Effect of calcium oxide on the properties and Fischer-Tropsch synthesis activities of the Co/ZrO$_2$ catalyst prepared by flame spray pyrolysis.

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Abstract – In this research, the effect of calcium oxide on the catalytic properties of zirconia supported cobalt catalyst for Fischer-Tropsch synthesis (FTS) was investigated under atmospheric pressure. All catalysts were prepared by flame spray pyrolysis (FSP). Mixing of calcium and zirconium precursors in flame spray pyrolysis step and then impregnation of cobalt precursor can inhibit the monoclinic phase formation. The interaction between cobalt and zirconia on the 20Co-5CaO/Z catalyst was slightly changed by calcium oxide. The 20Co-5CaO/Z catalyst showed the highest cobalt active sites compared with the CaO-modified catalysts. The 20Co-5CaO-Z and 20Co/5CaO-Z catalysts were promising. They showed high FTS reaction rate and high selectivity to heavy hydrocarbons.

Keyword: Co/ZrO$_2$ catalyst/ Fischer-Tropsch synthesis/ CaO/ syngas / flame spray pyrolysis
1. Introduction

The Fischer-Tropsch synthesis (FTS) was the pathway to convert syngas (CO+H\textsubscript{2}) to liquid hydrocarbons of various forms \cite{1,2}. Considerable development has taken place in the FT process in terms of improved design of reactors and synthesis of efficient cobalt (or iron)-based catalysts leading to optimization of a fully integrated gas-to-liquids (GTL) process for commercial scale application.

Typical catalysts used are based on iron and cobalt. The cobalt-based catalyst is usually used in FTS because of their high activity and selectivity for linear hydrocarbons, the lower cost compared with other catalyst and low activity for water-gas shift reaction (WGS). Their activity mainly depends on the density of surface metallic cobalt, which is usually correlated to their dispersion and reducibility. The kinds of supports generally used for this purpose are oxides such as ZrO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, SiO\textsubscript{2}, and TiO\textsubscript{2}. The support shows effect to the different metal-support interaction, which relates to catalytic activity of FTS. Use of zirconia as a cobalt catalyst support has showed the high activity and selectivity of long chain hydrocarbon in FTS. Cobalt supported zirconia catalyst increases longer chain hydrocarbons selectivity and enhances the chain growth probability \cite{3,4}.

In the previous work \cite{7-9}, study the catalytic performance of Co impregnated on the Co incorporated with ZrO\textsubscript{2} by FSP. Effect of the Co and Ru ratio between impregnation and incorporation was investigated over ZrO\textsubscript{2} prepared by FSP on the Fischer-Tropsch synthesis. Although ruthenium can obviously improve the properties of catalyst in Fischer-Tropsch synthesis, it includes highly prices. In attitude of commercialization, other metal promoters lowering the catalyst costs have been studied to supplant the noble metal. Bimetallic catalyst was interested in this case, the kinds of metals were selected to use with cobalt catalyst to according the need of properties. Metal oxide added in bimetallic form of catalyst can be used to modified the support leading to increased dispersions, the result of this promotion is an increase in the number of active sites and therefore a higher catalyst activity. The metal oxide was useful in FTS catalyst such as MgO, K\textsubscript{2}O, CaO, MnO\textsubscript{2}, Ni\textsubscript{2}O\textsubscript{3}, ZnO, Mo\textsubscript{2}O\textsubscript{5} and La\textsubscript{2}O\textsubscript{3}. Addition of calcium oxide on cobalt catalyst to produce bimetallic catalyst can enhance the catalytic activity, decrease the catalyst reducibility and inhibit selectivity of methane.

In this research, the effect of calcium oxide on the properties and Fischer-Tropsch synthesis activities of the Co/ZrO\textsubscript{2} catalyst prepared by flame spray pyrolysis is investigated.

2. Experimental

2.1. Catalyst preparation

In this research, the flame spray pyrolysis (FSP) and impregnation techniques were used to prepare the catalyst. All the catalysts containing cobalt (20 wt%) were promoted by calcium oxide (5 wt%). Some cobalt and/or calcium oxide was partially incorporated with ZrO\textsubscript{2} during the FSP step whereas some of it was impregnated. The six types of catalysts were shown in table 1.

<table>
<thead>
<tr>
<th>Catalyst preparation method</th>
<th>Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 wt% Co incorporated with ZrO\textsubscript{2} by FSP</td>
<td>20Co-Z</td>
</tr>
<tr>
<td>20 wt% Co impregnated on ZrO\textsubscript{2} by FSP</td>
<td>20CoZ</td>
</tr>
<tr>
<td>20 wt% Co and 5 wt% CaO were incorporated with ZrO\textsubscript{2} by FSP</td>
<td>20Co-5CaO-Z</td>
</tr>
<tr>
<td>5 wt% CaO was impregnated on 20 wt% Co incorporated with ZrO\textsubscript{2} by FSP</td>
<td>5CaO20Co-Z</td>
</tr>
<tr>
<td>20 wt% Co was impregnated on 5 wt% CaO incorporated with ZrO\textsubscript{2} by FSP</td>
<td>20Co5CaO-Z</td>
</tr>
<tr>
<td>20 wt% Co and 5 wt% CaO were impregnated on ZrO\textsubscript{2} prepared by FSP</td>
<td>20Co-5CaO/Z</td>
</tr>
</tbody>
</table>

2.2. Catalyst characterization

The crystallite sizes of the catalysts were characterized by X-ray diffraction (XRD). Temperature programmed reduction (TPR) was used to determine the reducibility of catalysts and H\textsubscript{2} chemisorption was used to determine the cobalt dispersion on the catalyst surface.

2.3. Catalyst evaluation

The catalytic activity and product selectivity of all samples were tested by Fischer-Tropsch synthesis in a fixed-bed reactor. Prior the reaction, 0.2 ml of catalyst was reduced by H\textsubscript{2} with flow rate of 30 ml/min at 350°C for 2 h. After the reduction, the reactor temperature was decreased to 220°C under atmospheric pressure. The syngas (molar ratio of H\textsubscript{2}/CO = 2.33 and GHSV = 9000 h\textsuperscript{-1}) was introduced at this condition. The total volumetric flow rate was 30 ml/min. The composition of the product stream was analyzed by two on-line gas chromatographs (GC) connecting with GC-FID and GC-TCD detector.
3. Results and Discussion

Figures 1 and 2 show the X-ray diffraction patterns of the samples. The XRD peaks at 30°, 35°, 50° and 60° indicated the ZrO$_2$ in tetragonal phase [5] while the XRD peaks at 29° and 32° were assigned to the presence of monoclinic zirconia [6]. The FSP catalysts can stabilize tetragonal phase of the ZrO$_2$ while the phase transformation take place with the impregnated catalyst. The introduction of Co or CaO in FSP step can inhibit the phase transformation as shown in Figure 2.

![XRD patterns of the Co based catalysts prepared by FSP and impregnation](image1)

![XRD patterns of the Co based catalysts with bimetallic calcium oxide](image2)

CaO on FSP catalysts can increase cobalt dispersion and therefore decrease the particle size.

![TPR patterns of the Co-Z based catalysts](image3)

![TPR patterns of the Co/Z based catalysts](image4)

The activation of the catalyst in hydrogen atmosphere was disclosed by temperature programmed reduction (TPR) experiment. Figure 3 shows the TPR peaks of the Co-Z based catalysts. The first and second peak indicated the reduction of Co$_3$O$_4$ to Co metal and the reduction of cobalt oxide interaction with ZrO$_2$ respectively. The second peak was shifted to higher reduction temperature when the CaO was modified. Co/Z based catalyst with CaO loading reduced slightly the reduction temperature, as shown in Figure 4. The result of H$_2$ chemisorption indicated that addition of CaO on FSP catalysts can increase cobalt dispersion and therefore decrease the particle size.

![TPR patterns of the Co-Z based catalysts](image5)

Fig. 3. TPR patterns of the Co-Z based catalysts.

Fig. 4. TPR patterns of the Co/Z based catalysts.

The results of FTS activity test show that the cobalt catalyst with CaO gives higher CO conversion than that without catalyst. Figure 5 shows high selectivity to heavy hydrocarbons for the 20 Co-5CaO-Z catalyst.

![Selectivity of products for effect of CaO loading on cobalt catalyst at 180 min](image6)

Fig. 5. The selectivity of products for effect of CaO loading on cobalt catalyst at 180 min
4. Conclusions

The effect of CaO addition on the FTS catalytic performance of the Co/ZrO$_2$ catalyst was focused. The results of catalyst characterization and catalyst evaluation showed that the CaO affected some properties of the catalyst. These showed to prevent the ZrO$_2$ phase transformation of tetragonal to monoclinic phase, increase the reducibility and promote selectivity to heavy hydrocarbons.

5. Acknowledgement

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References