Effects of glycols on Fischer–Tropsch synthesis activity and coordination structure of Co species in Co/SiO$_2$: Mechanism for enhanced dispersion of Co^0 nanoparticles

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ABSTRACT

Co/SiO$_2$ catalysts with higher dispersion of Co^0 as well as high reducibility of Co were prepared by impregnation using an aqueous solution containing Co nitrate and a glycol under different glycol/Co^{2+} molar ratios. Glycols with different structures, i.e., straight chain and branched ones, were used for preparation of the catalysts to help understand the fundamental role of the glycols. The CO conversion was enhanced in the presence of these glycols. The highest conversion was around 60% under 503 K and 1.1 MPa regardless of the structures of the glycols, whereas the optimum glycol/Co^{2+} molar ratio for the highest conversion shifted toward higher values with decreasing molecular weight of the glycols. On the other hand, these conversions fell on one curve irrespective of the structures of the glycols when plotted against the C/Co^{2+} atomic ratios of the impregnation solutions, indicating that the C/Co^{2+} ratio was one of crucial factors for activity enhancement induced by the glycols. Furthermore, XRD and Co K-edge EXAFS measurements revealed that Co$_3$O$_4$ species with smaller sizes was formed after calcination in the presence of the glycols. Size of Co$_3$O$_4$ species fell on one curve when plotted against the C/Co^{2+} atomic ratios, which was consistent well with activity data. FT-IR measurements also provided evidence that Co species interacted with triethylene glycol (TEG) derivatives during calcination in the range of 400–470 K. In analogy to the polymerizable complex method, it was considered that this interaction included polymer complex-like species, in which Co species was immobilized in network of cross-linked structures formed by ester polymerization of TEG and dicarboxylic acid derived from TEG, resulting in the formation of smaller Co$_3$O$_4$ species after calcination, and the smaller Co^0 nanoparticles after H$_2$ reduction, i.e., enhanced FTS activity.

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1. Introduction

Fischer–Tropsch synthesis (FTS) is one of versatile processes for the synthesis of transportation fuels, since it enables syngas to be produced from, in principle, any carbon resources. Furthermore, diesel fraction of hydrocarbons synthesized by FTS has superior properties than the conventional one. It was reported that Co-based FTS catalysts gave high activity and selectivity for the synthesis of diesel fraction from syngas under relatively low temperatures and medium pressures [1–3]. Over the last two decades, many research groups have studied Co-based catalysts for the purpose of improving catalytic activity and selectivity for acquisition of the diesel fraction from both fundamental and technological aspects [3–13].

Co-based catalysts are usually prepared by impregnating Co precursors, calcining them and reducing Co$_3$O$_4$ to FTS active Co^0 particles. Several research groups demonstrated that dispersion of Co^0 was enhanced when the catalyst was prepared using some organic Co precursors such as of Co acetate (Co/SiO$_2$) [11], Co acethylacetonate, Co oxalate (Co/TiO$_2$) [14] and/or Co nitrate/Co acetate mixed salt (Co/SiO$_2$) [11] instead of conventional Co nitrate. Unfortunately, however, use of these Co precursors lowered reducibility of Co, indicating the trade-off relationships between dispersion of Co^0 and reducibility of Co. Several researchers suggested that such Co precursor effect was related to difference in modes of interaction between Co species and surface hydroxy groups during the impregnation step [15–17]. However, details of the origin of Co precursor effect have not been elucidated yet.

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Recently, we found that chelate-assisted Co/SiO$_2$ catalysts, which were prepared by novel co-impregnation method using an aqueous solution containing both Co nitrate and a chelating agent (Co^0 loading = 5 mass%), showed high catalytic activity for FTS under pressurized conditions [18–21]. Maximum FTS activity was achieved with the catalyst prepared using Co nitrate and nitrilo-triacetic acid (NTA) as the chelating agent. This catalyst showed a 3-fold higher CO conversion than the catalyst prepared using Co nitrate alone. In spite of large activity enhancement of NTA, however, Co loading of the catalysts prepared by co-impregnation method was limited to maximum of 5 mass% because of low solubility of the chelating agents in the presence of Co nitrate. Later, Co loading of the catalysts prepared using the chelating agents was successfully increased up to 20 mass% by stepwise impregnation method [22,23]. For the catalysts prepared in this stepwise impregnation method, the CO conversion increased with increasing K_{Co} of the chelating agents [24]. Chelating agents with larger K_{Co} than NTA, in particular *trans*-1,2-diaminocyclohexane-*N,N,N′,N′*-tetraacetic acid (CyDTA), exhibited a noticeable activity enhancement [22]. Furthermore, the development of both high dispersion of Co^0 and high reducibility of Co took place when Co/SiO$_2$ was prepared by not only co-impregnation method using NTA [19] but also stepwise impregnation method using CyDTA [24]. Physicochemical characterization of the stepwise-impregnated catalysts suggested that only a part of Co species was involved in the complex formation with CyDTA during the impregnation and drying steps, which drastically enhanced dispersion of Co$_3$O$_4$ species formed after calcination [24].

To investigate the role of these organic additives from a different point of view, searching for tractable and inexpensive ones compared with the chelating agents, Co/SiO$_2$ catalysts were then prepared by co-impregnation method using Co nitrate and some glycols with much lower affinity for Co^{2+} than NTA and CyDTA, and their FTS activity and selectivity were investigated [25]. In our recent report, it was found that FTS activity of Co/SiO$_2$ was enhanced even in the presence of ethylene glycol (EG), diethylene glycol (DEG) or triethylene glycol (TEG). Especially, 20% Co/SiO$_2$ prepared using TEG exhibited the space-time yield of C$_{10}$–C$_{20}$ hydrocarbons comparable with that of 20% Co/SiO$_2$ prepared by stepwise impregnation method using CyDTA under the same reaction conditions [25]. Furthermore, use of these glycols enhanced dispersion of Co^0, whereas reducibility of Co was high regardless of whether the catalysts were prepared with or without using the glycols. These results are of importance to clarify the chemistry involved in the activity enhancement of Co-based FTS catalysts induced by the organic additives. Fundamental understanding of the role of these glycols in the formation of small Co^0 particles will lead us to general ideas for the mechanism of enhanced dispersion of Co^0 induced by organic additives. Before our study, only a few research groups reported that dispersion of Co^0 (or Co$_3$O$_4$ species) was influenced in part by the presence of mannitol and EG [26–29]. However, the effect of glycols on coordination structures of Co species in the preparation steps was not investigated in these studies. The role of these organic compounds has not been fully figured out yet.

To improve understanding of the fundamental role of the glycols, Co/SiO$_2$ catalysts were prepared using several glycols with different structures, i.e., straight chain (EG, DEG, TEG) and branched (glycerol, pentaerythritol) ones. Their FTS activity was investigated under pressurized conditions using a fixed bed reactor system for clarifying factors related to activity enhancement induced by the glycols. The catalysts were also employed for several physicochemical characterizations including XRD, Co K-edge EXAFS and FT-IR spectroscopy to study the effects of the glycols on coordination structure of Co species during and after calcination.

2. Experimental

2.1. Preparation of catalysts

All the catalysts studied in this work were prepared by a pore-filling incipient wetness impregnation method. SiO$_2$ powder (BET surface area = 224 m^2 g^{-1}, average pore diameter = 15 nm, pore volume = 1.24 mL g^{-1}, particle size = 150–250 × 10^{-6} m) was purchased from Fuji Silysia, and calcined at 823 K for 12 h before use. This SiO$_2$ powder was impregnated with aqueous solution containing Co(NO$_3$)$_2$·6H$_2$O (Wako Pure Chemical Industries) and one glycol selected from ethylene glycol, diethylene glycol, triethylene glycol, glycerol and pentaerythritol. Diglycolic acid was also used for preparation of the catalyst. The impregnated sample was then dried at 393 K and 3 h followed by calcination at 723 K and 4 h in static air. The catalysts thus prepared are denoted as Co(X)-Glycol(Y)/SiO$_2$ in this paper, where X and Y stand for Co loading (as mettalic Co) and glycol to Co^{2+} molar ratio of the impregnating solution, respectively. Co/SiO$_2$ was also prepared using aqueous solution containing only Co(NO$_3$)$_2$·6H$_2$O.

2.2. Activity test

The effects of the glycols on FTS activity and selectivity of the silica supported Co catalysts were studied under pressurized conditions using a high-pressure fixed bed reactor system. The reactor consisted of the stainless steel tube with internal diameter of 7 mm, and placed in an electrically heated oven. 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 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 and 6 h. After H$_2$ reduction, temperature was down to ambient temperature. The feed gas was changed into CO/H$_2$/Ar at the pressure of 1.1 MPa (W/F = 1.25 g-cat h mol^{-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. An on line GC/TCD (Shimadzu, GC-8A) was used for analysis of CO, CO$_2$ and CH$_4$, whereas another on line GC/FID (Shimadzu, GC-2014) was used for analysis of C$_1$–C$_7$ hydrocarbons. Ar was used as internal standard for GC/TCD analysis. Liquid products were collected with an ice trap, and analyzed with an off line GC/FID (Agilent Technologies, Agilent 6850A) after the reaction.

2.3. XRD

XRD measurements were carried out using a MiniFlex (Rigaku) and a RINT (Rigaku) powder X-ray diffractometer. Cu Kα radiation was used as the X-ray source with the X-ray tube operating at 30 kV and 15 mA for the MiniFlex, and 40 kV and 200 mA for the RINT, respectively. The observed diffraction peaks were assigned by reference to Joint Committee on Powder Diffraction Standards (JCPDS) data. The crystalline size of Co species was calculated by Debye–Scherrer equation (1) using the (3 1 1) diffraction peak of Co$_3$O$_4$.

$$D_{hkl} = \frac{k_{hkl}\lambda}{\beta_{hkl}\cos\theta} \tag{1}$$

In this equation, λ is the wavelength of the X-rays (λ = 0.15405 nm), and β_{hkl} is the full width at half maximum (FWHM) of the diffraction peak. The shape factor (k_{hkl}) was equal to 0.9 in this work.