[Regular Paper]

Hydrogenation of Carbon Monoxide in the Presence of Solvent Using Novel Carbon–Oxide Composite Supported Cobalt and Iron Catalysts

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(Received July 5, 2017)

Hydrogenation of carbon monoxide in the presence of solvent under low pressure of 0.5 MPa was developed to easily evaluate catalysts, and was used to examine novel carbon–oxide composite supported cobalt catalysts. CO conversion increased in the order 16Co63C21TiO2 ≈ 16Co63C21Al2O3 < 16Co63C21SiO2 < 16Co63C21ZrO2 (16Co: 16 wt% Co; 63C: 63 wt% carbon in PEG; 21TiO2, Al2O3, SiO2 or ZrO2: 21 wt% TiO2, Al2O3, SiO2 or ZrO2). This reaction was performed for easy evaluation of catalysts under high temperature and low pressure conditions, which are not usually used for Co catalysts, so most product was methane for all cobalt catalysts. 16Co63C21ZrO2 catalyst showed the highest conversion of 31 % at 340 °C, probably because 16Co63C21ZrO2 catalyst consists of only mesopores which have advantages for mass transfer and was unchanged after the reaction. Furthermore, cobalt metal species did not change and were detected by XRD after the reaction, which would also maintain the higher activity. Novel carbon–oxide composite supported iron catalysts were similarly prepared and reactivity for the hydrogenation of carbon monoxide in the presence of solvent was examined. CO conversion increased in the order 16Fe63C21SiO2 ≈ 16Co63C21TiO2 < 16Fe63C21Al2O3 < 16Fe63C21ZrO2 (calcined at 500 °C) < 16Fe63C21ZrO2 (calcined at 700 °C). Most product was methane for all iron catalysts under low pressure in the presence of solvent, but 16Fe63C21ZrO2 calcined at 700 °C also produced C2-C6 hydrocarbons. These results may be related to the increased surface area and pore volume for ZrO2 supported catalysts with higher calcination temperature and the decreased iron particle sizes after the reactions, specifically from 42 to 7.2 nm for the catalyst calcined at 700 °C.

1. Introduction

Global industrial progress has rapidly increased the mass consumption of resources. In particular, carbon-based fuel reserves are declining, resulting in potential shortages. In addition, consumption of carbon-based fuels causes environmental degradation including global warming, and the emission of harmful particles has severe effects on organisms including humans. Consequently, drastic increases in the price of crude oil and increasing demand for clean alternative fuels have occurred.

Hydrogenation of carbon monoxide, the so-called Fischer-Tropsch synthesis (FTS), converts synthesis gas produced by the gasification of biomass into completely sulfur-free fuels. Biomass is regarded as a carbon neutral renewable source. The FTS has been widely investigated in both the academic community and in the industrial world. This method of gas to liquid (GTL) conversion depends on the development of effective catalysts. Various heterogeneous transition metal catalysts containing Fe, Co, Ni and Ru have been developed, and Co-based catalysts are particularly advantageous for practical applications due to the high activity, selectivity for long chain linear hydrocarbons, high resistance toward deactivation, and lower cost than Ru. Generally, Co and Fe catalysts are deposited on supports with high surface area (e.g., SiO2, Al2O3, TiO2 and ZrO2) to increase the number of active Co, Fe metal species, and silica-supported cobalt is an especially promising catalyst. Alumina is one of the most effective support materials for Co or Fe based FT catalysts due to the high resistance to attrition and stabilization of small clusters. Most transition metal-supported catalysts are made by the impregnation method, but preparation of catalysts using the sol-gel method has become common.

Our research to prepare catalysts using the sol-gel
method concentrated on the preparation of transition metal-supported catalysts including carbon sources, because some such catalysts were found to show activity for steam reforming and hydrothermal gasification of ethanol and aqueous phenol. Furthermore, we have investigated the hydrogenation of carbon monoxide in the presence of a solvent because the presence of solvent has some advantages. Solvent can effectively remove reaction heat, which is important because the hydrogenation of carbon monoxide is exothermic and the excess heat often accelerates the sintering of active metal species. Solvent can also remove products with high molecular weight which often cover the catalyst surface or close the pores. Usually this reaction is performed under high pressure and larger amounts of high molecular weight products are formed. Liquids including the solvent and products and gases can be divided by a gas-liquid separator. Although solvent may prevent the access of feed gas to limit the formation of high molecular weight hydrocarbons under low pressure, analysis of products becomes easier. Therefore, high molecular weight products can be synthesized under high pressure even in the presence of solvent, and the solvent can be used to screen the catalysts under low pressure reaction.

The present study prepared Co and Fe catalysts supported on carbon-SiO$_2$, Al$_2$O$_3$, TiO$_2$ and ZrO$_2$ composites using polyethylene glycol as a carbon source. Catalytic reactivity for the hydrogenation of carbon monoxide in the presence of decalin solvent was investigated because the reaction used very low pressure where the formation of hydrocarbons with lower molecular weight than decalin might be expected.

2. Experimental

2.1. Preparation of Carbon–Oxide Composite Supported Cobalt and Iron Catalysts

Carbon-oxide composite supported cobalt and iron catalysts were prepared using the sol-gel method. Polyethylene glycol (PEG, av. MW 400, Nacalai Tesque, Inc.) was added as a carbon source. Starting materials for silica, alumina, titania and zirconia oxide supports were tetraethyl orthosilicate (TEOS, Nacalai Tesque, Inc.), aluminum tri-$s$-butoxide (ASB, Nacalai Tesque, Inc.), titanium tetraisopropoxide (TIP, Nacalai Tesque, Inc.) and zirconium butoxide (ZB, Nacalai Tesque, Inc.), respectively. Cobalt nitrate hexahydrate (Co(NO$_3$)$_2$$\cdot$6H$_2$O, Nacalai Tesque, Inc.) and iron nitrate nonahydrate (Fe(NO$_3$)$_3$$\cdot$9H$_2$O, Nacalai Tesque, Inc.) were used as the cobalt and iron sources, respectively. The typical preparation procedure was as follows: To an ethanol solution of TEOS, aqueous solution of cobalt nitrate was added at 0°C over 1 h, PEG was added, and the mixture was stirred at 0°C for 10 h. After that, the mixture was dried at 90°C for 3 h to obtain a clay-like paste. The solid obtained was calcined under a nitrogen atmosphere at 500°C for 3 h. Iron catalysts were prepared similarly, and were calcined at 500°C or 700°C for 3 h.

Naming of catalysts indicates the amounts of elements or oxides in wt% included in a catalyst as the numbers before elements or oxides. For example, 16Co63C21SiO$_2$ includes 16 wt% of Co, 63 wt% of carbon included in PEG added during the preparation and 21 wt% of SiO$_2$.

2.2. Characterization of Catalysts Using XRD, N$_2$ Adsorption and Desorption, XRF, TG-DTA and TEM

X-ray diffraction patterns of the catalysts before and after reaction were measured using a Ultima IV (Rigaku Corp.) diffractometer (nickel-filtered CuK$\alpha$). X-ray source ($\lambda$ = 0.15405 nm) operated at 40 kV and 20 mA under the following conditions: scan mode CONTINUOUS, slit (SS) 1° (DS) 1° (RS) 0.3 mm, present time 1 s, scan speed 4°/min, measurement range 2$\theta$ = 10-70°).

The pore size distributions of catalysts before and after reaction were measured using a BELSORP mini II (BEL Japan Inc.). Surface area (SA) and pore volume (PV) including micropores, and average pore diameter (PD) were calculated by the BET method. SA, PV and PD for mesopores larger than 3.3 nm of diameter were estimated with the BJH method. The sample catalyst was degassed under 10$^{-2}$ kPa at 300°C for 3 h before N$_2$ adsorption measurement.

X-ray fluorescence (XRF) analysis was performed using an EDX-720 (Shimadzu Corp.) to determine the composition of carbon–zirconia supported catalysts except for carbon content. This analysis assumed that Co, Fe and Zr were present as metal Co, metal Fe and ZrO$_2$, respectively.

Thermogravimetry-differential thermal analysis (TG-DTA, DTG-60AH, Shimadzu Corp.) was used to determine the carbon content of catalysts before and after reaction. The catalyst sample was added to a platinum pan and heated under 100 mL/min of air flow and heating rate of 10°C/min from 25 to 800°C. The carbon content was estimated from the total weight loss of sample in the exothermic period (about 350-500°C).

Transmission electron microscope (TEM) images of Fe/C/ZrO$_2$ catalysts before and after reaction were measured using a JEM-1011 (BEAM current: 60 μA).

2.3. F-T Reaction Using Carbon–Oxide Composite Supported Metal Catalysts

The F-T reaction was performed using a conventional fixed bed flow reactor equipped with a gas-liquid separator and mass flow controller in the inlet (Fig. 1) under the conditions, catalysts 1 g, gas flow 40 mL/min, syngas composition H$_2$ 66%, CO 33%, Ar 1%, pressure 0.5 MPa and reaction temperature 250-340°C. The liquid solvent decalin was introduced at 10 cm$^3$/h.
The collected liquid and gas were analyzed using gas chromatography with a GC-2010 FID (carrier He, column initial 5 °C to final 280 °C, Inj. 250 °C, Det. 250 °C, total 203 min. Products were assigned using a PONA solution data base) and GC-2014 TCD (carrier He, active carbon 1 m, column initial 40 °C to final 300 °C, Inj. 300 °C, Det. 300 °C, total 30 min, C1-C4 were assigned by reference to a standard gas), respectively.

3. Results and Discussion

3.1. Characterization of Novel Carbon–Oxide Composite Supported Cobalt and Iron Catalysts

X-ray diffraction (XRD) patterns of 16Co63C21SiO2, 16Co63C21Al2O3, 16Co63C21TiO2 and 16Co63C21ZrO2 catalysts before and after the reaction were measured. XRD detected no peaks for 16Co63C21SiO2 catalysts, indicating that Co metal was highly dispersed on the support. In contrast, 16Co63C21Al2O3 catalysts exhibited peaks of CoAl2O4 before and after the reaction. Cobalt is supported on alumina resulting in the formation of cobalt aluminate spinels. In this study, cobalt aluminate was formed on alumina despite the addition of carbon sources. 16Co63C21TiO2 showed very small peaks of anatase. Cobalt species were not observed even after the reaction, indicating that they were dispersed on the composite supports with TiO2. 16Co63C21ZrO2 catalyst exhibited peaks of both Co and ZrO2 before and unchanged after the reaction (Fig. 2). Therefore, the particle size of cobalt metal of 4.2 nm was maintained after the reaction.

XRD patterns of 16Fe63C21SiO2, 16Fe63C21Al2O3, 16Fe63C21TiO2 and 16Fe63C21ZrO2 catalysts before and after the reaction were measured. XRD detected no peaks for 16Fe63C21SiO2 catalysts, indicating that Fe metal was dispersed on the support. This result was very similar to that of the cobalt catalyst. 16Fe63C21Al2O3 catalysts exhibited peaks of FeO4 before and after the reaction. The particle size of FeO4 of 10.7 nm was maintained after the reaction. 16Fe63C21TiO2 showed very small peaks of anatase. Iron species were not observed even after the reaction,
indicating dispersion on the composite supports with TiO\(_2\). This result was also similar to that of the cobalt catalyst. 16Fe63C21ZrO\(_2\) (700 \(^\circ\)C) catalyst exhibited peaks of both Fe and ZrO\(_2\) before and after the reaction (Fig. 2). However, the particle size of Fe metal decreased from 42 nm before reaction to 7.6 nm after reaction, although the particle size of Fe\(_3\)O\(_4\), which was slightly observed before and after the reaction, did not change.

\(\text{N}_2\) adsorption and desorption of 16Co63C21SiO\(_2\), 16Co63C21Al\(_2\)O\(_3\), 16Co63C21TiO\(_2\) and 16Co63C21ZrO\(_2\) were measured (Table 1). Comparison of BET surface areas of 16Co63C21SiO\(_2\), 16Co63C21Al\(_2\)O\(_3\), 16Co63C21TiO\(_2\) and 16Co63C21ZrO\(_2\) found that those using SiO\(_2\) and Al\(_2\)O\(_3\) supports were more than 200 m\(^2\)/g whereas those using TiO\(_2\) and ZrO\(_2\) supports were about 150 m\(^2\)/g and 130 m\(^2\)/g, respectively. In contrast, the size of BET pore volume decreased in the order 16Co63C21Al\(_2\)O\(_3\)>16Co63C21ZrO\(_2\)>16Co63C21SiO\(_2\)>16Co63C21TiO\(_2\). Differences between BET and BJH methods were observed for 16Co63C21SiO\(_2\), 16Co63C21Al\(_2\)O\(_3\), 16Co63C21TiO\(_2\) but not for 16Co63C21ZrO\(_2\), indicating that almost all pores in 16Co63C21ZrO\(_2\) were mesopores. These results are confirmed by the BJH plots and MP plots of catalysts shown in Fig. 3. These four catalysts had mesopores but 16Co63C21ZrO\(_2\) contained few micropores. 16Co63C21ZrO\(_2\) and 16Co63C21Al\(_2\)O\(_3\) had wide distributions of mesopore size whereas 16Co63C21SiO\(_2\) and 16Co63C21TiO\(_2\) had narrow distributions of mesopore size.

\(\text{N}_2\) adsorption and desorption of 16Fe63C21SiO\(_2\), 16Fe63C21Al\(_2\)O\(_3\), 16Fe63C21TiO\(_2\), 16Fe63C21ZrO\(_2\) and 16Fe63C21ZrO\(_2\) (700 \(^\circ\)C) were measured (Table 2). Comparison of BET surface areas of these catalysts found that those using SiO\(_2\) and Al\(_2\)O\(_3\) supports were more than 120 m\(^2\)/g whereas those using TiO\(_2\), ZrO\(_2\) and ZrO\(_2\) (700 \(^\circ\)C) supports were about 50, 30 and 90 m\(^2\)/g, respectively. BET pore volume decreased in the order 16Fe63C21SiO\(_2\)>16Fe63C21Al\(_2\)O\(_3\)>16Fe63C21ZrO\(_2\)>16Fe63C21TiO\(_2\)>16Fe63C21ZrO\(_2\). Differences between BET and BJH methods were observed for all catalysts 16Fe63C21SiO\(_2\), 16Fe63C21Al\(_2\)O\(_3\), 16Fe63C21TiO\(_2\), 16Fe63C21ZrO\(_2\) and 16Fe63C21ZrO\(_2\) (700 \(^\circ\)C), indicating that these catalysts contained both micropores and mesopores. These results are confirmed by the BJH plots and MP plots of catalysts shown in Fig. 3. Compared to the cobalt-based catalysts, the iron-based catalysts had lower surface areas and pore volumes, probably because cobalt is reduced more easily than iron and hydrogen transfer by metallic cobalt may have inhibited significant condensation and polymerization of carbon materials from PEG which could develop micropores.

### Table 1  \(\text{N}_2\) Adsorption-desorption Measurements of Carbon–Oxide Composite Supported 16Co63C21SiO\(_2\), 16Co63C21Al\(_2\)O\(_3\), 16Co63C21TiO\(_2\) and 16Co63C21ZrO\(_2\) Catalysts before and after Reaction

| Sample name   | BET | BJH |
|---------------|-----|-----|
|               | SA  | PV  | PD  | SA  | PV  | PD  |
| 16Co63C21SiO\(_2\) \(b)\ | 203 | 0.18 | 3.55 | 124 | 0.13 | 3.70 |
| 16Co63C21SiO\(_2\) \(a)\ | 208 | 0.20 | 3.77 | 147 | 0.15 | 3.70 |
| 16Co63C21Al\(_2\)O\(_3\) \(b)\ | 212 | 0.37 | 7.00 | 163 | 0.33 | 3.72 |
| 16Co63C21Al\(_2\)O\(_3\) \(a)\ | 211 | 0.35 | 6.66 | 152 | 0.32 | 3.72 |
| 16Co63C21TiO\(_2\) \(b)\ | 148 | 0.14 | 3.69 | 49  | 0.083| 3.70 |
| 16Co63C21TiO\(_2\) \(a)\ | 143 | 0.13 | 3.73 | 46  | 0.080| 3.70 |
| 16Co84ZrO\(_2\) \(b)\ | 56  | 0.054| 3.86 | 25  | 0.033| 3.70 |
| 16Co84ZrO\(_2\) \(a)\ | 88  | 0.13 | 6.27 | 117 | 0.21 | 3.70 |
| 16Co21C63ZrO\(_2\) \(b)\ | 87  | 0.14 | 7.03 | 81  | 0.12 | 3.70 |
| 16Co21C63ZrO\(_2\) \(a)\ | 126 | 0.23 | 7.18 | 113 | 0.20 | 3.70 |
| 16Co63C21ZrO\(_2\) \(b)\ | 131 | 0.22 | 6.80 |     |     |     |
| \(b)\): before, \(a)\): after, SA: surface area, PV: pore volume, PD: pore diameter.

Conversions of carbon monoxide at 300 \(^\circ\)C in the FTS using 16Co63C21SiO\(_2\), 16Co63C21Al\(_2\)O\(_3\), 16Co63C21TiO\(_2\) and 16Co63C21ZrO\(_2\) catalysts were 6.4, 0.4, 0.3 and 17 %, respectively, as shown in Fig. 4A. The reaction temperature was too high for silica-supported cobalt catalysts and would not be appropriate for 16Co63C21SiO\(_2\). In general, cobalt catalysts are used at 190-240 \(^\circ\)C in the FTS of long-chain hydrocarbons and paraffins\(^3\), so the effects of supports on activity at higher temperatures are not very well known. 16Co63C21ZrO\(_2\) contained CoAl\(_2\)O\(_4\) which is not active. 16Co63C21TiO\(_2\) showed no cobalt species in XRD. These findings may indicate that the cobalt species were highly dispersed and covered with strong interactions by the carbon and oxide supports, resulting in the lower activity. Lower amounts of PEG as a carbon source in ZrO\(_2\)-supported catalysts resulted in decreased conversions as shown in Fig. 4B. The
conversions were 3.3 % and 1.7 % for 16Co21C63ZrO2 and 16Co84ZrO2 at 300 °C, respectively. 16Co63C21ZrO2 exhibited the highest CO conversion among the catalysts examined, presumably reflecting the pore size distribution of 16Co63C21ZrO2, because it only consists of mesopores which have advantages for the diffusion of products, reactants and solvent into the catalyst. Pore volumes and surface areas decreased significantly in the order 16Co63C21ZrO2 > 16Co21C63ZrO2 > 16Co84ZrO2 as shown in Table 1, while the pore structures of these catalysts were not changed before and after the reaction. Our catalyst system included decalin, and the trickle bed reactor system was presumably strongly affected by the mass transfer process. Another possibility was that Co metal was observed only for 16Co63C21ZrO2. Other two catalysts did not show cobalt species, indicating that cobalt species were highly dispersed. However, those fine particles may be covered and strongly interact with carbon and oxide supports, which would lead to the lower activity.

Figures 4A and 4B also show the carbon number distribution of products. Methane was a major product for all catalysts examined. C1-C3 products were confirmed with 16Co63C21SiO2 but C4 or higher products were not detected. 16Co63C21Al2O3 and 16Co63C21TiO2 catalysts only produced C1 and C2 compounds. In contrast, C1-C6 products were observed using 16Co63C21ZrO2.

Figure 5 shows the effect of temperature on the conversion and the product distribution for the F-T reaction using 16Co63C21ZrO2 catalyst. Conversion increased with higher temperature and reached 31 % at 340 °C probably because the Co metal species and pore structure of the catalysts were very stable and hardly changed even at 340 °C as shown by the XRD and N2 adsorption and desorption measurements. Cracking of decalin did not occur because only methane and ethane were formed at higher temperature. Catalytic decomposition of decalin would form products larger than methane and ethane.

Table 2  N2 Adsorption-desorption Measurements of Carbon-Oxide Composite Supported 16Fe63C21SiO2, 16Fe63C21Al2O3, 16Fe63C21TiO2 and 16Fe63C21ZrO2 (700 °C) Catalysts before and after Reaction

| Sample name                  | BET          | BJH          |
|------------------------------|--------------|--------------|
|                              | SA [m²/g]    | PV [cm³/g]   | PD [nm] | SA [m²/g]    | PV [cm³/g]   | PD [nm] |
| 16Fe63C21SiO2 8b             | 126          | 0.23         | 7.18    | 117          | 0.21         | 3.70    |
| 16Fe63C21SiO2 8a             | 131          | 0.22         | 6.80    | 113          | 0.20         | 3.70    |
| 16Fe63C21Al2O3 9b            | 148          | 0.14         | 3.69    | 49           | 0.083        | 3.70    |
| 16Fe63C21Al2O3 9a            | 143          | 0.13         | 3.73    | 46           | 0.080        | 3.70    |
| 16Fe63C21TiO2 5b             | 50           | 0.035        | 2.79    | 21           | 0.018        | 3.70    |
| 16Fe63C21TiO2 5a             | 55           | 0.038        | 2.78    | 23           | 0.019        | 3.70    |
| 16Fe63C21ZrO2 10b            | 30           | 0.017        | 2.32    | 4.31         | 0.0017       | 3.70    |
| 16Fe63C21ZrO2 10a            | 24           | 0.015        | 2.51    | 5.63         | 0.0033       | 3.70    |
| 16Fe63C21ZrO2 (700°C) 11b    | 98           | 0.065        | 2.66    | 15           | 0.023        | 3.28    |
| 16Fe63C21ZrO2 (700°C) 11a    | 92           | 0.067        | 2.88    | 21           | 0.030        | 3.70    |

b): before, a): after, SA: surface area, PV: pore volume, PD: pore diameter.
3.3. F–T Reaction Using Novel Carbon–Oxide Composite Supported Iron Catalysts in the Presence of Decalin

Conversions of carbon monoxide at 300°C in the FTS using 16Fe63C21SiO2, TiO2, Al2O3 or SiO2 Catalysts were 0.3, 3.3, 0.3 and 10%, respectively, as shown in Fig. 6A. Increase of the calcination temperature to 700°C for 16Fe63C21ZrO2 catalyst increased the conversion to 55%, the highest CO conversion among the catalysts examined, presumably resulting from the generation of very fine iron metal particles in 16Fe63C21ZrO2 calcined at 700°C which have advantages for the increase of active sites.

Figure 6A also shows the carbon number distribution of the products. Methane was a major product for all catalysts examined. C1-C6 products were confirmed with 16Fe63C21ZrO2. Increased reaction temperature from 300 to 320°C and 340°C using 16Fe63C21ZrO2 resulted in reduced conversions as shown in Fig. 6B. Deactivation occurred at higher temperature, as large decrease in conversion was observed with the temperature reduced to 280°C again.

Figure 7 shows transmission electron microscope (TEM) images of 16Fe63C21ZrO2 calcined at 700°C before and after reaction. Large
masses of metal and oxide species were observed after the reaction at 340°C, but small iron particles also appeared on the edge of the catalyst, consistent with the XRD findings.

Figure 8 shows model structures of carbon–oxide composite supported Co and Fe catalysts. Both catalysts showed higher activities with reduced metal species in the catalysts. Iron-based catalysts required higher temperature to obtain metallic iron, so that the initial carbon content decreased as shown in Table 3. The differences between initial and final amounts of carbon in the catalysts corresponded to the amounts of coke formation. The amount of coke formation for 16Co63C21ZrO2 was higher than that for 16Fe63C21ZrO2 (700°C). However, deactivation would occur for 16Fe63C21ZrO2 because of the small pore size and pore volume. 16Fe63C21ZrO2 would consist mainly of micropores because the BJH surface area was much smaller than the BET surface area. Therefore, the deposition of only small amounts of carbon may accelerate the deactivation. Iron metal species became small, indicating that oxygen from carbon monoxide may oxidize iron metals to form very fine FeO4 particles which are difficult to detect by XRD.

The presence of solvent, squalane or hexane reduces the conversion and shifts the product distribution to products with lower molecular weight8). Using a trickle bed reactor (TBR) with hexadecane showed slight decrease in CO conversion, but CO conversion using a TBR was double that using a slurry phase reactor11). Supercritical phase FTS (SFTS) technology uses solvents6),14),16). The selectivity for olefins increased in SFTS whereas the product distribution was not affected14). Propane, n-hexane, etc. were used as the supercritical fluid (SCF), and the positive effects were derived from the higher diffusivity of the reactants and products. The product distribution in SFTS also shifted to higher carbon number products16). The reaction rate and diffusion of reactants in SFTS are lower than those in the gas-phase reaction whereas the removal of reaction heat and waxy products from the catalyst surface was improved in comparison with the case in the gas-phase reaction17). Hydrogenolysis is important in shortening the chain length of the primary product and also in producing extra methane7),18). In our reaction system, carbon numbers of products were rather low and the solvent inhibited chain growth, consistent with some results for SFTS.

In general, Co-based catalysts produce high molecular weight and long chain hydrocarbons in FTS. The activities of Co-based catalysts were affected by the type of supports and decreased in the order Co/TiO2 > Co/Al2O3 > Co/SiO2 > Co > Co/MgO15),16). In our present study, the activities of carbon–oxide sup-

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**Table 3** Elemental Analyses of Carbon–Oxide Composite Supported 16Co63C21ZrO2 and 16Fe63C21ZrO2 (700°C) Catalysts before and after Reaction Using XRF and TG-DTA Measurement

| Catalyst         | Metal | Carbon | Support |
|------------------|-------|--------|---------|
| 16Co63C21ZrO2 before | 40.75 (Co) | 24.75 | 34.50 (ZrO2) |
| 16Co63C21ZrO2 after  | 36.29 (Co) | 28.56 | 35.15 (ZrO2) |
| 16Fe63C21ZrO2 before (700°C) | 35.85 (Fe) | 16.97 | 47.18 (ZrO2) |
| 16Fe63C21ZrO2 after (700°C) | 34.47 (Fe) | 19.48 | 46.05 (ZrO2) |

Average pore diameter and pore volume were much smaller than those of Co catalysts. Coke deposition after 340°C may lead to deactivation.
ported Co catalysts decreased in the order Co/C/ZrO$_2$ > Co/C/SiO$_2$ > Co/C/Al$_2$O$_3$ = Co/C/TiO$_2$ under relatively high temperature and low pressure. Although the formations of methane and ethane were major routes, Co/C/ZrO$_2$ did not lose activity in the hydrogenation of carbon monoxide. Co metal species were considered to persist only on this catalyst, resulting in the higher activity.

4. Conclusions

- Novel carbon-oxide composite supported Co and Fe catalysts with high metal content were prepared.
- F-T reaction in the presence of solvent was evaluated over Co/C/ZrO$_2$ catalysts.
- Conversions using Fe catalysts decreased in the order Fe/C/ZrO$_2$ : 21 wt% TiO$_2$, Al$_2$O$_3$, SiO$_2$ over Co/C/ZrO$_2$ catalysts.
- Catalytic activity increased with higher calcination temperature over Fe/C/ZrO$_2$ catalysts.

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