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Improvement of the Fischer–Tropsch Synthesis Activity of Co/SiO_2 Catalyst by the Stepwise Impregnation Method with Chelating Agents

**Takehisa Mochizuki · Daichi Hongo ·
Takuya Satoh · Naoto Koizumi · Muneyoshi Yamada**

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Abstract Co/SiO_2 catalysts were prepared by a stepwise impregnation of aqueous solutions containing Co nitrate or chelating agent, nitrilotriacetic acid (NTA) or *trans*-1,2-diaminocyclohexane-*N,N,N′,N′*-tetraacetic acid (CyDTA), with various concentrations of Co^{2+} and the chelating agent. Fischer–Tropsch synthesis activity of Co/SiO_2 catalysts having Co loadings of 5–20 mass% as metallic Co was improved by the stepwise impregnation method with these chelating agents. The catalyst prepared with CyDTA (Co loading = 20 mass%, Co^{2+}/CyDTA = 4 mol mol^{-1}) yielded 1,500 and 815 g kg-cat^{-1} h^{-1} of C_{5+} and C_{10-20} hydrocarbons at 503 K and 1.1 MPa, respectively, which was much greater than that with the catalyst prepared from the aqueous solution containing both Co nitrate and NTA.

Keywords Fischer–Tropsch synthesis · Co/SiO_2 catalyst · Chelating agents · *Trans*-1,2-diamino-cyclohexane-*N,N,N′,N′*-tetraacetic acid (CyDTA)

1 Introduction

Because of increasing demands for high-quality diesel fuels, many studies on both fundamental and technological aspects of Co-based FTS catalysts have been made in order to improve their activities and selectivities [1–9].

Co-based catalysts are usually prepared by the impregnation of Co precursor followed by drying, calcination and H_2 reduction [2]. Co nitrate is frequently used as a Co precursor, which is considered to decompose to Co_3O_4 species during the drying and/or calcination steps [8–10]. During H_2 reduction, Co_3O_4 species is reduced to CoO and then successively reduced to metallic Co or Co–SiO_2 interaction species [11–14]. Iglesia et al. [4] have reported that the dispersion of metallic Co species correlates well with its FTS activity. Although it has been often reported that the dispersion of metallic Co species (i.e. the FTS activity) depends on the type of Co precursors, pH of the impregnating solution, and calcination temperatures, the detail mechanism of the dependencies is still unknown [15–17]. For example, it has been reported that the FTS activity of Co/SiO_2 is improved when Co nitrate is co-impregnated with Co acetate, whereas the impregnation of Co nitrate or Co acetate alone results in lower FTS activities [15, 16]. The catalyst prepared with both Co nitrate and Co acetate shows CO conversion ca. 1.4 times higher than the catalyst with Co nitrate alone (42.5 vs. 29.8%) [16]. Since Co acetate is known to form highly dispersed Co oxide species that is hard to be reduced by H_2 reduction, the higher activity induced by the co-impregnation method is interesting. However, the detail mechanism is still unclear.

Apart from these studies, the authors recently investigated the FTS activity of Co/SiO_2 catalysts prepared from an aqueous solution containing both Co nitrate and the chelating agent or organic acid (Co^{2+}/chelating agent or organic acid = 1 mol mol^{-1}, Co loading = 5 mass% as metallic Co) having various complex formation constants with Co^{2+} [18]. It was found that the use of the aqueous solution of Co nitrate and nitrilotriacetic acid (NTA) as an impregnating solution improves CO conversion over Co/SiO_2 catalyst by a factor of 3. The space time yield (STY) of C_{10-20} hydrocarbon obtained with this catalyst

T. Mochizuki · D. Hongo · T. Satoh · N. Koizumi ·
M. Yamada (✉)
Department of Applied Chemistry, Graduate School of Engineering, Tohoku University, Aoba 6-6-07, Aramaki, Aoba-ku, Sendai 980-8579, Japan
e-mail: yamada@erec.che.tohoku.ac.jp

was 110 g kg-cat^{-1} h^{-1} at 503 K and 1.1 MPa, which was ca. 3 times greater than that with the catalyst without chelating agents [19]. On the contrary, the use of the aqueous solution of Co nitrate and the chelating agents having larger complex formation constants such as ethylenediamine-*N,N,N′,N′*-tetraacetic acid (EDTA) and/or *trans*-1,2-diaminocyclohexane-*N,N,N′,N′*-tetraacetic acid (CyDTA) showed relatively weaker effects. A volcano-type dependency was found when CO conversion over these catalysts was plotted against their logarithmic complex formation constants [18]. The maximum conversion was obtained with the catalyst prepared with the chelating agent having an intermediate complex formation constant, i.e. NTA. Furthermore, H_2 uptakes on these catalysts correlate well with their conversions. Therefore, it was suggested that the complex formation with Co^{2+} (1:1 complex) having an intermediate stability in the impregnating solution increases the number of surface metallic Co sites, leading to an active Co/SiO_2 catalyst [18, 19]. However, detailed mechanism of the activity improvement by these chelating agents is still unclear yet.

In the present study, in order to investigate the role of these chelating agents from different point of view, the catalysts were prepared by the stepwise impregnation of aqueous solutions containing Co nitrate or the chelating agent (NTA or CyDTA). The concentrations of Co^{2+} and the chelating agent (and thus the molar ratio of Co^{2+} to the chelating agent) were varied in a wide range. Their FTS activity and selectivity were investigated at 503 K and 1.1 MPa, and compared with those of the catalysts prepared from the aqueous solution containing both Co nitrate and the chelating agents, i.e. from the aqueous solution containing 1:1 complex. The crystalline structure of Co species formed on calcined catalysts was also investigated by XRD analysis.

2 Experimental

2.1 Catalyst Preparation

All the catalysts investigated here were prepared by a stepwise incipient wetness impregnation method with aqueous solutions of the chelating agent and Co nitrate. SiO_2 granule (Q-15, Fuji Silisia, BET surface area = 192 m^2 g^{-1}, pore volume = 1.03 mL g^{-1}) was sieved to yield 150–250 μm powder and calcined at 823 K before use. The aqueous solution containing NTA (Dojindo Chemicals, purity, purity >99%) or CyDTA (Dojindo chemicals, purity >99%) was firstly impregnated into sieved SiO_2 powder followed by drying at 393 K and 12 h. The aqueous $Co(NO_3)_2·6H_2O$ solution (Wako Pure Chemicals, purity: >99.5%) with different Co^{2+} concentrations was subsequently impregnated into dried material followed by drying (393 K, 12 h) and calcination (723 K, 4 h). The ratio of Co^{2+} to these chelating agents was varied in a range from 1 to 32 mol mol^{-1}. In this paper, the catalysts thus prepared are denoted as $Co(X)/L/SiO_2$ (L = NTA or CyDTA, X = Co loading as metallic Co), whereas those prepared from the aqueous solution containing both Co nitrate and the chelating agent are denoted as L-Co(5)/SiO_2 (Co^{2+}/NTA or CyDTA = 1 mol mol^{-1}, Co loading = 5 mass% as metallic Co) [18, 19].

In our previous studies, it was found that the FTS activity and selectivity of the NTA-Co(5)/SiO_2 and CyDTA–Co(5)/SiO_2 catalysts depend on various preparation conditions such as the type of SiO_2 support, pH of the impregnating solution, calcination temperature and so on [20, 21]. The type of SiO_2 support and other preparation conditions for $Co(X)/L/SiO_2$ catalysts mentioned above were chosen according to these previous studies. These preparation conditions were effective for obtaining the higher activity with NTA–Co(5)/SiO_2 catalyst. The optimization of the preparation conditions for $Co(X)/L/SiO_2$ catalysts is now under investigations, and will be reported in a separate paper.

2.2 FTS Reaction

FTS activities and selectivities of the reduced catalysts were investigated using a fixed bed reactor. The reactor consisted of a stainless steel tube with an internal diameter of 7 mm in an electronically heated oven. Two sets of temperature controllers and thermocouples regulated the temperature in the catalyst bed within ±1 K. The gases, H_2 (purity: >99.995%) and 33% CO/62% H_2/5% Ar (purity >99.99995%), were used without further purification. The flow rate and the pressure of these gases were regulated with mass flow controllers and a backpressure regulator. The calcined catalyst mixed with glass beads was charged into the reactor, and then reduced in a stream of H_2 at 773 K for 6 h. After H_2 reduction, the temperature was down to room temperature in H_2 stream. The feed gas was changed into CO/H_2/Ar at the pressure of 1.1 MPa (W/F = 1.25 or 5.0 g-cat h mol-CO^{-1}). The catalyst was heated to 503 K for the activity evaluation.

Gaseous products were periodically sampled with computer-controlled gas samplers and analyzed with two on line GCs after the reaction temperature reached 503 K. CO, CO_2 and CH_4 were quantified with on line GC/TCD (Shimadzu, GC-8A) while C_1–C_7 hydrocarbons were quantified with on line GC/FID (Shimadzu, GC-2014). Ar was used as an internal standard for the quantification with GC/TCD. Liquid products were collected with an ice trap during on stream and analyzed with off line GC/FID

(Agilent Technologies, Agilent 6850A) after the reaction. The chain growth probability of liquid hydrocarbons (α) was calculated from molar fractions of obtained C_{10}–C_{20} hydrocarbon.

2.3 Characterization of the Calcined Catalysts

XRD measurements were carried out on the calcined catalysts, in order to investigate the effect of modification with the chelating agents on the crystalline structure of Co oxide species. XRD patterns of the calcined catalysts were measured on a MiniFlex powder X-ray diffractometer (Rigaku). Cu Kα radiation was used as the X-ray source, with the X-ray tube operating at 30 kV and 15 mA. Diffraction intensities were recorded from 20 to 90° at the rate of 2.00° min^{-1} with a sampling width of 0.02°. The observed diffraction peaks were assigned by reference to Joint Committee on Powder Diffraction Standards (JCPDS) data.

3 Result and Discussion

3.1 FTS Activity

The effect of NTA on the FTS activity of the catalyst prepared by the stepwise impregnation method was firstly investigated, and compared with that observed for the catalyst prepared from the aqueous solution containing both Co nitrate and NTA. Figure 1 compares CO conversions (at 20 h on stream) over Co(5)/SiO_2, NTA–Co(5)/SiO_2, Co(5)/NTA/SiO_2 and NTA/Co(5)/SiO_2 catalysts. The stepwise-impregnated catalysts were prepared by different orders of the impregnating solutions. Co^{2+}/NTA molar ratio was unity for the catalysts prepared with NTA. FTS reactions were carried out at 503 K and 1.1 MPa with $W/F = 5$ g h mol^{-1}. Under these reaction conditions, Co(5)/SiO_2 catalyst shows CO conversion of 20%. Both Co(5)/NTA/SiO_2 and NTA/Co(5)/SiO_2 catalysts show higher conversions as well as NTA–Co(5)/SiO_2 catalyst than the catalyst without NTA. The conversions over Co(5)/NTA/SiO_2 and NTA–Co(5)/SiO_2 catalysts are comparable with each other (60%), while NTA/Co(5)/SiO_2 catalyst shows a slightly lower conversion than these catalysts. This figure clearly shows that promoting effects of NTA are observed even though the catalysts are prepared by the stepwise impregnation method.

As reported in our previous studies [18, 19], Co loading of L-Co/SiO_2 catalyst is limited to a maximum of 5 mass% because it is difficult to prepare the homogeneous solutions of Co nitrate and the chelating agent having higher Co^{2+} concentrations. On the contrary, Co loading of the catalysts can be increased when the catalysts are prepared by the stepwise impregnation method with the chelating agent. Then, effects of NTA and CyDTA on the FTS activity of the catalyst having higher Co loadings were further investigated at the same reaction conditions. Co loading was varied from 5 to 20 mass% as metallic Co, whereas the loading of the chelating agents was kept constant. In Fig. 2, CO conversions (at 20 h on stream) over Co(X)/SiO_2 and Co(X)/L/SiO_2 (L = NTA or CyDTA) catalysts are plotted as a function of their Co loading. This figure also includes the conversions over NTA–Co(5)/SiO_2 and CyDTA–Co(5)/SiO_2 catalysts as references [18, 19]. CO conversion over Co(X)/SiO_2 catalyst increases with increasing Co loading, and reaches to 60% at Co loading of 20 mass% as metallic Co. The conversion over Co(X)/NTA/SiO_2 catalyst is always higher than that over Co(X)/SiO_2 catalyst, and

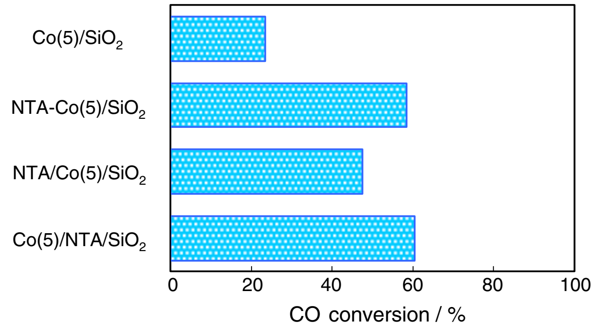

Fig. 1 Promoting effects of NTA on CO conversions over Co/SiO_2 catalyst prepared by the stepwise impregnation method. Reaction conditions: 503 K, 1.1 MPa, 5 g-cat h mol^{-1}

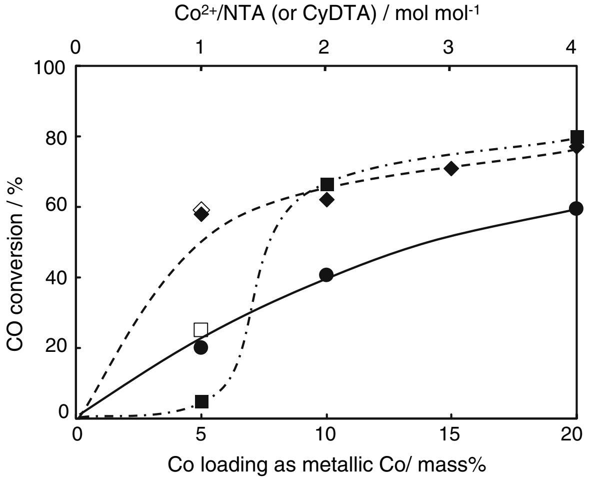

Fig. 2 Effect of Co loading on CO conversions over Co(X)/SiO_2 (●), Co(X)/NTA/SiO_2 (◆) and Co(X)/CyDTA/SiO_2 (■) catalysts. The conversions over NTA–Co(5)/SiO_2 (◇) and CyDTA–Co(5)/SiO_2 (□) catalysts are also plotted in this figure. NTA and CyDTA loadings were fixed at 16 and 31 mass%, respectively, for the catalysts prepared by the stepwise impregnation method. Reaction conditions: 503 K, 1.1 MPa, 5.0 g-cat h mol^{-1}

eventually reaches to ca. 80%. On the contrary, the conversion is quite low over Co(5)/CyDTA/SiO_2 catalyst. This catalyst shows the lower conversion than CyDTA–Co(5)/SiO_2 catalyst. An abrupt increase in the conversion is observed over Co(X)/CyDTA/SiO_2 catalyst when Co loading increases from 5 to 10 mass%. The conversion further increases with Co loading, and reaches a similar level to Co(20)/NTA/SiO_2 catalyst. Both NTA and CyDTA show the promoting effects on the FTS activity of Co/SiO_2 catalyst having higher Co loadings (10–20 mass%). The stepwise impregnation method has important advantages that Co loading of the catalysts with NTA and/or CyDTA can be increased at least up to 20 mass%, and the promoting effects of these chelating agents are clearly observed for the catalyst having higher Co loadings.

3.2 FTS Selectivity and Productivity of Hydrocarbons

Table 1 summarizes FTS selectivities and hydrocarbon productivities over Co(20)/NTA/SiO_2 and Co(20)/CyDTA/SiO_2 catalysts (Co^{2+}/NTA or CyDTA = 4 mol mol^{-1}) in comparison with those over Co(20)/SiO_2 catalyst. FTS reactions were carried out at $W/F = 1.25$ g h mol^{-1} because the conversions over Co(20)/NTA/SiO_2 and Co(20)/CyDTA/SiO_2 catalysts reach to 80% at $W/F = 5$ g h mol^{-1} (Fig. 2). The selectivities and productivities over Co(5)/SiO_2 and NTA–Co(5)/SiO_2 catalysts are also included in this figure as references ($W/F = 5$ g h mol^{-1}) [18, 19]. The C_{5+} selectivity over Co(20)/SiO_2 catalyst is 80.2 °C-mol%. The chain growth probability of C_{10-20} hydrocarbon (α) over this catalyst is 0.85. Both the C_{5+} selectivity and α value over Co(20)/SiO_2 catalyst are identical to those over Co(5)/SiO_2 catalyst. Co(20)/SiO_2 catalyst yields 360 g kg-cat^{-1} h^{-1} of C_{5+} hydrocarbons, which is ca. 2.5 times greater than that obtained with Co(5)/SiO_2 catalyst.

Concerning effects of the chelating agents, the C_{5+} selectivities over Co(20)/NTA/SiO_2 and Co(20)/CyDTA/SiO_2 catalysts are comparable with that over Co(20)/SiO_2 catalyst, whereas the α values over Co(20)/NTA/SiO_2 and Co(20)/CyDTA/SiO_2 catalysts are slightly lower. Besides, the use of these chelating agents greatly improves the STY of hydrocarbons. 608 and 1,500 g kg-cat^{-1} h^{-1} of C_{5+} hydrocarbon are obtained with Co(20)/NTA/SiO_2 and Co(20)/CyDTA/SiO_2 catalysts, respectively, whereas the STY of C_{5+} hydrocarbon over Co(20)/SiO_2 catalyst is no more than 360 g kg-cat^{-1} h^{-1}. Furthermore, the STY of C_{10-20} hydrocarbon (equivalent to the diesel fraction) reaches 815 g kg-cat^{-1} h^{-1} over Co(20)/CyDTA/SiO_2 catalyst. The STY of C_{5+} and C_{10-20} hydrocarbons obtained with this catalyst is ca. 4.3 and 7.4 times greater than those obtained with NTA–Co(5)/SiO_2 catalyst. These differences in the STY of hydrocarbons (Co(20)/CyDTA/SiO_2 vs. NTA–Co(5)/SiO_2) are evidently greater than those observed for the catalyst without chelating agents (Co(20)/SiO_2 vs. Co(5)/SiO_2).

In open literatures, the champion data for the STY of C_{5+} and C_{10-20} hydrocarbons has been reported to be 710 and 350 g kg-cat^{-1} h^{-1}, respectively, over SBA-15 supported Co catalyst (Co loading: 20 mass% as metallic Co) at 503 K and 2.0 MPa with W/F of 2.4 g h mol^{-1} [22]. Co(20)/CyDTA/SiO_2 catalyst yields C_{5+} and C_{10-20} hydrocarbons more than 2 times greater than Co/SBA-15 catalyst even under lower reaction pressure.

3.3 Crystalline Structure of Co Oxide Species on the Calcined Catalysts

XRD measurement was then carried out on the calcined catalysts, in order to investigate the effect of the chelating agents on the crystalline structure of Co oxide species. Figure 3 shows XRD patterns of Co(20)/NTA/SiO_2 and

Table 1 Effects of modification with the chelating agents on the FTS selectivity and hydrocarbon productivity over the reduced Co catalysts[a]

	W/F (g-cat h mol-CO^{-1})	CO conversion (%)	Product selectivity (C-mol%)			α[c]	STY of C_{5+} (g kg-cat^{-1} h^{-1})	STY of C_{10}–C_{20} (g kg-cat^{-1} h^{-1})
			CO_2	CH_4	C_{5+}			
Co(5)/SiO_2	5	19	0.7	8.4	79.2	0.86	145	46
Co(20)/SiO_2	1.25	19	–[d]	9.8	80.2	0.85	360	209
NTA–Co(5)/SiO_2	5	53	0.7	12.7	74.2	0.82	348	110
Co(20)/NTA/SiO_2[b]	1.25	30	–[d]	10.5	78.8	0.83	608	270
Co(20)/CyDTA/SiO_2[b]	1.25	60	0.5	14.1	76.7	0.81	1,500	815

[a] Reaction conditions: 503 K, 1.1 MPa

[b] Co^{2+}/NTA or CyDTA = 4 mol mol^{-1}

[c] Chain growth probability of liquid hydrocarbons

[d] Not detected

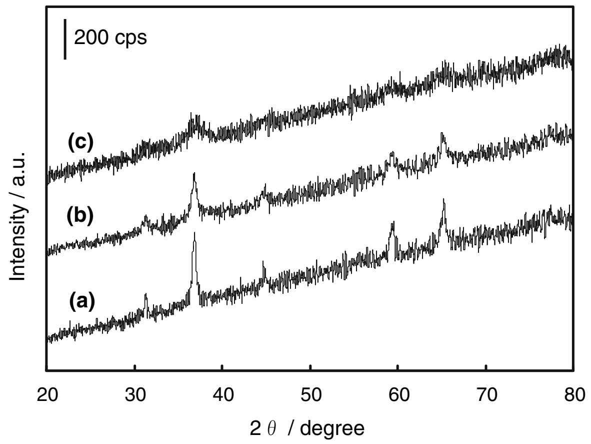

Fig. 3 XRD patterns of the calcined Co(20)/SiO_2 (a), Co(20)/NTA/SiO_2 (b) and Co(20)/CyDTA/SiO_2 (c) catalysts (Co^{2+}/NTA or CyDTA = 4 mol mol^{-1})

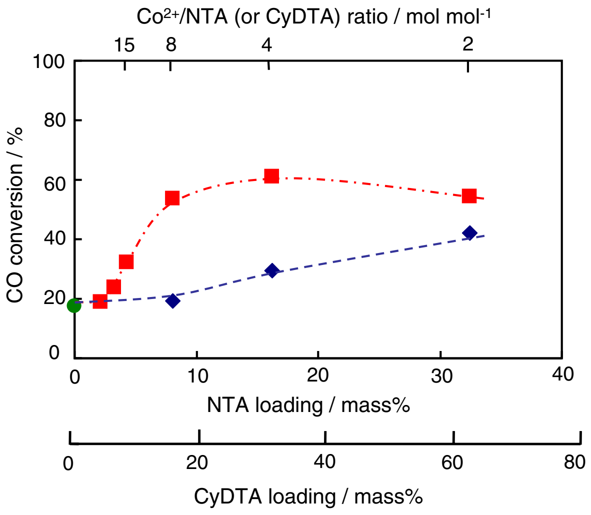

Fig. 4 Effect of the molar ratio of Co^{2+} to NTA or CyDTA lon CO conversions over Co(20)/NTA/SiO_2 (◆) and Co(20)/CyDTA/SiO_2 (■) catalysts. Reaction conditions: 503 K, 1.1 MPa, 1.25 g-cat h mol^{-1}

Co(20)/CyDTA/SiO_2 catalysts (Co^{2+}/NTA or CyDTA = 4 mol mol^{-1}) in comparison with Co(20)/SiO_2 catalyst. XRD pattern of Co(20)/SiO_2 catalyst shows sharp peaks originated from the crystalline Co_3O_4 species. The crystalline size of this specie was estimated to be 25 nm by the Scherrer equation. In the patterns of the calcined catalysts with the chelating agents, several peaks are observed as well at identical positions to those observed in the pattern of Co(20)/SiO_2 catalyst. However, these peaks are evidently broader and weaker compared with Co(20)/SiO_2 catalyst. The crystalline size of the Co_3O_4 species over Co(20)/NTA/SiO_2 and Co(20)/CyDTA/SiO_2 catalysts was estimated to be 17 nm and less than 5 nm, respectively, clearly showing that the use of these chelating agents decreases the (average) crystalline size of the Co_3O_4 species formed after the calcination.

3.4 Role of the Chelating Agents

Our previous study showed that the FTS activity (CO conversion) of NTA–Co(5)/SiO_2 catalyst changes depending on the Co^{2+}/NTA molar ratio of the impregnating solution (0–2 mol mol^{-1}) [23]. The maximum conversion was obtained at the Co^{2+}/NTA molar ratio of unity, suggesting that the formation of 1:1 complex in the impregnating solution is responsible for the higher FTS activity of this catalyst. In the present study, it was found that the promoting effects of NTA and CyDTA are observed even though the catalysts were prepared by the stepwise impregnation method as mentioned above. In order to investigate the role of these chelating agents in view of the complex formation, the FTS activities of Co(20)/NTA/SiO_2 and Co(20)/CyDTA/SiO_2 catalysts having various Co^{2+}/L (L = NTA or CyDTA) molar ratios were further investigated. In these experiments, the loadings of NTA and CyDTA were varied, while Co loading was kept constant (20 mass% as metallic Co). It should be noted that the catalysts having the Co^{2+}/L molar ratio below 2 mol mol^{-1} could not be prepared because of difficulties in the preparation of homogenous solutions containing these chelating agents at higher concentrations. Their FTS activities were evaluated at $W/F = 1.25$ g h mol^{-1}. Obtained results are summarized in Fig. 4. Over Co(20)/NTA/SiO_2 catalyst, CO conversion gradually increases with increasing NTA loading (Co^{2+}/NTA molar ratio from 15 to 2 mol mol^{-1}). On the contrary, CO conversion over Co(20)/CyDTA/SiO_2 catalyst steeply increases at CyDTA loading of 8 mass% (Co^{2+}/CyDTA = 15 mol mol^{-1}). The conversion over this catalyst shows a broad maximum in a wide range of CyDTA loading (Co^{2+}/CyDTA molar ratio from 8 to 2 mol mol^{-1}). These two catalysts show different dependencies upon the Co^{2+}/L molar ratio, and Co(20)/CyDTA/SiO_2 catalyst always shows higher conversions irrespective of this ratio. It is noted that this result is in contrast with our previous results, where the higher conversion was obtained by the catalyst with NTA rather than CyDTA when the catalyst is prepared from the aqueous solution containing Co nitrate and these chelating agents [18, 19].

The increasing conversion over Co(20)/NTA/SiO_2 catalyst with decreasing the Co^{2+}/NTA molar ratio is consistent with the dependency observed for NTA–Co(5)/SiO_2 catalyst upon the Co^{2+}/NTA molar ratio. On the contrary, the conversion over Co(20)/CyDTA/SiO_2 catalyst shows a broad maximum in the wide range of the Co^{2+}/CyDTA molar ratio (8 to 2 mol mol^{-1}). Much smaller

CyDTA is enough for obtaining a higher activity over this catalyst compared with NTA–Co(5)/SiO_2 catalyst. Such the dependency upon the Co^{2+}/CyDTA molar ratio cannot be explained simply in terms of the stoichiometric complex formation during the preparation step in the catalyst pores. It is suggested that the interaction between not only CyDTA and Co^{2+}, but also CyDTA and SiO_2 surface is indispensable during the preparation steps for obtaining higher activities of this catalyst. Because the number of surface sites on SiO_2 surface that can be interacted with CyDTA will be definite, the interaction between CyDTA and SiO_2 surface will be saturated by the addition of certain amount of CyDTA. Such the interaction may result in the formation of dispersed Co_3O_4 species after the calcinations as shown in Fig. 3, leading to the higher activity.

4 Conclusion

In order to make clear the role of the chelating agents found in our previous studies from different point of view, the catalysts were prepared by the stepwise impregnation of the aqueous solutions containing Co nitrate or the chelating agent (NTA or CyDTA). The loadings of Co and the chelating agents were varied in wide ranges, and their FTS activity and selectivity were investigated at 503 K and 1.1 MPa.

It was found that the chelating agent-modified catalysts having higher Co loadings (at least up to 20 mass%) can be prepared by the stepwise impregnation method, and the promoting effects of NTA and CyDTA are clearly observed for these catalysts. Co(20)/CyDTA/SiO_2 catalyst (Co^{2+}/CyDTA $= 4$ mol mol^{-1}) yielded 1,500 and 815 g kg-cat^{-1} h^{-1} of C_{5+} and $C_{10–20}$ hydrocarbons at 503 K and 1.1 MPa, respectively, which were much greater than those with the previously reported NTA–Co(5)/SiO_2 catalyst. Furthermore, the promoting effect of CyDTA was observed in the wide range of the Co^{2+}/CyDTA molar ratio (8–2 mol mol^{-1}). Although it was suggested in our previous studies that the formation of 1:1 complex is responsible for the higher activity of NTA–Co(5)/SiO_2 catalyst, the promoting effect of CyDTA observed for Co(20)/CyDTA/SiO_2 catalyst cannot be explained simply in terms of the stoichiometric complex formation during the preparation steps in the catalyst pores. It is suggested that the interaction between not only CyDTA and Co^{2+}, but also CyDTA and SiO_2 surface during the preparation steps is responsible for obtaining higher activities of this catalyst.

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