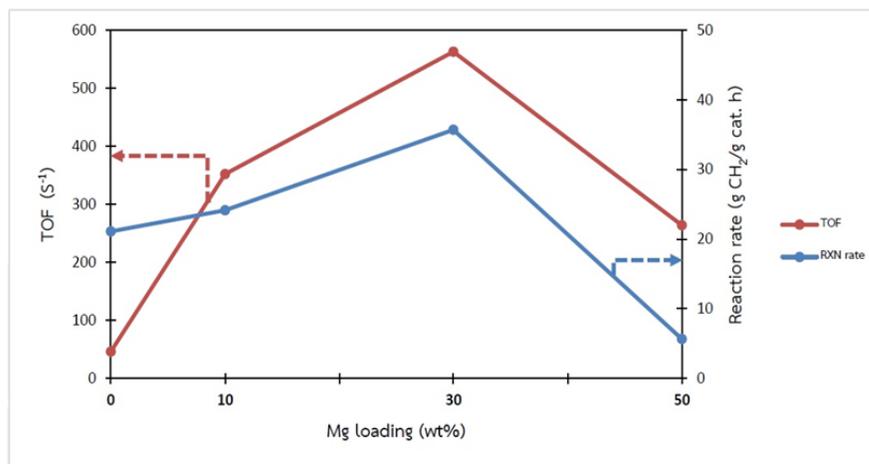


Figure 5 The FTS reaction rate and TOF of the Co/MgO-ZrO₂ catalyst with various Mg loadings

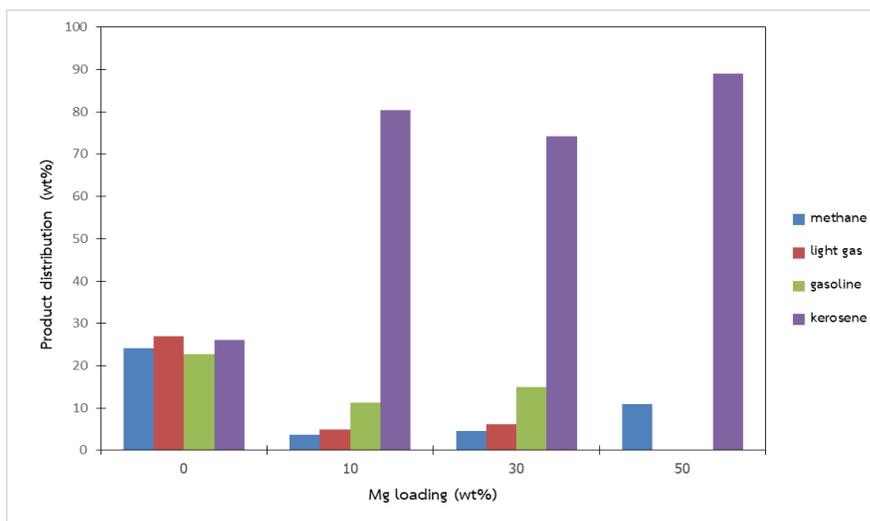


Figure 6 The FTS product distribution of the Co/MgO-ZrO₂ catalyst with various Mg loadings

Conclusion

The presence of Mg in the binary mixed MgO-ZrO₂ support accelerated the phase transformation of zirconia from monoclinic to tetragonal phases. It enhanced a strong interaction of cobalt and support leading to suppress hydrogen adsorption. This strong interaction was an important role to promote the selectivity to heavy hydrocarbons in Fischer-Tropsch synthesis. The optimum Mg loading was 30 wt % to show high reaction rate and maintain high kerosene selectivity.

Acknowledgements

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