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Article

Effect of Cobalt Precursors on Properties of Co/CoAl₂O₄ Catalysts Synthesized by Solvothermal Method

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Abstract. In the present study, different cobalt precursors, such as cobalt acetylacetonate (CoAA), cobalt acetate (CoAC), cobalt nitrate (CoN) and cobalt chloride (CoCL), were employed to synthesize the cobalt on cobalt-aluminate catalysts by the solvothermal process. The calcined samples were characterized by means of N₂ physisorption, XRD, SEM/EDX, TEM and TPR. The CO hydrogenation under methanation condition was performed to measure the activity and product distribution. It revealed that the CoN sample exhibited the highest activity due to high reducibility and large crystallite size having fewer interactions. The similar trend was observed for the CoAC and CoAA samples. However, the CoCL sample had the lowest activity, but highest selectivity to C₂-C₄ products. This was likely attributed to the different form of cobalt oxide species obtained from CoCl₂ as seen from XRD.

Keywords: Cobalt aluminate, cobalt catalyst, CO hydrogenation, solvothermal, methanation, cobalt precursor.

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1. Introduction

Fischer-Tropsch synthesis (FTS) has been considered as a part of gas-to-liquid technology, which converts natural gas that is the basis for a number of large-scale chemical industrial processes to more valuable middle distillates and clean transportation fuels. Natural gas is first transformed into synthesis gas, which is a mixture of carbon monoxide and hydrogen as the starting material to produce heavy hydrocarbons or synthetic fuels, which generally contain negligible sulfur and aromatic compounds compared to gasoline or diesel from crude oil, through carbon monoxide hydrogenation or FTS [1].

Many transition metals of Group VIII can be used as catalysts for FTS, such as iron (Fe), cobalt (Co), nickel (Ni), and ruthenium (Ru) [2-4]. However, supported cobalt catalysts are preferred for FTS because of their high activities for FTS based on natural gas, high selectivity for linear hydrocarbons, and low activity for the competitive water-gas shift (WGS) reaction [5-7]. To increase their activities, cobalt is usually deposited on a high surface area support to obtain a high metal dispersion. Many inorganic supports, such as SiO₂, Al₂O₃, TiO₂ and zeolites [8-11] have been extensively studied for supported Co catalyst for years. It is known that in general, the catalytic properties depend on reaction conditions, catalyst composition, metal dispersion, and types of inorganic supports used. Furthermore, the catalytic performance of all FT catalysts strongly depends on the methods of catalyst preparation. The preparation of cobalt supported catalysts involves choice of the appropriate catalyst support, deposition of active phase, its promotion, oxidative and reductive treatments. The deposition of the precursor on the support surface is a complex phenomenon, which involves physical or chemical interactions between the precursor and the support. It is known that cobalt dispersion depends on the type of cobalt precursors. Van De Loosdrecht *et al.* [12] showed that alumina-supported cobalt catalysts prepared by incipient wetness impregnation using cobalt EDTA and cobalt citrate precursors resulted in smaller cobalt oxide particles compared to the one prepared from cobalt nitrate. The use of cobalt oxalate, cobalt acetate, or cobalt acetylacetonate as cobalt precursors for titania-supported cobalt catalysts has been found to give higher cobalt dispersions than the catalysts prepared from cobalt nitrate [13]. Rosynek and Polansky [14] reported that use of cobalt acetate yields higher dispersion than cobalt chloride on silica. Sun *et al.* [15] concluded that catalysts prepared by mixed impregnation of cobalt nitrate and cobalt acetate result in higher Fischer-Tropsch synthesis activity than catalysts prepared from either monoprecursor. In previous study, Panpranot *et al.* [16] has presented a comprehensive model for how cobalt precursors on MCM-41 support influenced the catalytic activity of the cobalt catalysts. A balance between dispersion-enhancing strong support-precursor interaction and metal loss by retarded reduction was suggested. However, compound formation between cobalt and the supports such as cobalt-aluminate, cobalt-silicate can occur during the catalyst activation and/or reaction conditions resulting in irreversible catalyst deactivation [16, 17].

The main objective of this present research was to investigate the effect of cobalt precursors on the catalytic properties of cobalt dispersed on cobalt-aluminate synthesized by the solvothermal having only a single step to disperse cobalt oxide species on the cobalt-aluminate. The great benefit of this study is that the cobalt on cobalt-aluminate can be prepared in only single step compared to the one obtained from the conventional impregnation method. Moreover, the cobalt-aluminate as cobalt-support compound formation (Co-SCF) [17] is not formed further due to the limitation of Co/Al ratio upon stoichiometry to form cobalt-aluminate. The cobalt-aluminate formation can result in low activity of the cobalt catalysts. The samples were prepared and characterized by means of N₂ physisorption, XRD, SEM/EDX, TEM and TPR. The samples were tested under methanation condition in order to measure the catalyst activity and product distribution.

2. Experimental

2.1. Catalyst Preparation

Cobalt on cobalt-aluminate was synthesized by solvothermal method [18]. It was prepared using the mixture of aluminium isopropoxide (AIP, [(CH₃)₂CHO]₃•Al), 15.0 g (0.07344 mole) and appropriate amount of cobalt precursors [cobalt (II) acetylacetonate, cobalt (II) acetate, cobalt (II) nitrate and cobalt (II) chloride] that the Co/Al molar ratio equal to 1.0. The starting materials were suspended in 100 mL of toluene in a beaker, and then set up in 1000 mL autoclave. In the gap between the beaker and autoclave wall, toluene (40 mL) was added. After the autoclave completely purged with nitrogen, the suspension was heated to 250°C at the rate of 2.5°C/min and was hold at that temperature for 2 h. Autogenous pressure

during the reaction gradually increased as temperature was raised. Then the autoclave was cooled to room temperature. After the autoclave was cooled, the resulting product was washed repeatedly with methanol by centrifugation and dried at 110°C for 24 h. The calcination of the obtained product was carried out in a furnace with air (30 cc/min) using the ramp rate of 10°C/min at 300°C for 1h.

2.2. Catalyst Characterization

2.2.1. N₂ Physisorption

The specific surface area of catalysts was performed using Micromeritic Chemisorb 2750. It was calculated based on nitrogen uptake at liquid-nitrogen temperature using the Brunauer-Emmett-Teller (BET) equation by the single point method.

2.2.2. X-ray Diffraction

XRD was performed to determine the bulk crystalline phases of catalyst. It was conducted using a SIEMENS D-5000 X-ray diffractometer with CuK_α ($\lambda = 1.54439 \text{ \AA}$). The spectra were scanned at a rate of 2.4 deg/min in the range $2\theta = 20\text{-}80^\circ$.

2.2.3. Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy

SEM and EDX were used to determine the catalyst morphologies and elemental distribution throughout the catalyst granules, respectively. The SEM of JEOL mode JSM-5410LV was applied using the secondary electron mode at 15 kV. EDX was performed using Link Isis series 300 program.

2.2.4. Transmission Electron Microscopy

The morphology and size of the catalysts were determined using a JEOL-TEM 200CX transmission electron spectroscopy operated at 160 kV.

2.2.5. Temperature-Programmed Reduction

TPR was used to determine the reduction behaviors of the samples. It was carried out using 20 mg of a sample and a temperature ramp from 35 to 800°C at 10°C/min. The carrier gas was 5% H₂ in Ar. A cold trap was placed before the detector to remove water produced during the reaction. A thermal conductivity detector (TCD) was used to determine the amount of H₂ consumed during TPR.

2.3. Reaction study

CO hydrogenation (H₂/CO = 10/1) was performed to measure the overall activity of the catalyst samples. Hydrogenation of CO was carried out at 220°C and 1 atm. A flow rate of H₂/CO/Ar = 20/2/8 cc/min in a fixed-bed flow reactor was used. A relatively high H₂/CO ratio was used to minimize deactivation due to carbon deposition during reaction. Typically, 0.2 g of a catalyst sample was reduced *in situ* in flowing H₂ (30 cc/min) at 350°C for 3 h prior to the reaction. Reaction effluent samples were taken at 1 h intervals and analyzed by GC. In all cases, steady-state was reached within 5 h.

2.4. Catalyst nomenclature

The nomenclature used for the catalyst samples in this study is as follows:

- **CoAA** refers to the cobalt on cobalt-aluminate catalyst synthesized from the cobalt (II) acetylacetonate precursor.
- **CoAC** refers to the cobalt on cobalt-aluminate catalyst synthesized from the cobalt (II) acetate precursor.
- **CoN** refers to the cobalt on cobalt-aluminate catalyst synthesized from the cobalt (II) nitrate precursor.

- **CoCL** refers to cobalt on cobalt-aluminate catalyst that synthesized from cobalt (II) chloride precursor.

3. Results and Discussion

In the present study, the effect of different cobalt precursors, such as cobalt (II) acetylacetonate, cobalt (II) acetate, cobalt (II) nitrate and cobalt (II) chloride employed to synthesize the cobalt dispersed on cobalt-aluminate catalysts using the solvothermal process was investigated. After calcination of samples, they were further characterized by means of N₂ physisorption, XRD, SEM/EDX, TEM and TPR. The samples were also tested under methanation condition in order to measure the activity and product distribution. Details are discussed as follows:

All the calcined samples were measured for the BET surface areas using the N₂ physisorption. The BET surface areas are listed in Table 1.

Table 1. N₂ physisorption and reaction study.

Samples	BET Surface Area (m ² /g)	Rate (x10 ² gCH ₂ /g.cat.h)	Selectivity to CH ₄ (%)	Selectivity to C ₂ -C ₄ (%)
CoAA	130	37	99.5	0.5
CoAC	61	41	99.9	0.1
CoN	85	69	99.9	0.1
CoCL	124	1	89.9	10.1

It was found that the BET surface areas of samples obtained from different cobalt precursors were in the range of 61-130 m²/g within the order of CoAA > CoCL > CoN > CoAC. The XRD patterns for all samples are shown in Fig. 1. As seen, various forms of cobalt oxides (Co_xO_y) are dispersed on CoAl₂O₄. The noises can be attributed to the presence of various Co_xO_y on the support. It indicated that the CoAA, CoAC and CoN samples exhibited the similar short-broaden XRD peaks at 31, 37, 46, 59 and 65° assigned to Co₃O₄ and CoAl₂O₄ species, which were overlapped [17, 19-21]. The observed short-broaden peaks suggested the good dispersion of Co₃O₄ and CoAl₂O₄ species. However, the XRD patterns for CoCL sample showed a short-broaden XRD peaks at 28, 37, 39, 49, 66 and 73° indicating the other forms of chlorinated cobalt oxide species.

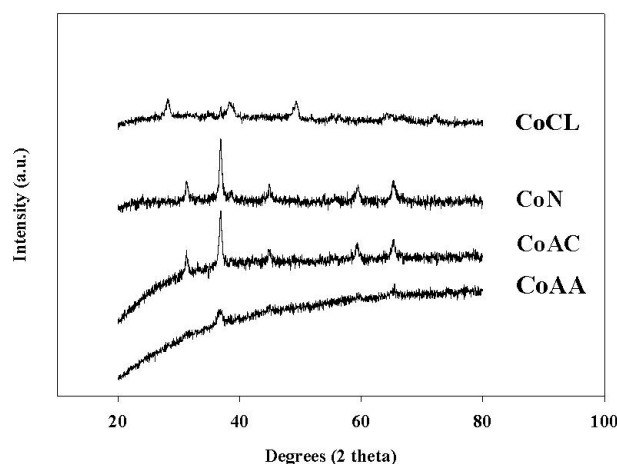


Fig. 1. XRD patterns of the calcined cobalt dispersed on cobalt-aluminate catalysts using different cobalt precursors.

SEM and EDX were performed to study the morphologies of catalyst samples and the elemental distribution on the external surface of the catalyst granule. It was found that no significant change in morphologies was observed upon different cobalt precursors employed. All catalyst granules were appeared in irregular shapes regardless to different cobalt precursors. A typical SEM micrograph and EDX mapping for cobalt on cobalt-aluminate are shown in Fig. 2.

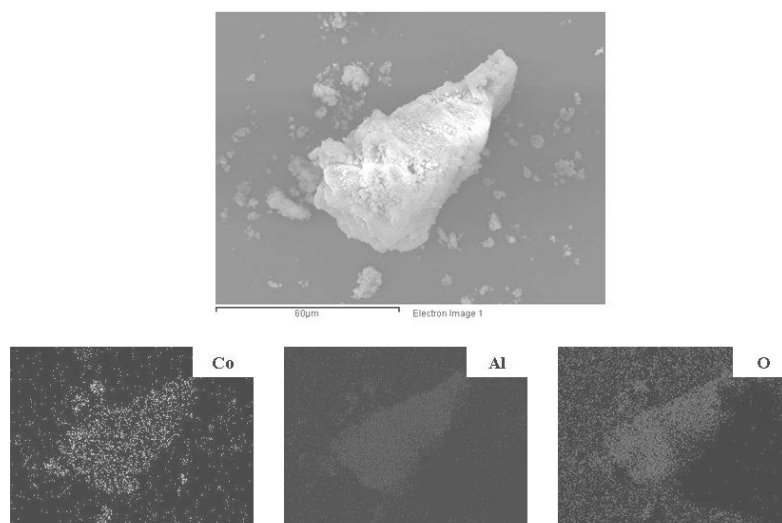


Fig. 2. A typical SEM micrograph and EDX mapping for the calcined CoN catalyst.

It was also observed that cobalt was well distributed on the catalyst granule. In order to determine the dispersion of cobalt oxide species and crystallite size of them, the more powerful technique, such as TEM was performed. The TEM micrographs for all samples are shown in Fig. 3.

The dark spots represented the cobalt species dispersing on the catalyst granule. It was found that different cobalt precursors were result in different crystallite size of cobalt oxide species in the order of $\text{CoN} > \text{CoAC} > \text{CoAA} > \text{CoCL}$. In addition, all samples exhibited the agglomeration of the crystals as seen in the cluster of polycrystals.

It is known that the active form of cobalt catalyst for CO hydrogenation reaction is cobalt metal (Co^0). Thus, reduction of cobalt oxide species is essentially performed in order to transform cobalt oxide species obtained after calcination process into the active cobalt atoms for catalyzing the reaction. Therefore, TPR was performed in order to determine the reduction behaviors and reducibility of cobalt oxide species. The TPR profiles for all catalyst samples are shown in Fig. 4. It was found that the CoAA and CoAC samples exhibited reduction peaks at ca. 450°C and at ca. 650°C, whereas the TPR reduction peaks for the CoN sample were located at ca. 350°C and 700°C. The CoAA sample exhibits two shoulders at low temperature area indicating more non-uniform cobalt oxides species present. The reduction peak for the CoCL sample was located at ca. 450 °C. All the peaks observed were assigned to the overlap of two step reduction of Co_3O_4 to CoO and, then to Co metal [17, 19-21]. Upon the TPR conditions, the two-step reduction may or may not be observed. In fact, the TPR peak locations are affected by reduction kinetics. The kinetics of reduction can be affected by a wide range of variables, including crystallite size, support interaction, and reduction gas composition [17, 22]. The effects of crystallite size and support interaction can be superimposed on each other. Thus, while a decrease in metal oxide crystallite size can result in faster reduction due to greater surface area/volume ratio, smaller particles may interact more with the support, slowing reduction. As seen from Fig. 4, the amounts of H_2 consumed during TPR related to the reducibility of each sample were different as seen from the area below the TPR profiles. It can be observed that the CoCL sample exhibited the lowest reducibility among other samples even though it rendered the smallest crystallite size of cobalt oxide species as seen from the TEM results. This was suggested that highly dispersed forms of cobalt oxide species be not only the factor that insures the high degree of

reducibility [23]. Here, the effect of crystallite size was more pronounced where the smaller particle can interact more retarding reduction. The similar phenomenon was also observed for the Co/ZrO₂ catalyst as reported by Kittiruangrayab *et al.* [24]. Thus, the larger particle, such as the cobalt oxide from CoN sample can be reduced more easily based on the TEM and TPR results.

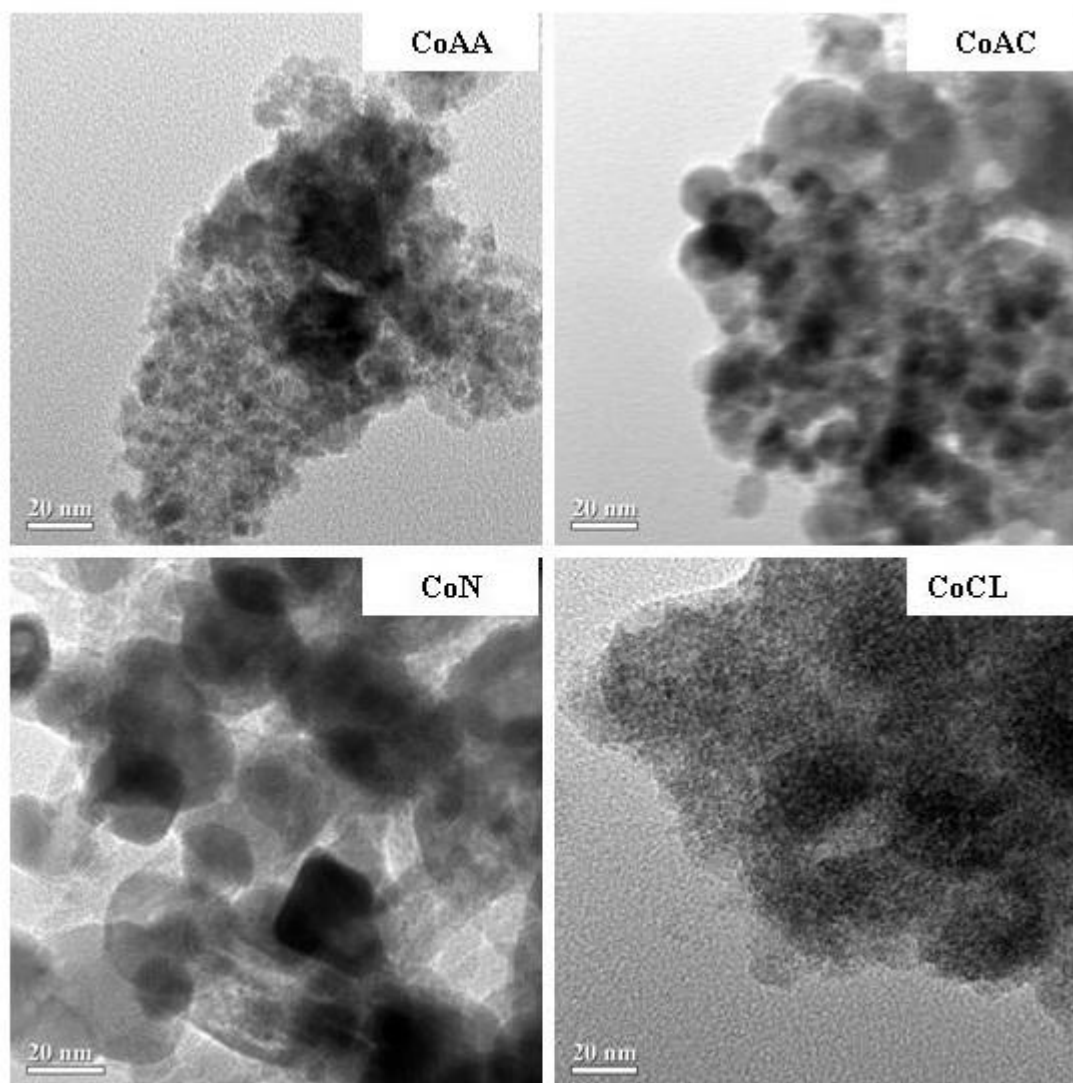


Fig. 3. TEM micrographs of the calcined cobalt dispersed on cobalt-aluminate catalysts using different cobalt precursors; top-left (CoAA), top-right (CoAC), bottom-left (CoN), bottom-right (CoCL).

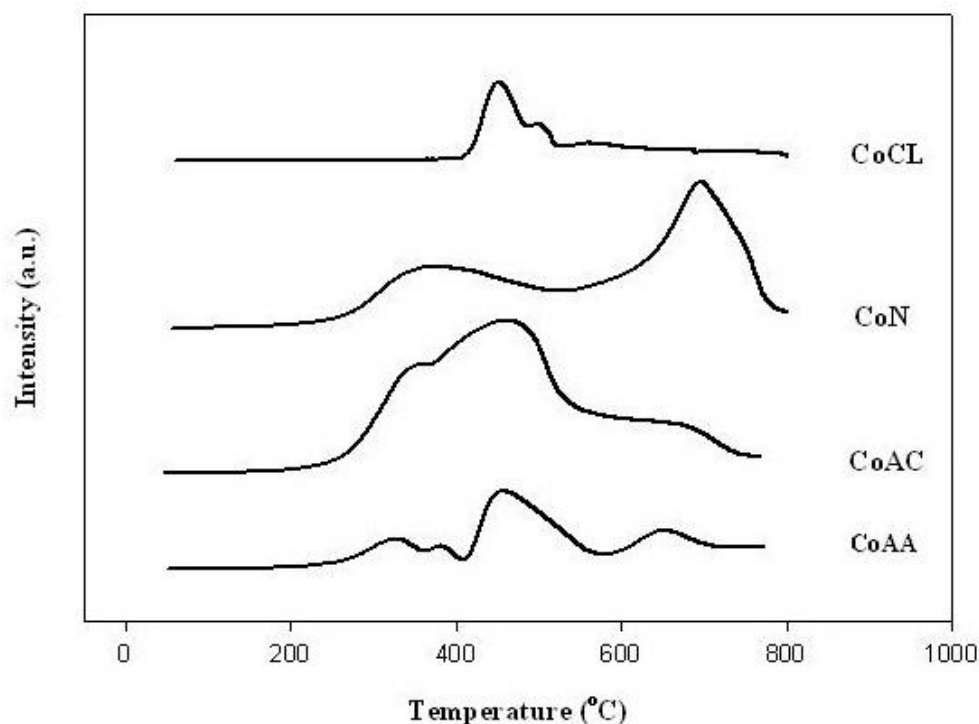


Fig. 4. TPR profiles for cobalt dispersed on cobalt-aluminate catalysts using different cobalt precursors.

In order to determine the catalytic behaviors of the samples obtained from different cobalt precursors, CO hydrogenation ($H_2/CO = 10$) under methanation condition was performed to determine the overall activity and product selectivity of the samples. In fact, hydrogenation of CO was carried out at 220°C at atmospheric pressure. A flow rate of $H_2/CO/Ar = 20/2/8$ cc/min in a fixed-bed flow reactor was used. The relatively high H_2/CO ratio was employed to minimize deactivation due to carbon deposition during reaction. The resulted reaction study is also shown in Table 1. The CoN sample exhibited the highest activity among other samples with in agreement as the results from the TPR measurement. The CoAC and CoAA samples also showed adjacent high activity as well. However, the CoCL sample exhibited the lowest activity during methanation due to strong interaction. Considering the product selectivity, it revealed that for the CoN, CoAC and COAA samples, cobalt precursors did not affect on the selectivity of product during methanation where methane was still the product majority in the effluent. On contrary, the selectivity of C_2-C_4 products apparently increased with the use of $CoCl_2$ as the cobalt precursor. This was suggested that the cobalt oxide species derived from $CoCl_2$ might have different form compared to those obtained from other cobalt precursors as mentioned for the XRD results. The different forms of cobalt oxide species likely respond for the chain growth probability resulting in different values of C_2-C_4 selectivity during methanation.

4. Summary

Here, different cobalt precursors, such as cobalt (II) acetylacetonate, cobalt (II) acetate, cobalt (II) nitrate and cobalt (II) chloride, were employed to synthesize the cobalt on cobalt-aluminate catalysts. It revealed that the CoN sample exhibited the highest activity during methanation due to high reducibility and large crystallite size having fewer interactions. The similar trend was observed for the CoAC and CoAA samples. However, the CoCL sample had the lowest activity, but highest selectivity to C_2-C_4 products. This was likely attributed to the different form of cobalt oxide species obtained from $CoCl_2$ as seen from XRD.

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