

XAS studies on promoted and un-promoted silica supported cobalt catalysts for Fischer-Tropsch synthesis

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Abstract. An investigation on the performance of cobalt catalysts for Fischer-Tropsch synthesis, 100Co/20ZrO₂/100Aerosil and 100Co/20ZrO₂/100Aerosil/0.66Ru, was carried out. These catalysts were prepared by co-precipitation method. Cobalt phases in fresh catalysts were characterized by means of XRD and XAS techniques including XANES and EXAFS. From XRD, fresh catalysts showed the presence of cobalt in the form of Co₃O₄. XANES analysis showed the oxidation state of Co as Co₃O₄ which corresponded to the result from XRD. EXAFS showed that the small addition of ZrO₂ and Ru in the catalyst resulted in the change of cobalt coordination shells. Preliminarily, hydrocarbon products in the range of C₁ to C₉ catalyzed by the prepared catalyst were observed.

Keywords: XANES, EXAFS, promoted cobalt catalyst, Fischer-Tropsch synthesis

1. Introduction

The Fischer-Tropsch synthesis (FTS) is a catalytic process that converts CO and H₂ (so-called as synthesis gas or syngas) into a mixture of linear gaseous, liquid, and solid hydrocarbons using as alternative energy sources. This synthesis has received considerable attention in recent years by both of industrial and academic worlds as a way of exploiting the huge natural gas reserves located in remote areas, leading to high-grade fuels [1]. In fact, FTS derived products are excellent high performance and clean diesel fuels due to their cetane number and the absence of sulphur [2] and aromatic compounds [1].

Both Co and Fe are used as FTS catalysts, however, Co catalysts are preferred for gas to liquid (GTL) applications because of the lower gas shift activity and the higher paraffinic nature of the resulting synthetic crude [3]. The most active metals for FTS are Co, Fe, Ru, and Ni. Co and Ru are preferred for the synthesis of higher hydrocarbons at low temperature and high pressure [4]. Cobalt-based catalysts have been successfully applied in the industrial processes due to their high FTS activity and low oxygenates selectivity, which makes this catalyst suitable for the H₂-rich syngas obtained from natural gas [5]. In the case of cobalt-based catalyst, the ability to prepare well-dispersed cobalt clusters on supports such as silica, alumina or titania and their promotion with Ru, Re, or Pt are considered to be the most promising aspects in obtaining high FTS activity [6]. These promoters normally help increasing the catalytic activity by increasing reducibility of cobalt particles, decreasing the deactivation rate, and retaining high activity for longer duration, whereas ZrO₂ is also used to help suppression the cobalt particle aggregation [7].

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In this study, we are investigating the catalytic activity of the doubly promoted Co/ZrO₂/Ru/SiO₂ catalyst and looking at the local structure of un-promoted and promoted Co using X-ray absorption techniques of X-ray Absorption Near Edge Structure (XANES) and Extended X-Ray Absorption Fine Structure (EXAFS).

2. Experiment

2.1. Catalyst Preparation

The cobalt catalysts were prepared by discontinuous co-precipitation of aqueous Co(NO₃)₂·6H₂O and ZrO₂·8H₂O solutions in the presence of Aerosil (Aerosil 200, Evonik) (final composition in mass ratio: 100Co/20ZrO₂/100Aerosil). Then, it was further impregnated with RuCl₃·xH₂O (final composition in mass ratio: 100Co/20ZrO₂/100Aerosil/0.66Ru). The prepared samples were pre-treated by calcination in air with temperature programmed of 2°C/min from ambient temperature to 400 °C, and kept for 6 h.

2.2. X-ray absorption

X-ray absorption (XANES and EXAFS) measurements on Co⁰, CoO, Co₃O₄ reference compounds and prepared catalysts were carried out at the beam line 8, Synchrotron Light Research Institute (SLRI), Nakorn Ratchasima, Thailand with synchrotron radiation using beam line with energy of 1.2 GeV. The X-ray energy was monochromatized with channel-cut Ge (220) crystal monochromator. A Si (111) monochromator was used to vary the energy within the desired range. Measurements were carried out at the K-edge of Co. The calibration was performed with a Co foil using the first point of inflection of Co at 7709 eV. The X-ray absorption measurements were performed in the transmission mode.

2.3. Fischer-Tropsch synthesis activity test

The Fischer-Tropsch synthesis was carried out in a stainless steel fixed-bed reactor with 2 g of catalyst loading and operated at 190°C and total pressure of 10 bars. Hydrogen (99.9990%, Air liquid) and carbon monoxide (99.997%, Air liquid) were introduced to the reactor through mass flow controller (Bronkhorst High-Tech). The H₂/CO ratio was 2 in all experiments. 0.5% Cyclopropane in N₂ was used as internal standard.

Prior to the activity test, the catalyst was activated under the flow of H₂ (0.6 lh⁻¹, 16 h.) at atmospheric pressure at 450°C. The temperature of reduction was chosen in order to get Co or Ru at the metallic state [5]. The catalyst was cooled to the reaction temperature (190°C) and the pressure was increased up to 10 bars. Then, the H₂ flow was adjusted to the value for the reaction testing and CO was introduced. Analysis of gaseous products was carried out by gas chromatography equipped with flame ionization detector (FID). The schematic diagram of FTS setup was briefly shown in Figure 1.

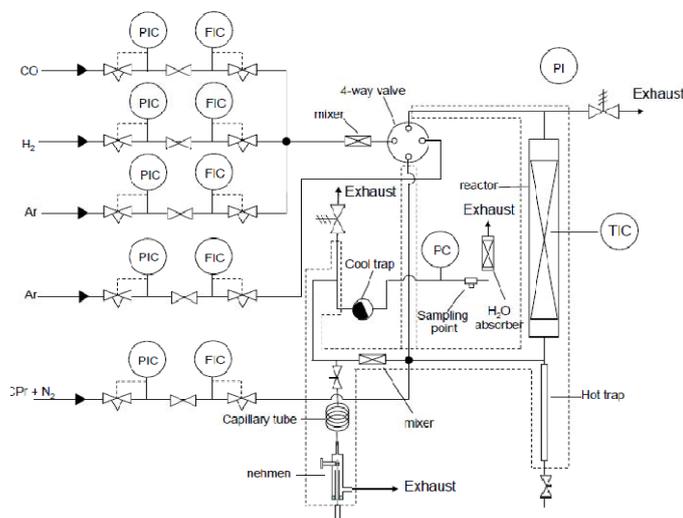


Fig. 1: Schematic diagram of fixed-bed reactor for FTS testing.

3. Results and discussion

3.1. Silica supported cobalt catalysts

XRD patterns (not shown here) revealed the cobalt phase of Co_3O_4 ($2\theta = 19.09, 31.39, 36.91, 37.31, 44.91, 55.77, 59.41, 65.33$, JCPDS card No. 76-1802) with its particle size of approximately 3 nm using Scherrer's equation, indicating the good distribution of cobalt. Co_2SiO_4 (cobalt silicate) and CoO were not detected over prepared catalysts. Also, there was no evidence of ZrO_2 and Ru crystalline components.

3.2. X-ray absorption

From X-ray absorption measurements, Figure 2 summarized the XANES analysis of prepared 100Co/20ZrO₂/100Aerosil and 100Co/20ZrO₂/100Aerosil/0.66Ru catalysts compared with reference compounds. From Figure 2 (left) the spectra of 100Co/20ZrO₂/100Aerosil showed the pre-edge and edge energies of Co at 7702 and 7720 eV, respectively and there was a small increase at 7709 eV which was close to the small increase at 7709 eV of the Co_3O_4 reference. From Figure 2 (right), the spectra of 100Co/20ZrO₂/100Aerosil/0.66Ru showed the pre-edge and edge energies of Co at 7706 and 7720 eV, respectively, and there was a small increase at 7709 eV close to the small increase at 7709 eV of the Co_3O_4 reference. By comparing the pre-edge of Co foil, CoO, and Co_3O_4 references at 7702, 7705 and 7702 eV, and edge energies at 7709, 7716, and 7720 eV, respectively, both 100Co/20ZrO₂/100Aerosil and 100Co/20ZrO₂/100Aerosil/0.66Ru catalysts had the pre-edge and edge energies close to Co_3O_4 reference and Co/Aerosil studies [9]. The XANES spectra showed that cobalt phase was in the form of Co_3O_4 which agreed with the XRD result and the small addition of ZrO_2 and/or Ru in Co/Aerosil did not cause any changes in cobalt oxidation state.

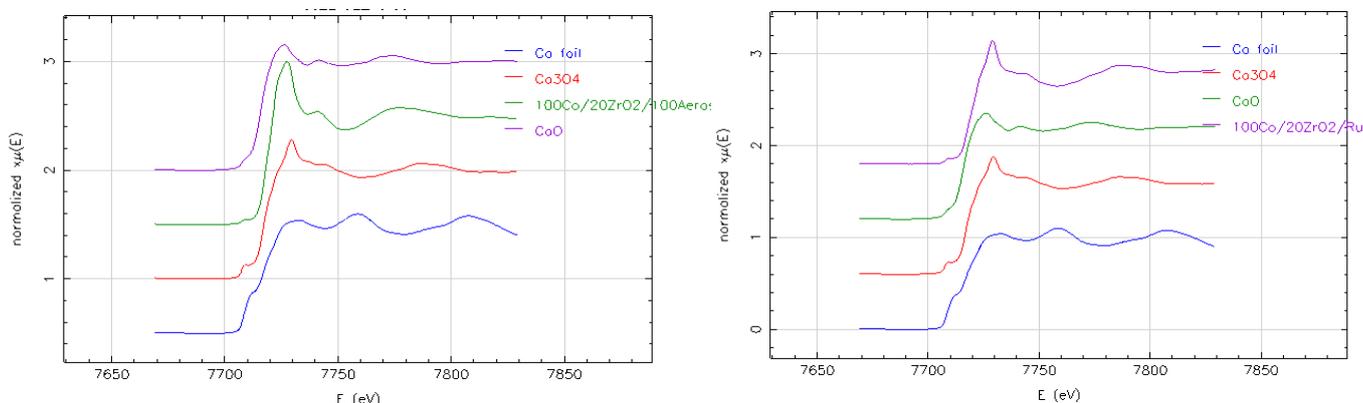


Fig. 2: Normalized XANES spectra of 100Co/20ZrO₂/100Aerosil (left) and 100Co/20ZrO₂/100Aerosil/0.66Ru (right) compared with reference compounds.

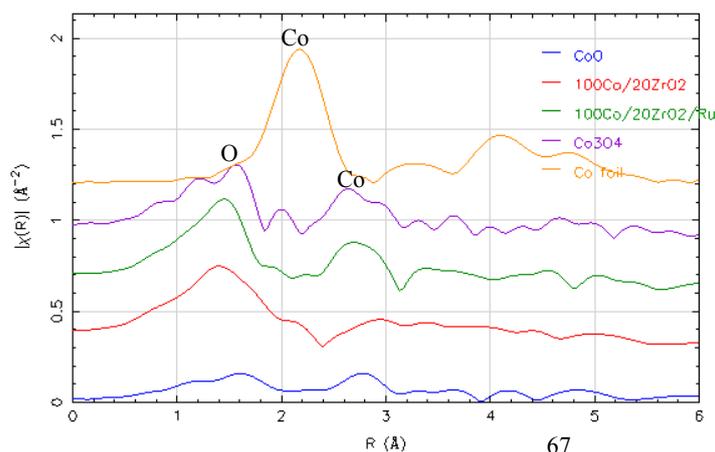


Fig.3: EXAFS Fourier transform measured for 100Co/20ZrO₂/100Aerosil and 100Co/20ZrO₂/100Aerosil/0.66Ru compared with reference compounds.

From the results of XANES, the cobalt phase of both 100Co/20ZrO₂/100Aerosil and 100Co/20ZrO₂/100Aerosil/0.66Ru catalysts was almost identical to that of Co₃O₄ by having a spinel structure with Co²⁺ ions in tetrahedral coordination and Co³⁺ in octahedral coordinated with oxygen atoms [8,10]. The EXAFS spectra of 100Co/20ZrO₂/100Aerosil and 100Co/20ZrO₂/100Aerosil/0.66Ru catalysts were shown in Fig 3. By Fourier transformation of Co₃O₄, the peaks attributed to Co-O and Co-Co coordination shells were stated in Table 1 [8]. By comparing the Co-O and Co-Co shells in the Co₃O₄ with the EXAFS spectra, the results showed the slight decrease of Co-O distance and the increase of Co-Co distance in 100Co/20ZrO₂/100Aerosil and 100Co/20ZrO₂/100Aerosil/0.66Ru. It was indicated that the small addition of ZrO₂ and/or Ru in Co/Aerosil altered the Co-O and Co-Co distance resulting in the change in coordination shells of cobalt in the prepared catalysts.

Table 1: Interatomic distance (R) and coordination numbers (N) of the Co model compounds [8].

Sample	R, Å	N	Sample	R, Å	N
Co foil (Co metal)			CoO		
Co-Co	2.51	12	Co-O	2.13	6
Co-Co	3.57	6	Co-Co	3.02	12
Co-Co	4.36	24	Co-O	3.69	8
Co-Co	5.02	12	Co-Co	4.27	6
Co-Co	5.62	24			
Co₃O₄					
Co-O	1.89	4			
Co-O	1.98	1.33			
Co-Co	2.85	4			
Co-Co	3.35	8			

3.3. Reaction testing

From the preliminary reaction testing on FTS by the prepared 100Co/20ZrO₂/100Aerosil/0.66Ru catalyst, the products were analyzed by gas chromatography as shown in Fig. 4. The hydrocarbon products from C₁ to C₉ were obtained. The large amount of methane was observed showing that the prepared catalyst could also be a methanation catalyst. The further catalyst preparation and reaction testing will be studied.

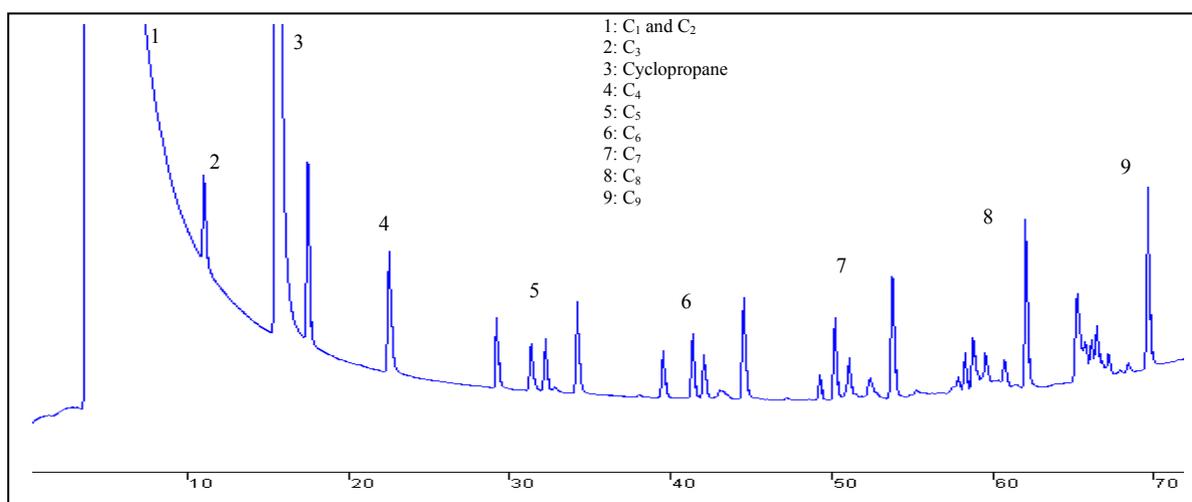


Fig. 4: A representative of GC chromatogram for preliminary Fischer-Tropsch synthesis activity test over 100Co/20ZrO₂/100Aerosil/0.66Ru.

4. Conclusion

From XAS studies, the small addition of ZrO₂ and/or Ru to the silica supported cobalt catalysts did not change the oxidation state of cobalt after pre-treatment by calcinations but it was a cause of change in coordination shells of cobalt catalysts. From the preliminary studies on FTS reaction over the 100Co/20ZrO₂/100Aerosil/0.66Ru catalyst, the hydrocarbons in the range of C₁ to C₉ were produced and there was a high selectivity on methane production. This was leading to the further studies on the catalyst preparation, characterization, and the catalytic activity on Fischer-Tropsch synthesis.

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6. References

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