

The Effect of Promoters on Reduction of Ru/ZrO₂/Co/SiO₂ Catalyst for Fischer-Tropsch Synthesis as Studied by *in situ* XANES

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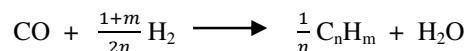
ABSTRACT

Ru/ZrO₂/Co/SiO₂ was prepared via a co-precipitation and an incipient wetness impregnation methods and characterized by XRD and XANES. To study the effect of promoters on reduction of active cobalt species on the catalyst, Ru/ZrO₂/Co/SiO₂, ZrO₂/Co/SiO₂, Ru/Co/SiO₂, and Co/SiO₂ were observed by *in situ* XANES. The results showed no Co(0) on Co/SiO₂ whereas Ru/Co/SiO₂ was reduced to 37.5% Co(0). ZrO₂ exhibited less effect on the reduction of Co species. Ru/ZrO₂/Co/SiO₂ diluted with quartz as the same composition ratio in the synthetic reaction was investigated producing 34.9% Co(0) and 65.1% CoO after reduction. Fischer-Tropsch product selectivity from the reaction over Ru/ZrO₂/Co/SiO₂ catalyst was observed in terms of chain growth probabilities of n-paraffins as a function of carbon numbers and as a function of time during self-organization of the catalyst. The growth probability of paraffins with high carbon number was high at 72 h indicating the steady state of Fischer-Tropsch synthesis.

Keywords: FTS cobalt catalyst, FTS Ru/ZrO₂/Co/SiO₂ catalyst, FTS cobalt catalyst promoter, FTS *in situ* XANES reduction.

1 INTRODUCTION

Fischer-Tropsch synthesis (FTS) is considered as a promising route for converting natural gas, coal and biomass to liquid fuels and other chemicals via syngas as shown in the following equation.



It synthesizes hydrocarbons through a -CH₂-polymerization reaction using Co or Fe as a catalyst. Cobalt is favorable for the synthesis of long chain hydrocarbons due to its high activity, high selectivity to linear paraffins and low water-gas shift activity [1].

Addition of zirconia (ZrO₂) as a promoter has been used to improve the FTS activity of the Co-based catalysts [2,3].

It is also found that C⁵⁺ selectivity or chain growth probability of hydrocarbons could be promoted upon such addition. Promoters such as Ru, Pt, and Re are often employed to facilitate the reduction of cobalt species interacting with the support and thereby generate more available active cobalt metal surface sites to participate in synthesis [4,5,6].

However, the FTS is highly dependent on the redox state of the active components, i.e. cobalt. The distribution of cobalt phase changes during reaction on stream. The cobalt catalyst agglomerates and sinters during high temperature operation, therefore, various kinds of the inorganic oxides support such as SiO₂ [7], MCM-41 [8], Al₂O₃ [9] and TiO₂ [10] have been used to disperse Co metal particles and prevent sintering for improving stability and activity of cobalt based catalyst. The product selectivities are closely related to the state of the catalyst together with the type of the catalyst support.

There is a controversy concerning the structure sensitivity in the FT reaction when the metals are promoted on the catalysts. It has been shown that the dispersion of the cobalt active phase which might change to other forms of cobalt during the synthesis, has an influence on the chain growth and the hydrocarbon distributions.

This study is aimed to investigate the real promoted cobalt (Ru/ZrO₂/Co/SiO₂) for the FTS. The structures of the FT catalysts will be characterized to study the influence of the promoters on dispersion and reduction of the catalyst active species. The real catalyst structures before the FTS reactions will be observed together with product selectivities during the FTS analyzing by an adapted instantaneous sampling unit.

2 EXPERIMENTAL

2.1 Catalyst preparation

The Co-based catalyst was prepared via a co-precipitation using an aqueous solution of cobalt nitrate (Co(NO₃)₂·6H₂O) and zirconyl nitrate (ZrO(NO₃)₂·xH₂O). Silica (aerosil) (BET surface area = 200 m² g⁻¹) was used as a catalyst support. Subsequently, the dried prepared

sample was immersed into ruthenium chloride solution ($\text{RuCl}_3 \cdot x\text{H}_2\text{O}$) to achieve a desired ruthenium loading. The impregnated catalyst was dried then calcined at 873 K with a heating rate of 2 K/min in flowing 40 cm^3/min of argon for 6 hours. The desired chemical composition of cobalt samples are present in Table 1.

2.2 Catalyst characterization

XRD was used to determine the crystalline phases of the catalysts. It was performed using diffractometer with $\text{Cu}_{K\alpha}$ ($\lambda=1.54 \text{ \AA}$), electron current of 45 mA with an accelerating voltage of 35 kV. The spectra were scanned with step size of 0.02° in the range $2\theta = 20 - 70^\circ$. The identification of crystalline phase is accomplished by comparing the pattern results with ICSD databases.

X-ray absorption spectroscopic experiment (XAS) was performed at Synchrotron Light Research Institute (SLRI), Thailand. The *in situ* Co *K*-edge XANES measurements under reductive condition were measured in transmission mode using Si(111) bent crystal monochromator, providing the energy dispersive XAS to disperse and focus a range of X-ray energies. The transmitted X-ray was detected simultaneously with linear image NMOS sensor, of which the readout is 1000 ms. Data analysis was performed using Athena. Cobalt foil, CoO and Co_3O_4 were used as references.

2.3 Fischer – Tropsch synthesis

The catalyst was dried at 333 – 363 K under 30 cm^3/min of Ar for 1 hour then was reduced at 723 K under 30 cm^3/min of Ar and 10 cm^3/min of H_2 for 16 hours. The reactor was cooled down to 463 K then reactant gases (20 cm^3/min H_2 , 10 cm^3/min CO and 30 cm^3/min Ar) flowed continuously to the reactor through the catalyst bed at a

| Co-samples | Content (wt%) | | | |
|---|------------------|-------|------------------|------|
| | SiO ₂ | Co | ZrO ₂ | Ru |
| Co/SiO ₂ | 50.00 | 50.00 | - | - |
| 0.33Ru/Co/SiO ₂ | 49.84 | 49.84 | - | 0.33 |
| 7ZrO ₂ /Co/SiO ₂ | 46.51 | 46.51 | 6.98 | - |
| 9ZrO ₂ /Co/SiO ₂ | 45.45 | 45.45 | 9.09 | - |
| 13ZrO ₂ /Co/SiO ₂ | 43.48 | 43.48 | 13.04 | - |
| 0.07Ru/7ZrO ₂ /Co/SiO ₂ | 46.48 | 46.48 | 6.97 | 0.07 |
| 0.15Ru/7ZrO ₂ /Co/SiO ₂ | 46.44 | 46.44 | 6.97 | 0.15 |
| 0.31Ru/7ZrO ₂ /Co/SiO ₂ | 46.37 | 46.37 | 6.96 | 0.31 |

Table 1: The weight percentages of each component in cobalt samples. space velocity of 180 $\text{dm}^3 \text{ g}^{-1} \text{ h}^{-1}$ at 10 bar. Another Ar line was connected before the needle valve to hold the reaction

pressure up to 10 bar. Cyclopropane in N_2 of 0.5 vol% used as reference was added at the atmospheric pressure into the product stream, mixed in a mixer and was sampling with an adapted ampoule sampling unit [11,12].

3 RESULTS AND DISCUSSION

The XRD patterns of 0.07Ru/7ZrO₂/Co/SiO₂ and 0.31Ru/7ZrO₂/Co/SiO₂ before reduction are shown in Fig. 1. The patterns showed the peaks at 2θ 31.3°, 36.9°, 59.4° and 65.3° corresponded to Co_3O_4 as the major cobalt phase.

Table 2 presents linear combination analyses of XANES spectra of all Co-samples before reduction (sample no. 1-8) and *in situ* XANES reduction (sample no. 9-16). Cobalt on SiO₂ without any promoters was not reduced to Co after reduction (sample no. 9). When ruthenium was added (0.33Ru/Co/SiO₂), the reducibility of the Co-species was better. Co_3O_4 was reduced to 37.5% Co and 61.4% CoO with some trace of Co_3O_4 left (sample no. 10). When ZrO₂ was added (7ZrO₂/Co/SiO₂), Co_3O_4 was also reduced well to 33.7% Co and 66.3% CoO. The reducibility was decreased with decreasing the ZrO₂ content in the samples (sample no. 11-13). It can be proposed that ZrO₂ interacts with SiO₂ via bonding through oxygen. At the same time, Co species (both CoO and Co_3O_4) coordinate with ZrO₂ via oxygen which is more polar than that on SiO₂. Therefore, ZrO₂ has the influence on Co species dispersion causing high reducibility to small Co particles. Khodakov *et. al* [13] showed that the reduction of CoO to Co was strongly influence by the particle size, with the smaller being more difficult to reduce. Therefore with high ZrO₂ content (13 ZrO₂/Co/SiO₂) the percentage of Co from reduction decreased to 11.0%. For the catalyst composition (Ru/ZrO₂/Co/SiO₂), the reducibility to Co increased with the increase amount of Ru (0.07% to 0.31%) producing 67.2% Co and 32.8% CoO (Table 3).

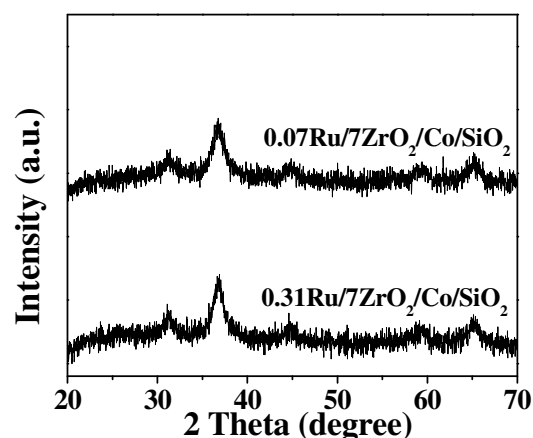


Figure 1 The XRD patterns of 0.07Ru/7ZrO₂/Co/SiO₂ and 0.31Ru/7ZrO₂/Co/SiO₂ before reduction.

| Sample No. | Co-samples | Linear combination analysis | | |
|------------|---|-----------------------------|------|--------------------------------|
| | | Co | CoO | Co ₃ O ₄ |
| 1 | Co/SiO ₂ | 0.0 | 52.2 | 47.8 |
| 2 | 0.33Ru/Co/SiO ₂ | 0.0 | 58.1 | 41.9 |
| 3 | 7ZrO ₂ /Co/SiO ₂ | 0.0 | 33.8 | 66.2 |
| 4 | 9ZrO ₂ /Co/SiO ₂ | 0.0 | 22.3 | 77.7 |
| 5 | 13ZrO ₂ /Co/SiO ₂ | 0.0 | 45.8 | 54.2 |
| 6 | 0.07Ru/7ZrO ₂ /Co/SiO ₂ | 0.0 | 24.3 | 75.7 |
| 7 | 0.15Ru/7ZrO ₂ /Co/SiO ₂ | 0.0 | 34.3 | 65.7 |
| 8 | 0.31Ru/7ZrO ₂ /Co/SiO ₂ | 0.0 | 35.6 | 64.4 |
| 9 | reduced Co/SiO ₂ | 0.0 | 83.9 | 16.1 |
| 10 | reduced 0.33Ru/Co/SiO ₂ | 37.5 | 61.4 | 1.1 |
| 11 | reduced 7ZrO ₂ /Co/SiO ₂ | 33.7 | 66.3 | 0.0 |
| 12 | reduced 9ZrO ₂ /Co/SiO ₂ | 29.3 | 70.7 | 0.0 |
| 13 | reduced 13ZrO ₂ /Co/SiO ₂ | 11.0 | 89.0 | 0.0 |
| 14 | reduced 0.07Ru/7ZrO ₂ /Co/SiO ₂ | 42.4 | 57.6 | 0.0 |
| 15 | reduced 0.15Ru/7ZrO ₂ /Co/SiO ₂ | 44.1 | 55.9 | 0.0 |
| 16 | reduced 0.31Ru/7ZrO ₂ /Co/SiO ₂ | 68.0 | 32.0 | 0.0 |

Table 2: Linear combination analysis of catalysts before and after reduction at 723 K. Reduction condition was 30 cm³/min of H₂. (ramp rate 5 K/min).

| Catalysts | Linear combination analysis | | |
|---|-----------------------------|------|--------------------------------|
| | Co | CoO | Co ₃ O ₄ |
| 0.07Ru/7ZrO ₂ /Co/SiO ₂ | 0.0 | 10.5 | 89.5 |
| 0.31Ru/7ZrO ₂ /Co/SiO ₂ | 0.0 | 15.3 | 84.7 |
| reduced 0.07Ru/7ZrO ₂ /Co/SiO ₂ | 34.9 | 65.1 | 0.0 |
| reduced 0.31Ru/7ZrO ₂ /Co/SiO ₂ | 67.2 | 32.8 | 0.0 |

Table 3: Linear combination analysis of catalysts diluted with quartz before and after reduction. Reduction condition was 10 cm³/min of H₂ and 30 cm³/min of Ar, at 723 K 16 h. (ramp rate 2 K/min).

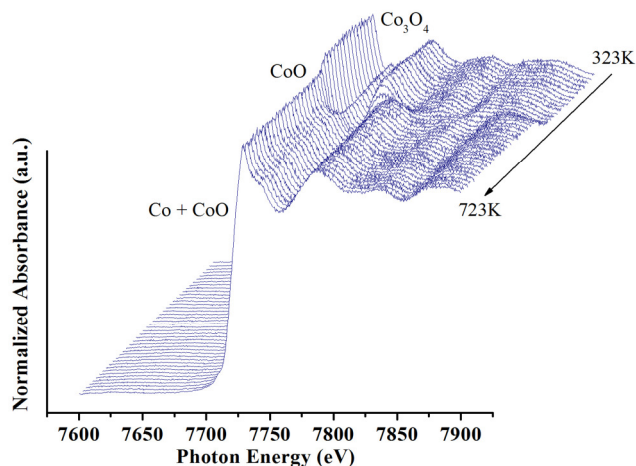


Figure 2: *in situ* XANES of 0.07Ru/7ZrO₂/Co/SiO₂ diluted with quartz as the same composition ratio in the FTS.

XANES spectra resulted from the *in situ* reduction of 0.07Ru/7ZrO₂/Co/SiO₂ catalyst, diluted with quartz as the same composition ratio for the FTS, are illustrated in Fig. 2. Before reduction at 323 K, the Co active species were 10.5% CoO and 89.5% Co₃O₄. The Co₃O₄ gradually changed to CoO and Co upon reduction at high temperature. At 723 K, which was used for reduction of the FTS catalyst (0.07Ru/7ZrO₂/Co/SiO₂) in the fixed bed reactor, the Co species were 34.9% Co and 65.1% CoO after reduction. Whereas, the higher Ru content (0.31Ru/7ZrO₂/Co/SiO₂) showed higher percentage (84.7%) of Co after reduction. For the FTS, the low Ru content catalyst (0.07Ru/7ZrO₂/Co/SiO₂) was used in order to reduce the hydrogen dissociation activity which could decrease the CH₄ formation as a result.

The ideal -CH₂- polymerization of the FTS is defined by the value of growth probability, p_g and represented with horizontal line [14]. Fig. 3 shows the low p_g value at $N_c = 1$ due to high activity for CH₄ formation and the high p_g value at $N_c = 2$ corresponded to high ethylene re-adsorption on growth sites. The growth probability was 0.7 at 72 h and was constant to 120 h indicating the steady state of the FTS. The p_g value in the range of 0.6 – 0.7 was independent of carbon number, whereas the increasing values upto $p_g = 0.8$ corresponded to the increasing probability of olefin re-adsorption on the growth sites of the reconstruction catalyst with increasing carbon number. To observe the product selectivities of the FTS on the 0.07Ru/7ZrO₂/Co/SiO₂ catalyst at the steady state in more details, the product selectivities of n-paraffin, i-paraffin and olefin together with the %CO conversion at 96 h reaction time were illustrated in Fig. 4(a) and 4(b). Fig. 4(a) exhibits 80% CO conversion upto 120 h reaction time. The n-paraffin selectivity was high at C₂ with low fraction of long chain hydrocarbon upto C₁₆ and there was some trace of i-paraffin and olefin at low C-number.

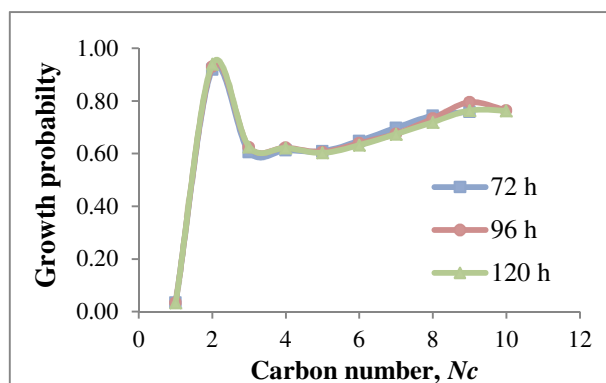


Figure 3 : The growth probabilities of n-paraffins from FT over 0.07Ru/7ZrO₂/Co/SiO₂ at 72, 96 and 120 h.

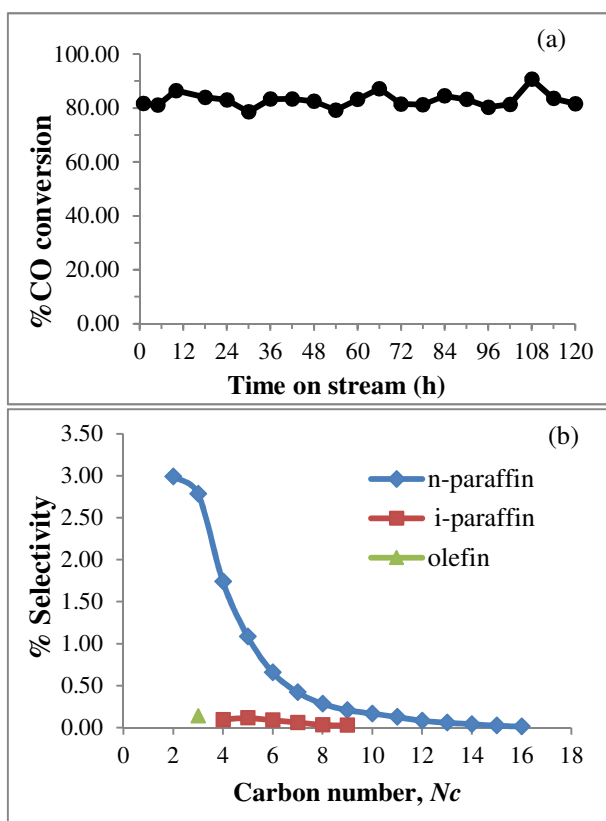


Figure 4 (a) %CO conversion of FT reaction over 0.07Ru/7ZrO₂/Co/SiO₂ and (b) FT product selectivities of n-paraffin, i-paraffin and olefin from the reaction over 0.07Ru/7ZrO₂/Co/SiO₂ at 96 h

4 CONCLUSIONS

The investigation of Ru/ZrO₂/Co/SiO₂ catalyst structure by *in situ* XANES indicating that both Ru and ZrO₂ had the influence on reduction of the Co-species. The reducibility of Co-species increased with the increasing content of Ru whereas the high content of ZrO₂ reduced the reduction activity due to high Co-species dispersion on the catalyst support. For the FTS, the activity of the catalyst was high

for CO conversion and CH₄ formation. The growth probability value (p_g) was independent of carbon number in the range of 0.6 – 0.7 at the steady state from 72 h and increased to 0.8 indicating the olefin re-adsorption on the growth sites of the reconstruction catalyst. However, at the FTS steady state of 96 h the long chain hydrocarbon was produced together with some traces of i-paraffin and olefin.

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