A study of Cobalt-based Fischer-Tropsch Catalyst for the Production of High Calorific Synthetic Natural Gas

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Abstract: We investigated the performances of the Co-based catalysts with various supporters to develop the new high calorific Synthetic Natural Gas (SNG) process. The CO conversion of the Co-based catalysts supported with alumina, non-porous silica and porous silica were 95, 80 and 91%, respectively. And it was maintained for 400 min without deactivation. The C_2-C_4 selectivity were 18, 30 and 23%, respectively. In particular, the porous silica-supported catalyst shows high C_2-C_4 selectivity and low C_{5+} selectivity, even though the CO conversions was lower than that of the alumina supported catalyst.

Keywords: Co catalyst, high calorific, Synthetic Natural Gas, Fischer-Tropsch.

1. Introduction

Natural gas is expected to produce the least amount of carbon dioxide (CO_2) to produce the unit energy of hydrocarbon fuels, increasing demand for natural gas to mitigate global warming. However, natural gas has a higher proportion of transportation costs and the production countries are limited. So the studies on how to produce Synthetic Natural Gas (SNG) by gasifying relatively inexpensive and abundant coal have been actively conducted for energy security of each country. The heating value of natural gas is one of the most important factors in the use of natural gas. Typical SNG has 99% of methane, of which the heating value is 8,107 kcal/Nm^3. In general, the heating value of domestic city gas was enhanced by adding the Liquefied Propane Gas (LPG) up to 10,400 ± 100 kcal / Nm^3 in Korea. However the LPG is directly affected by the price of petroleum, a new process for producing high calorific natural gas is needed.

In this study, we developed the new Fischer-Tropsch catalyst to produce light hydrocarbon (C_2-C_4) less than 5 atoms of carbon using the coal gasification syngas. We investigated the CO conversion and CH_4, C_2-C_4 and C_{5+} selectivity of the Co-based catalysts with various supports.

2. Experimental

Co-Mn-Ru-based catalysts were prepared by typical impregnation method. Ruthenium was first impregnated to the support materials. $RuCl_3 \cdot H_2O$ (Aldrich) was dissolved in ethanol with the support. And dried at 40-60°C using rotary vacuum evaporator. After drying at 120°C overnight, Ru/support was calcined at 400°C for 3 h. At the second impregnation step, the cobalt and manganese precursors ($Co(NO_3)_2 \cdot 6H_2O$ and $Mn(NO_3)_2 \cdot 4H_2O$, Sigma-Aldrich) dissolved in ethanol were then impregnated on Ru/support. And then the sample was dried and calcined at the same condition.

3. Results and discussion

Figure 1 shows the CO conversion and C_2~C_4 selectivity of the various Co-Mn-Ru-based catalysts supported with α-alumina, non-porous silica and porous silica in a fixed bed reactor at 300 °C, 10 bar, and 5000 ml/g-catalyst·h using the syngas (H_2/CO=3.1). In the case of the alumina-supported catalyst, the CO

conversion was 95%, which is higher than that of the other catalysts, but the C_2-C_4 and C_{5+} selectivity were about 17.6% and 9.4%, which are lower. In the case of the non-porous silica-supported catalyst, the C_2-C_4 selectivity was highest than that of the other catalysts, but the C_{5+} selectivity was highest, too. And the CO conversion is 80%, which is the worst of all the performances of the catalyst. However, the porous silica-supported catalyst shows good performances which are the high C_2-C_4 selectivity and low C_{5+} selectivity, even though the CO conversions was lower than that of the alumina supported catalyst. These results were due to the phase and particle size of the Co metal that caused by metal-support interaction.

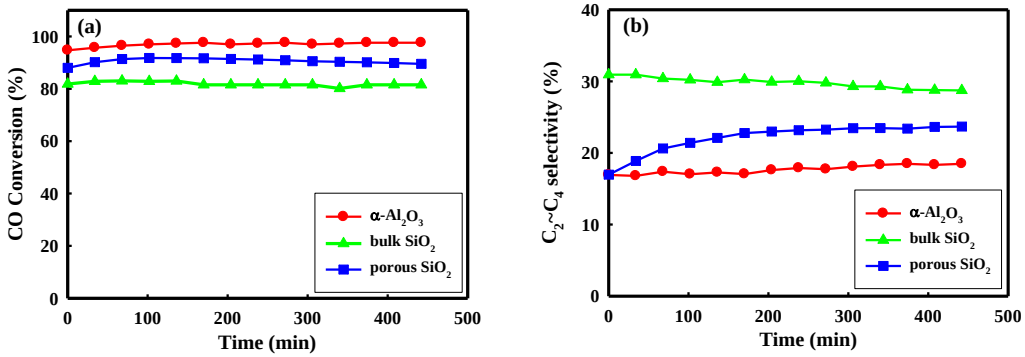

Figure 1. The (a) CO conversion and (b) C_2-C_4 selectivity of the Co-Mn-Ru-based catalysts using α-alumina, non-porous silica, and porous silica as a supporter.

4. Conclusions

We investigated the performances of the Co-based catalysts with various supports at 300 °C, 10 bar, H_2/CO=3.1, 5000 ml/g-catalyst·h to develop the catalyst for the new high calorific SNG process using coal gasification syngas. The CO conversions of the catalyst supported with alumina, non-porous silica and porous silica were 99, 80 and 91%, respectively. In particular, the porous silica-supported catalyst shows the high C_2-C_4 selectivity and low C_{5+} selectivity. So the porous silica-supported Co-based catalyst can be used for the new high caloric SNG process.