

Article

Time-resolved XANES studies on used silica supported cobalt catalysts

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Abstract. In order to investigate the phases of used Co/SiO₂ catalysts, one of the most commonly used catalysts for Fischer-Tropsch synthesis, time-resolved X-ray absorption near edge structure (TR-XANES) technique was introduced. The catalysts were prepared by incipient wetness impregnation method with %Co loading of 15% and 20% and used for Fischer-Tropsch synthesis at the reaction temperature of 190°C and the pressure of 10 and 20 bar, called 15%Co/Aerosil_wi_used_10_bar, 15%Co/Aerosil_wi_used_20_bar, and 20%Co/Aerosil_wi_used_20_bar. TR-XANES showed the edge energy of 7721 eV for all used catalysts and by looking at the feature of their spectra, the results implied that the major phase was CoO. To further investigate their ability of being oxidized at elevated temperatures, the catalysts were oxidized by heating from ambient to 450°C with the heating rate of 8°C/min at the pressure of 1 bar with the O₂:N₂ flow rate of 70:30 ml/min. Once reaching 450°C, the temperature was held at 450°C for 90 min before cooling down to room temperature. During heating, holding, and cooling, the catalyst properties were measured by TR-XANES. When all catalysts heating up from 300 to 400°C, the edge energy of 15%Co/Aerosil_wi_used_10_bar, 15%Co/Aerosil_wi_used_20_bar, and 20%Co/Aerosil_wi_used_20_bar at 7719, 7717, and 7718 eV, respectively, showed the main phase of CoO mixed with Co₃O₄. There were no significant changes in phase while holding the temperature at 450°C. Once cooling from 450°C to room temperature, the edge energy of 15%Co/Aerosil_wi_used_10_bar at 7724 eV showed the main Co₃O₄ phase, the ones of 15%Co/Aerosil_wi_used_20_bar and 20%Co/Aerosil_wi_used_20_bar at 7717 and 7718 eV showed the mixed phase of Co₃O₄ and CoO. All results would be confirmed by further studies on temperature programmed oxidation (TPO).

Keywords: Time-resolved X-ray absorption near edge structure (TR-XANES), Fischer-Tropsch synthesis, cobalt catalyst.

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1. Introduction

The Fischer-Tropsch synthesis (FTS) process is one of most promising processes to produce clean liquid fuels from syngas (mixture of carbon monoxide and hydrogen). It allows rational utilization of fossil and renewable resources (natural gas, coal and biomass) [1]. 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. FT synthesis derived products are excellent high-performance and clean. The obtained diesel fuel has high cetane number and contains sulfur and aromatic compounds free [2, 3].

A key element in improved the Fischer-Tropsch technology is the development of active and stable catalysts with high wax selectivity. Today cobalt catalysts for FT diesel production from natural gas are designed for a maximum wax selectivity [4, 5]. Cobalt is considered as the most favorable metal for the synthesis of long chain hydrocarbon due to its high activity and selectivity to linear paraffins and low water gas shift (WGS) activity. The chain growth CH_2 - (monomer) formation involves the restructuring of cobalt catalysts including segregation of the metal surface and thus sites disproportionation. The catalysts usually consist of Co metal particles dispersed on an oxide support [5]. The FT cobalt catalyst is of dynamic nature. All relative rates of elemental reaction are depending on reaction time, temperature and partial pressures (mainly CO and H_2). The structure of site appears to be thermodynamically controlled, as linked to CO-adsorption-induced surface segregation [6]. Solving problem on catalyst deactivation is the major challenge in cobalt based Fischer-Tropsch synthesis [5]. The structural studies utilizing synchrotron radiation are well suited for in situ time-resolved measurements of catalysts [7]. X-ray absorption spectroscopy (XAS) provides powerful structural and chemical information about a selected element in a material. A particular strength of this technique is that penetrating nature of the X-rays make possible studies of materials under the conditions of their use, including high temperature, pressure and reactive atmosphere [1].

Normally, Co^0 is the active phase in Fischer-Tropsch synthesis. However, after FT reaction testing, the Co^0 could oxidize to CoO and Co_3O_4 . Prior to reuse these catalysts, their surface should be clean. Oxidation is introduced in the process in order to remove the carbon/hydrocarbons that contaminate the catalyst surface causing the deactivation and by doing so, Co species would be fully oxidized to Co_3O_4 phase before proceeding to reduction and another reaction testing. In this study, we investigated the oxidation of cobalt species in the used silica supported cobalt catalysts by time-resolved XANES technique.

2. Experiment

2.1. Catalysts Preparation

The cobalt catalysts were prepared by the incipient wetness impregnation method using silica (Aerosil 200, Evonik) as the catalyst support (BET surface area of $\sim 200 \text{ m}^2/\text{g}$). The impregnating solution of cobalt(II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) were at the concentrations of 15 and 20 %wt, the prepared catalysts were called 15% Co/Aerosil_wi and 20% Co/Aerosil_wi. After impregnation, the catalysts were dried at 110°C for 20 h and calcined in Ar at 400°C for 6 h.

2.2. Fischer-Tropsch Synthesis

The catalyst loading of 2 g was reduced by H_2 diluted with Ar in a stainless steel fixed-bed reactor at 550°C for 5 h. The Fischer-Tropsch synthesis was carried out at the temperature of 190°C and the pressure of 10 and 20 bars. Hydrogen (99.9990%, Air liquid) and carbon monoxide (99.997%, Air liquid) were introduced to the reactor through mass flow controllers (Bronkhorst High-Tech) at the H_2/CO molar ratio of 2:1 for 12 h. 0.5%/cyclopropane in N_2 was used as the internal standard for product analysis using gas chromatography with flame ionization detector (FID). Three catalysts, 15%Co/Aerosil_wi_used_10_bar, 15%Co/Aerosil_wi_used_20_bar, and 20%Co/Aerosil_wi_used_20_bar, would be preliminarily focused in this study. The schematic diagram of FTS setup was briefly shown in Fig. 1.

2.3. Time-Resolved X-Ray Absorption near Edge Structure (TR-XANES)

The oxidation of three used catalysts was investigated using Time-Resolved X-ray Absorption Near Edge Structure (TR-XANES). The measurements were performed at the Time-Resolved X-ray Absorption Spectroscopy (TRXAS) station, Beam line 4, Synchrotron Light Research Institute (Public Organization) (SLRI), Nakorn Ratchasima, Thailand with synchrotron radiation using beam line with energy of 1.2 GeV to observe the changes in Co species during oxidation. TR-XANES on 15%Co/Aerosil_wi_used_10_bar, 15%Co/Aerosil_wi_used_20_bar, and 20%Co/Aerosil_wi_used_20_bar catalysts were carried out at *K*-edge of Co and the results were compared to the measurements on Co⁰, CoO, and Co₃O₄ reference compounds. The catalysts were oxidized by heating from ambient to 450°C with the heating rate of 8°C/min at the pressure of 1 bar with the O₂:N₂ flow rate of 70:30 ml/min. Once reaching 450°C, the temperature was held at 450°C for 90 min before cooling down to room temperature.

2.4. Temperature Programmed Oxidation

The oxidation behavior of a used silica supported cobalt catalyst was investigated using the temperature programmed oxidation (TPO) technique (TPDO/MS 1100 at The Petroleum And Petrochemical College, Chulalongkorn University, Bangkok, Thailand). Oxidation of 15%Co/Aerosil_wi_used_10_bar was performed in a 60 ml/min 4.99% O₂ in Helium at the temperature from 0 to 950°C with heating rate of 10°C/min and held for 240 min. The procedure, involved pretreatment of the sample with N₂ at temperature of 120°C for 30 min, was measured by thermal conductivity detector (TCD).

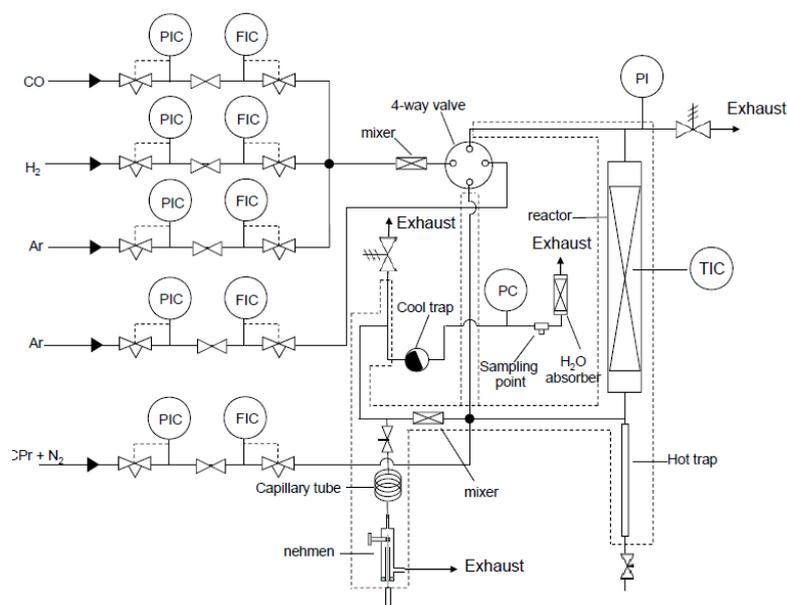


Fig. 1. Schematic diagram of FTS reaction testing. (PIC: pressure indicator controller, PC: pressure controller, PI: pressure indicator, FIC: flow indicator controller and TIC: temperature indicator controller).

3. Results and Discussion

3.1. Time-Resolved X-Ray Absorption near Edge Structure

Three used catalysts of 15%Co/Aerosil_wi_used_10_bar, 15%Co/Aerosil_wi_used_20_bar, and 20%Co/Aerosil_wi_used_20_bar were studied by TR-XANES. The edge energy of reference compounds was reported in Table 1. The measurements included heating the used catalysts in O₂/N₂ atmosphere (70:30 by volume) from ambient to 300, 400, and 450°C, holding at 450°C for 90 min, and cooling from 450 °C to room temperature. At ambient, the results were compared to the reference edge energy and corresponded to the phase of CoO as shown in Fig. 2. When heating to 400°C, by looking at the edge

energies of 15%Co/Aerosil_wi_used_10_bar, 15%Co/Aerosil_wi_used_20_bar, and 20%Co/Aerosil_wi_used_20_bar at 7719, 7717, and 7718 eV, respectively, cooperated with the feature of spectra, the results indicated the main phase of CoO mixed with Co₃O₄, as shown in Fig. 3(a). When reaching 450°C and holding for 90 min, there were no significant changes in phase of cobalt Fig. 3(b).

Table 1. The edge energy of cobalt reference compounds.

Reference compounds	Edge Energy (eV)
Co foil	7709
CoO	7720
Co ₃ O ₄	7727

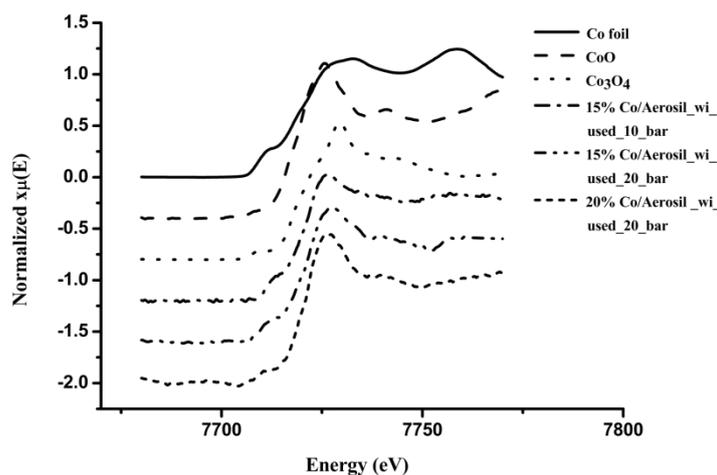


Fig. 2. The normalized Co *K*-edge XANES spectra of the 15%Co/Aerosil_wi_used_10_bar, 15%Co/Aerosil_wi_used_20_bar, and 20%Co/Aerosil_wi_used_20_bar catalysts at ambient compared with cobalt reference compounds.

The composition of cobalt phase was analyzed by linear combination analysis of Athena program. After holding at 450°C for 90 min, the species of Co₃O₄ in all catalysts was increased and dominated when compared to the results at 400°C. It was indicated that the oxidation was increased with the reaction time. However, the change from Co⁰ and/or CoO to Co₃O₄ phase was not significantly evident which could be resulted from the incomplete oxidation of cobalt. After holding for 90 min, their catalysts were cooling down from 450°C to room temperature, the XANES spectra are illustrated in Fig. 4. The 15%Co/Aerosil_wi_used_10_bar, 15%Co/Aerosil_wi_used_20_bar, and 20%Co/Aerosil_wi_used_20_bar catalysts showed the edge energies at 7724, 7717, and 7718 eV, respectively. From the feature of spectra, both 15%Co/Aerosil_wi_used_10_bar and 15%Co/Aerosil_wi_used_20_bar showed the main structure of Co₃O₄, whereas 20%Co/Aerosil_wi_used_20_bar showed the mixed structure of CoO and Co₃O₄. When looking at the linear combination analysis, the 15%Co/Aerosil_wi_used_10_bar and 15%Co/Aerosil_wi_used_20_bar catalysts indicated the main composition of Co₃O₄ phase, showing the highest percentage of Co₃O₄ in 15%Co/Aerosil_wi_used_20_bar. In terms of Co loading, when comparing 15%Co/Aerosil_wi_used_20_bar with 20%Co/Aerosil_wi_used_20_bar, 15%Co/Aerosil_wi_used_20_bar showed the higher percentage of Co₃O₄, due to the correspondence in shape between both spectra and the Co₃O₄ spectrum.

From the linear combination analysis, the Co₃O₄ phase increased when increasing the pressure of FTS. The results implied that at high pressure, the surface rearrangement would play role that involves the distribution of Co⁰ and CoO species on the catalyst surface causing the high extent of oxidation to Co₃O₄. When comparing the percentage of Co loading, the high %Co loading catalyst would require more amount

of oxygen to fully oxidize Co^0 to CoO and CoO to Co_3O_4 . Under static oxygen atmosphere and limitation of oxygen concentration, a two-step of oxidation would completely occur only at the low Co loading catalyst, thus low content of Co_3O_4 species was investigated at the high Co loading.

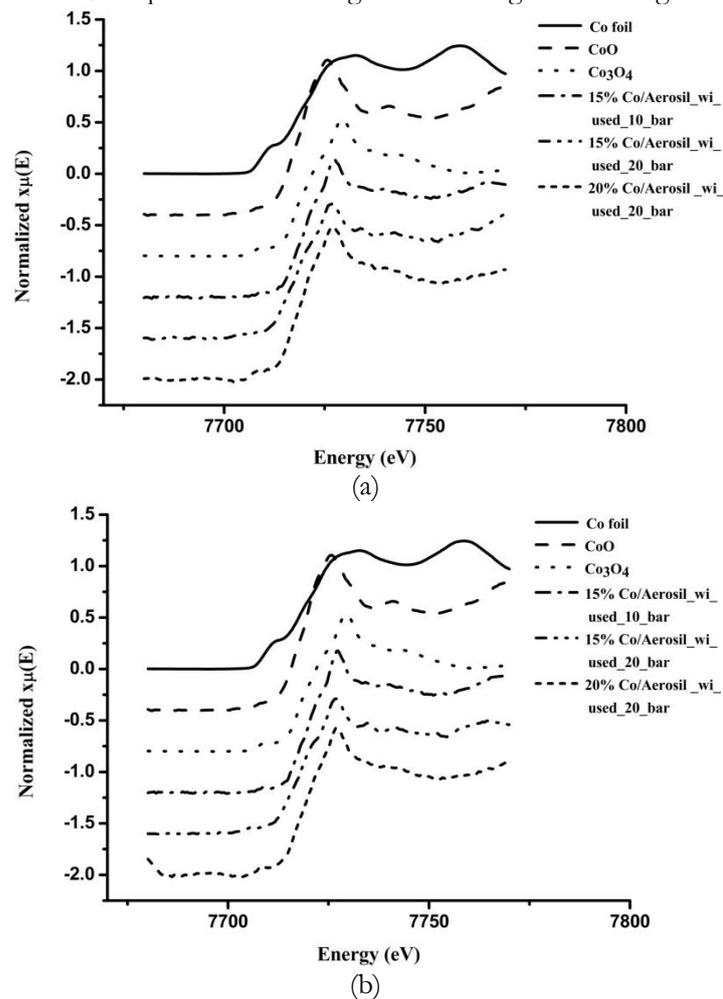


Fig. 3. The normalized Co *K*-edge XANES spectra of the 15%Co/Aerosil_wi_used_10_bar, 15%Co/Aerosil_wi_used_20_bar, and 20%Co/Aerosil_wi_used_20_bar catalysts (a) at temperature of 400°C and (b) after holding at temperature of 450°C for 90 min compared with cobalt reference compounds.

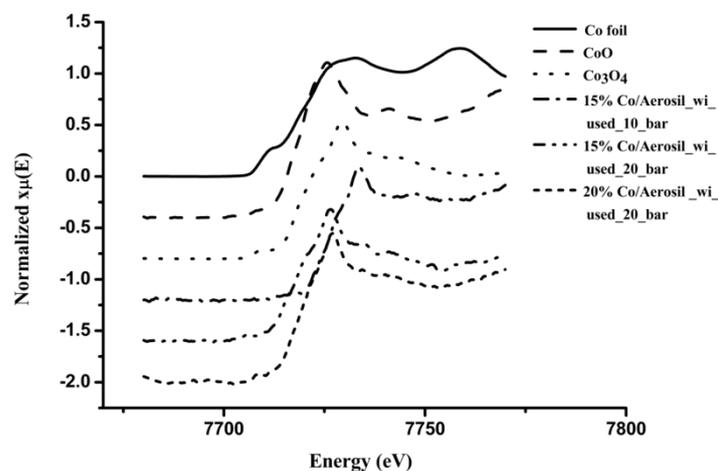


Fig. 4. The normalized Co *K*-edge XANES spectra of the 15%Co/Aerosil_wi_used_10_bar, 15%Co/Aerosil_wi_used_20_bar, and 20%Co/Aerosil_wi_used_20_bar catalysts when cooling down to room temperature compared with cobalt reference compounds.

3.2. Temperature Programmed Oxidation

From literatures [8, 9], temperature programmed oxidation (TPO) of unsupported cobalt metal showed two oxygen consumption maxima at 298 and 583°C, corresponding to the sequential oxidation of metallic cobalt first to CoO and then to Co₃O₄ (reaction (1) and (2)). At the temperature of 872°C, the spinel Co₃O₄ decomposed to form the thermodynamically more stable CoO with a stoichiometric release of oxygen (reaction (3)).



The result obtained from the TPO measurements on the 15%Co/Aerosil_wi_used_10_bar catalyst showed the oxidizing step of Co⁰ to CoO at 296°C and second step of CoO to Co₃O₄ at 655°C as shown in Fig. 5. At the temperature of 894°C, the result showed the decomposition of Co₃O₄ to CoO. The deviation in temperatures compared to the metallic cobalt was due to the interaction between the catalyst and its support in the supported silica cobalt catalysts.

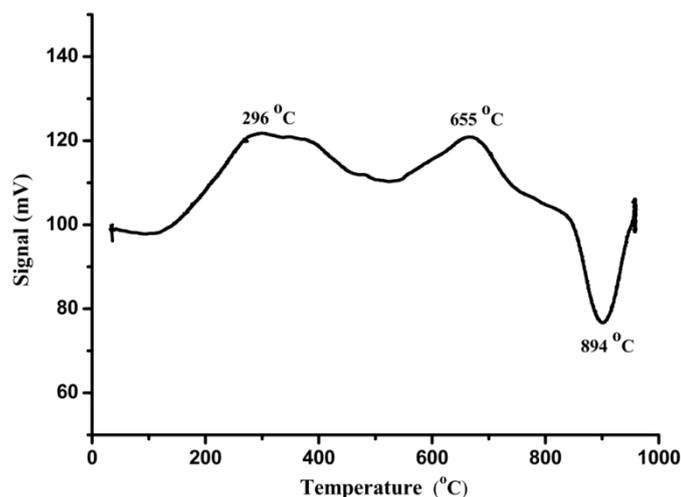


Fig. 5. Temperature programmed oxidation profile of the 15%Co/Aerosil_wi_used_10_bar catalyst.

4. Conclusions

The oxidation of Co species from three used silica supported cobalt catalysts was preliminarily studied by using TR-XANES and TPO techniques. All used catalysts, 15%Co/Aerosil_wi_used_10_bar, 15%Co/Aerosil_wi_used_20_bar, and 20%Co/Aerosil_wi_used_20_bar, showed the main CoO phase at ambient. When heating up to 450°C then holding for 90 min, all used catalysts showed the mixed phase of CoO and Co₃O₄. The whole oxidation process led to the increase of Co₃O₄ in all used catalysts. The increase in the FTS reaction pressure could cause the surface rearrangement and affect the Co species on the surface. This would lead to the higher Co₃O₄ content. At high %Co loading, the Co₃O₄ species was decreased which could be resulted from the incomplete oxidation.

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