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Novel preparation method of highly active Co/SiO$_2$ catalyst for Fischer-Tropsch synthesis with chelating agents

Takehisa Mochizuki,* Takeshi Hara, Naoto Koizumi, and Muneyoshi Yamada

Department of Applied Chemistry, Graduate School of Engineering, Tohoku University, Aoba 6-6-07, Aramaki, Aoba-ku, Sendai 980-8579, Japan

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Co/SiO$_2$ catalysts were prepared by the incipient wetness method using the aqueous Co nitrate solution modified with various organic acids and/or chelating agents followed by drying and calcination. After H$_2$ reduction at 773 K, the catalyst prepared with nitrilotriacetic acid (NTA) showed Fischer-Tropsch synthesis (FTS) activity ca. 3 times higher than the catalyst without additives under mild reaction conditions (503 K, 1.1 MPa).

KEY WORDS: Co/SiO$_2$ catalyst; Fischer-Tropsch synthesis; chelating agents; nitrilotriacetic acid (NTA).

1. Introduction

Because of increasing demands for the high-quality diesel fuel, many studies on both fundamental and technological aspects of Co-based FTS catalysts have been made in order to improve their activities and selectivities [1–7].

Co-based catalysts are usually prepared by impregnation followed by drying, calcination and H$_2$ reduction [1]. Co nitrate, a conventional Co precursor, is considered to decompose to Co$_3$O$_4$ particles after drying and calcination [6–8]. During H$_2$ reduction, the Co$_3$O$_4$ particles are reduced to CoO particles and then successively reduced to metallic Co particles or Co–SiO$_2$ interaction species [9–12]. Iglesia *et al.* [2] have reported that the dispersion of metallic Co well correlates with its FTS activity.

Although it has been often reported that the dispersion of metallic Co (i.e. the FTS activity) depends on Co precursors, pH of impregnating solution, and calcination temperatures, the detail mechanism of the dependencies is not known [13–15]. For example, it has been reported that the FTS activity of Co/SiO$_2$ is dramatically improved when Co nitrate is co-impregnated with Co acetate, while impregnation of Co nitrate and/or Co acetate alone results in lower FTS activities [13,14]. 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 versus 29.8%). Since Co acetate is known to form highly dispersed Co oxide species which is hard to be reduced by H$_2$, the high activity induced by co-impregnation is interesting. However the detail mechanism is still unclear. Kraum and Baerns [16] have reported that Co/TiO$_2$ catalysts prepared by using Co acetate, Co acetylacetonate and/or Co oxalate show higher FTS activities than the catalyst prepared by using Co nitrate. CO conversion over the catalysts prepared with these organic precursors is in a range from 23.6% to 32.0%, which is ca. 1.6 to 2.2 times higher compared with the catalyst prepared with Co nitrate. Although, the detail mechanism of these phenomena is still unclear, these works suggest that the use of organic Co compounds and organic Co complex strongly affects the dispersion of Co oxide species after drying and calcinations.

On the other hand, we have already found that HDS activities of Co(or Ni)Mo(or W)/A1$_2$O$_3$ are highly improved when some chelating agents are added in impregnating solutions containing Co (or Ni) ions and Mo (or W) ions [17–21]. The role of chelating agents is considered to form stable chelate–Co complex and to control the timing of sulfiding of Co. Especially, it is noticed to find that the stability of chelate–Co (or Ni) complex strongly affects the HDS activity after sulfiding.

Considering these previous reports, it is expected that some chelating agents affect the dispersion Co species on SiO$_2$ through formation of chelate–Co complex. In the present work, we have tried to investigate the effect of chelating agents on the FTS activity of Co/SiO$_2$. In order to make clear the effect of stability of chelate–Co complex on the activity, some chelating agents and organic acids which have various stability constants when they are complexed with Co ions.

2. Experimental

2.1. Catalyst preparation

All the catalysts investigated here were prepared by pore-filling incipient wetness method. SiO$_2$ granule

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*To whom correspondence should be addressed.
E-mail: mochizuki@erec.che.tokohu.ac.jp

(Japan Reference Catalyst, JRC-SIO-5, 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. Sieved SiO_2 powder was then impregnated with the aqueous solution containing both $Co(NO_3)_2 \cdot 6H_2O$ (Wako Pure Chemicals, purity: >99.5%) and one of organic acids and/or chelating agents shown in table 1. Molar ratio of the additive to Co was unity, which is equivalent for the stoichiometric ratio of the complex formation reaction. The pH of the impregnating solutions was maintained at 9–10 (at room temperature) for all the catalysts. The impregnated sample was dried at 393 K for 12 h and then calcined at 723 K for 4 h in static air. The catalysts thus prepared are denoted as L-Co/SiO_2 (L: organic acid or chelating agent) in this paper. Co/SiO_2, i.e. the catalyst without additives, was also prepared from the impregnating solution containing only Co nitrate for the comparison purpose. Co loading of these catalysts was restrict to 5 mass% on a SiO_2 weight basis (as metallic Co) because it was difficult to prepare the homogeneous solution containing higher amount of Co nitrate and chelating agents.

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 (Brooks, 5850E) and a backpressure regulator (TESCOM). Typically, 0.4 g of 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 with the flowing rate of 30 mL (SIP) min^{-1} (W/F: 5.0 g-cat h mol-CO^{-1})The catalyst was heated to 503 K for the activity evaluation.

Table 1

Organic acids and chelating agents used for the preparation of catalysts and their complex formation constants with Co^{2+} [22–25]

Compound (Notation)	Complex formation constants with Co^{2+}
Organic acid	
Glycine (Glycine)	0.6
Citric acid (Citric)	5.0
L-Asparatic acid (Asparatic)	5.9
Chelating agents	
Nitrilotriacetic acid (NTA)	10.4
Ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid (EDTA)	16.3
trans-1,2-diaminocyclohexane-*N*,*N*,*N*′,*N*′-tetraacetic acid (CyDTA)	18.9
Triethylenetetramine-*N*,*N*,*N*′,*N*″,*N*‴,*N*‴-hexacetic acid (TTHA)	28.8

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-14B). 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 (Shimadzu, GC-17A) after the reaction.

2.3. Characterization of the reduced catalysts

The calcined catalyst was reduced in a stream of H_2 at the same conditions as used for the activity measurements. After H_2-reduction, the catalyst was passivated in a stream of 1% O_2/He stream at room temperature, and then subjected to XRD and H_2 uptake measurements.

XRD patterns of the reduced catalysts were measured on a MiniFlex diffractometer (Rigaku). CuKα radiation was used 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 with a sampling width of 0.02°. The observed diffraction peaks were assigned by reference to Joint Committee on Powder Diffraction Standards (JCPDS)data.

H_2 uptakes of the reduced catalysts were measured by a volumetric method using AUTOSORB-1-C analyzer (Quantachrome INSTRUMENTS). H_2 adsorption was carried out at 373 K. after *in-situ* re-reduction at 573 K for 2 h in the adsorption cell.

3. Result and discussion

3.1. FTS activity and selectivity

At first, the present study investigated the FTS activity and selectivity of reduced Co/SiO_2 catalysts prepared from the impregnating solution modified with some organic acids and/or chelating agents. The complex formation constants of these additives with Co^{2+} lies in a range from 0.6 to 29 [22–25], which is suitable for investigating the effect of complex formation in the impregnating solution.

After H_2 reduction at 773 K, CO conversion over the prepared catalysts firstly increased with increasing time on stream, and reached their steady-state values within 3 h. No activity decline was observed on these catalysts for the duration investigated here (ca. 20 h on stream). Table 2 summarizes the steady-state CO conversion over the reduced catalysts. The steady-state conversion varies depending on the organic acids and/or chelating agents used for the modification of the impregnating solution. Except glycine and TTHA, modification of the impregnating solution with the organic acids and/or chelating agents improves the steady-state conversion. Especially, the steady-state conversion over reduced NTA-Co/SiO_2 is ca. 3 times higher than that over reduced Co/SiO_2. Such the large activity enhancement has never been reported in the previous studies with the catalysts prepared from the organic Co precursors. For example, Li et al [13,14] reported that CO conversion over Co/SiO_2 catalyst prepared with both Co nitrate and Co acetate (CO conversion: 42.5%) is ca. 1.4 times higher than that over Co/SiO_2 catalyst with only Co nitrate (29.8%). For the TiO_2-supported catalysts, Kraum and Baerns [16] reported that CO conversion over the catalyst prepared with Co oxalate (CO conversion: 32.0%) was ca. 2.2 times higher than that over the catalyst with Co nitrate (14.7%). It is also noted here that modification with EDTA results in the catalyst with relatively higher activity, which is in contrast to the previous results [15], where the use of Co–EDTA precursor instead of Co nitrate strongly depresses the conversion over Co/$A1_2O_3$ catalyst.

Product selectivities over the reduced catalysts are also shown in table 2. The selectivity for C_{5+} hydrocarbons over the reduced catalysts is above 60 mol% except reduced TTHA–Co/SiO_2. The chain growth probability of the hydrocarbons (α) is in a range from 0.77 to 0.86. CH_4 selectivity is less than 16 mol%, and CO_2 formation is negligible over these catalysts. Concerning effects of the organic acids and/or chelating agents, both the selectivity for C_{5+}. hydrocarbons and the chain growth probability are slightly lower when the impregnating solution is modified with these additives. However, the improvement on the steady-state conversion are larger compared with the decreases in the selectivity for C_{5+} hydrocarbons and the chain growth probability. Thus, modification of the impregnating solution with these organic acids and/or chelating agents increases the yield of hydrocarbons.

3.2. Surface structure of the reduced catalysts

Then, XRD measurement was carried out on the reduced catalysts, in order to investigate the effects of the organic acids and/or chelating agents on the structure of metallic Co species. Figure 1 shows XRD pattern of the reduced catalysts after the passivation at room temperature. XRD pattern of reduced Co/SiO_2 shows a broad peak originated from the metallic Co species. The crystalline size of the metallic Co species over this catalyst was estimated to be 19 nm by Sherrer equation. In the patterns of the reduced catalysts with the organic acids and/or chelating agents except CyDTA and TTHA, relatively broader and weaker peaks of the metallic Co species were observed, suggesting that modification with these additives decreases the crystalline size of the metallic Co species. On the contrary, the reduced catalysts modified with CyDTA and/or TTHA show no diffraction peaks in their XRD patterns.

In order to get more quantitative information, surface metallic Co sites were then titrated by H_2 uptake measurements. H_2 uptakes of the reduced catalysts are summarized in table 3. From this table, we can see that H_2 uptakes of the reduced catalysts with the organic acids and/or chelating agents (except glycine and TTHA) are evidently larger than that of reduced Co/SiO_2. Especially, H_2 uptake of reduced NTA–Co/SiO_2 is ca. 3 times larger than that of reduced Co/SiO_2. We further calculated the dispersion of Co, i.e. the number of metallic Co sites normalized to total amount of Co atoms in the reduced catalysts (Co_s/Co_{total}; Co_s: the number of metallic Co sites, Co_{total}: total amount of Co atoms in the reduced catalysts, table 3) from H_2 uptakes of the reduced catalysts assuming that the stoichiometry for the hydrogen adsorption on the metallic Co sites is unity. As can be seen from table 3, the dispersion of Co is higher when the impregnating solution is modified

Table 2

Effects of modification with the organic acids and/or chelating agents on the FTS activity and selectivity of reduced Co/SiO_2 catalyst

	Steady-state CO conversion/%	Product selectivity/mol%			α[a]
		CO_2	CH_4	C_{5+}	
Co/SiO_2	19.0	0.7	8.4	79.2	0.86
Glycine–Co/SiO_2	16.6	–	10.2	59.5	0.77
Citric–Co/SiO_2	32.6	–	10.5	62.9	0.81
Asparatic–Co/SiO_2	42.5	–	11.7	66.3	0.81
NTA–Co/SiO_2	53.4	0.7	12.7	74.2	0.82
EDTA–Co/SiO_2	37.1	–	8.8	78.9	0.83
CyDTA–Co/SiO_2	32.1	0.9	16.1	68.6	0.79
TTHA–Co/SiO_2	7.8	1.7	24.8	39.9	–

[a] Chain growth probability of liquid hydrocarbons.

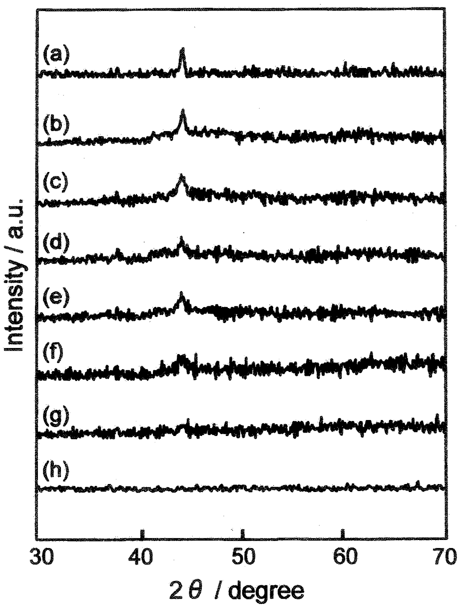

Figure 1. X-ray diffraction patterns of the reduced catalysts after the passivation in 1% O_2/He stream at room temperature: (a) Co/SiO_2, (b) Glycine–Co/SiO_2, (c) Citric–Co/SiO_2, (d) Aspartic–Co/SiO_2, (e) NTA–Co/SiO_2, (f) EDTA–Co/SiO_2, (g) CyDTA–Co/SiO_2, (h) TTHA–Co/SiO_2.

with the organic acids and/or chelating agents except glycine and TTHA, which is apparently consistent with XRD result. Furthermore, the dispersion of Co increases in the same order as that for the steady-state conversion. Therefore, it can be said that modification of the impregnating solution with some organic acids and/or chelating agents improves the dispersion of Co, leading to the higher FTS activity.

3.3. *Effects of modification with the organic acids and chelating agents*

As mentioned above, the FTS activity of the reduced catalysts varies depending on the organic acids and/or chelating agents used for modification of the impregnating solution. Higher activities can be obtained when modified with some organic acids and/or chelating agents. Thus, we further investigated the relationship between the FTS activity and the complex formation constant of the organic acids and/or chelating agents. In figure 2, the steady-state conversions over the reduced catalysts are plotted against the complex formation constants of the organic acids and/or chelating agents used here. This figure shows that the steady-state conversion seems to show the maximum around the complex formation constant of 10 (NTA). Modification with the organic acids and/or chelating agents having much smaller and/or larger complex formation constants shows negligible and/or negative effects. Thus, this figure shows that modification of the impregnating solution with the additives having the appropriate complex formation constant with Co^{2+} is important for obtaining the higher FTS activity. Whether the catalysts prepared with these chelating agents show stable FTS activities even for long time duration (1 year or more) is not clear yet, and is beyond the scope of the present study. It can be only pointed out at present that no activity decline is observed on these catalysts for relatively short duration (ca. 20 h on stream) in our activity tests. The present study cannot provide experimental evidences for the regeneration of the deactivated catalysts either. However, they could be regenerated by the reductive and/or oxidative treatments under mild conditions when the catalyst deactivation caused by the oxidation of metallic Co species [26] and/or the deposition of carbonaceous compounds.

Table 3

Effects of modification with the organic acids and/or chelating agents on H_2 uptake and the dispersion of Co over reduced Co/SiO_2 catalyst

	H_2 uptake /μ mol-H_2 g^{-1}	Dispersion of Co/%
Co/SiO_2	20.3	4.8
Gilycine–Co/SiO_2	20.9	4.9
Citric–Co/SiO_2	39.4	9.3
Asparatic–Co/SiO_2	49.5	11.7
NTA–Co/SiO_2	65.0	15.3
EDTA–Co/SiO_2	37.9	8.9
CyDTA–Co/SiO_2	35.6	8.4
TTHA–Co/SiO_2	8.7	2.1

Because NTA has a large complex formation constant with Co^{2+}, it is suggested that modification of the impregnating solution with NTA results in the formation of a stable NTA–Co complex. On the other it is reasonable to assume that the dispersion of Co depends on the reducibility and cluster size of Co species on the calcined catalyst. Therefore, it is probable that the stability of the complex formed in the impregnating solution affects the reducibility and cluster size of Co species on the calcined catalyst. These points will be investigated in detail, and reported in the subsequent paper [27].

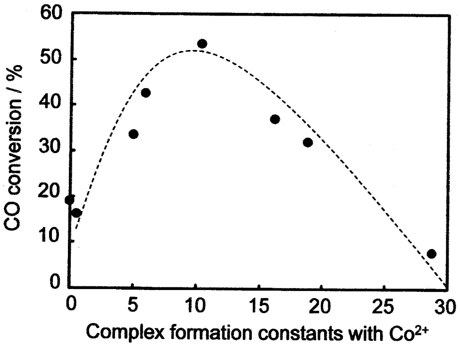

Figure 2. Relationship between the steady-state conversions over the reduced catalysts and the complex formation constants of the organic acids and/or chelating agents used for the preparation of the catalysts.

4. Conclusion

The present study investigated the FTS activity and surface structure of reduced Co/SiO_2 catalysts prepared by the incipient wetness method using the aqueous Co nitrate solution modified with the organic acids and/or chelating agents having various complex formation constants with Co^{2+}, followed by drying and calcination. Modification with some organic acids and chelating agents improved the dispersion of Co over the reduced catalyst, leading to the higher FTS activity. Especially, the steady-state CO conversion over the reduced catalyst modified with NTA was ca. 3 times higher than that over the catalyst without additives. The complex formation constant of the organic acids and/or chelating agents was crucial to the FTS activity of reduced Co/SiO_2 catalyst. Higher FTS activities could be obtained simply by modification of the impregnating solution with the additives having the appropriate complex formation constant with Co^{2+} (ca. 10).

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