CoO$_x$–FeO$_x$ composite oxide prepared by hydrothermal method as a highly active catalyst for low-temperature CO oxidation

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A series of CoO$_x$–FeO$_x$ composite oxides with different Co content was prepared using the hydrothermal method. Low-temperature activity of CoO$_x$–FeO$_x$ composite oxides for CO oxidation was significantly improved by the addition of 50 atm % CoO$_x$ into FeO$_x$. Further increase in Co content up to 70 atm % caused a decrease in low-temperature activity. Structural characterizations by X-ray diffraction, transmission electron microscope and Fourier transform infrared (FT-IR) revealed that Co species, which were not substituted with Fe sites to form CoFe$_2$O$_4$, are highly dispersed on the surface of CoFe$_2$O$_4$ particles with a perimeter interface for the samples with 50 atm % CoO$_x$. The surface valence state of CoO$_x$–FeO$_x$ composite oxides was found to be different by FT-IR spectroscopy following NO adsorption. CoO$_x$–FeO$_x$ with 50 atm % CoO$_x$ includes a relatively large amount of quasi-tetrahedrally coordinated Co$^{3+}$ sites on the surface, whereas that with 10 atm % CoO$_x$ consists of Fe$^{3+}$ sites on the surface. Temperature-programmed reduction by H$_2$ measurements suggested that CoO$_x$–FeO$_x$ with 50 atm % CoO$_x$ possesses the largest amount of active oxygen species, which can be reduced by H$_2$ in lower temperature region. The surface oxygen species of which the formation is related to the presence of quasi-tetrahedrally coordinated Co$^{3+}$ sites was concluded to participate in CO oxidation reaction on CoO$_x$–FeO$_x$ composite oxides.

Key-words: CoO$_x$–FeO$_x$ composite oxides, CO oxidation, NO adsorption, FT-IR, H$_2$-TPR

1. Introduction

The exhaust gas emitted from boilers, combustors and engines contains carbon monoxide (CO), which is a major harmful pollutant to human health. Catalytic oxidation is an effective method of CO abatement. Numerous kinds of catalysts showing the CO oxidation activity have been reported, and the development of highly active catalysts for low-temperature CO oxidation is still attracting attention in environmental emission control. Among the catalysts reported, supported precious metal catalysts are promising candidates for low-temperature CO oxidation. For example, Haruta et al. reported that Au nanoparticles supported on α-Fe$_2$O$_3$ and Co$_2$O$_4$ can effectively catalyze CO oxidation at temperatures as low as −70°C. They proposed the importance of the perimeter between Au nanoparticles and oxide support as catalytically active sites. Supported Pt and Pd catalysts are also effective CO oxidation catalysts. However, as precious metals are rare, the development of alternative catalysts is required.

Transition metal oxides can also catalyze the CO oxidation reaction. Boroskov measured the catalytic activity of the 4th period transition metal oxides for various catalytic oxidation reactions, and revealed a close correlation between the activity for oxidation reactions and that for homonuclear exchange of oxygen isotopes. Among them, cobalt oxide (CoO$_2$) is an active catalyst for low-temperature CO oxidation. Since the reaction mechanism of CO oxidation over metal oxide catalysts is believed to be the Mars-van Krevelen redox model, the high activity of CoO$_2$ would be due to the relatively low ΔH of O$_2$ vaporization originating from the Co$^{3+}$–Co$^{2+}$ ion pairs. Recently, Co$_3$O$_4$ with controlled nanostructures such as nanorods, nanobelts and nanocubes has been reported to show extremely high low-temperature CO oxidation activity. The high activity of nanostructured Co$_3$O$_4$ was explained by the favorable exposure of crystal facets on which active Co$^{3+}$ species are predominantly present such as {110} and {011} planes. Controlling the local structure surrounding the Co$^{3+}$ species is an effective strategy for the development of low-temperature active CO oxidation catalysts.

Composite oxide catalysts often exhibit extremely high catalytic activity compared with that of single metal oxides. Therefore, the activity of CoO$_x$ is expected to be improved by combining with other oxides. Among the candidates as oxide additive, iron oxide (Fe$_2$O$_3$) nanoparticles are reported to show unique catalytic behavior for CO oxidation at temperatures below 150°C. In addition, Fe$_2$O$_3$ can create cobalt-ferrite composite oxide with a spinel structure via the solid reaction with Co$_3$O$_4$, leading us to the expectation of a synergistic effect. In fact, Mountapmbeme Kouotou et al. reported that spinel type Co–Fe oxides with higher Fe contents synthesized by a special technique, the so-called cold-wall stagnation-point flow CVD method, exhibit higher CO oxidation activity than the corresponding bare α-Fe$_2$O$_3$. From a practical viewpoint, however, it is important to develop highly active low-temperature CO oxidation catalysts that can be prepared by conventional methods. In this study, we prepared CoO$_x$–FeO$_x$ composite oxides with different Co contents by using the hydrothermal method. In the
course of this work, we found that CoO$_x$–Fe$_2$O$_3$ composite oxide with a Co content of 50 atm% can effectively oxidize CO at temperatures below 150°C. Its unique catalytic property is discussed on the basis of its catalyst characterizations.

2. Experimental

Cobalt–iron composite oxides were prepared using the hydrothermal method. Cobalt(II) chloride (Wako Pure Chemicals Industry) and iron(III) chloride (Wako Pure Chemicals Industry) were dissolved in distilled water at room temperature under vigorous stirring, and then ethylene glycol (Wako Pure Chemicals Industry) was added to the solution. The solution thus obtained was transferred to a Teflon vessel and then an aqueous solution of sodium(I) hydroxide (Wako Pure Chemicals Industry) was added to adjust the pH value to 13. The resulting wet gel was treated at 180°C for 4 h in an autoclave. The product thus obtained was washed with ethanol and distilled water, followed by drying and calcination at 500°C for 1 h in air. The Co content was changed from 10 to 70 atm% as a metal. The samples are abbreviated as Co($x$)–Fe$_2$O$_3$, where $x$ is the atomic concentration of Co. Iron oxide and cobalt oxide are expressed as Fe$_2$O$_3$ and Co$_3$O$_4$, respectively.

The Brunauer–Emmett–Teller (BET) surface area of the catalysts was determined by $N_2$ physisorption at liquid nitrogen temperature using a BELSORP mini-II, after evacuating the background spectrum of Co$_3$O$_4$. When Co was added to Fe$_2$O$_3$, a structure transformation to CoFe$_2$O$_4$ with an inverse spinel structure was observed, suggesting a substitution of Fe sites by Co. The formation of CoFe$_2$O$_4$ is theoretically completed at the Co/Fe atomic ratio of 1/2. Therefore, CoFe$_2$O$_4$ is expected to be completely formed for Co(30)–Fe$_2$O$_3$ [Fig. 1(c)]. As summarized in Table 1, a gradual increase in the lattice constant of CoFe$_2$O$_4$ was observed for Co–Fe$_2$O$_3$ with Co content lower than 30 atm%, suggesting the formation of Co$_{3-x}$Fe$_x$O$_4$ ($x \leq 1$) solid solution. On the other hand, not only CoFe$_2$O$_4$ but also Co$_3$O$_4$ are suspected of being simultaneously formed in higher Co content than 30 atm%. 

![Fig. 1. XRD patterns of Co($x$)–Fe$_2$O$_3$ composite oxides with different Co content. (a) Fe$_2$O$_3$, (b) Co(10)–Fe$_2$O$_3$, (c) Co(30)–Fe$_2$O$_3$, (d) Co(50)–Fe$_2$O$_3$, (e) Co(70)–Fe$_2$O$_3$, (f) Co$_3$O$_4$.](image)

| Co/Fe atomic ratio | XRD measurements |
|--------------------|------------------|
|                    | Detected oxides  | Lattice constant of CoFe$_2$O$_4$/nm | Crystallite size of oxide/nm | BET surface area/m$^2$ g$^{-1}$ |
| Fe$_2$O$_3$       | 0/1              | $\alpha$–Fe$_2$O$_3$                 | —                           | 56.8                          | 72.7                          |
| Co(10)–Fe$_2$O$_3$| 1/9              | Fe$_2$O$_4$                          | 0.8357                      | 12.5                          | 74.1                          |
| Co(30)–Fe$_2$O$_3$| 3/7              | Fe$_2$O$_4$                          | 0.8352                      | 11.4                          | 75.4                          |
| Co(50)–Fe$_2$O$_3$| 1/1              | Fe$_2$O$_4$                          | 0.8351                      | 15.1                          | 42.1                          |
| Co(70)–Fe$_2$O$_3$| 7/3              | Fe$_2$O$_4$                          | 0.8341                      | 15.8                          | 26.6                          |
| Co$_3$O$_4$       | 1/0              | Co$_3$O$_4$                          | —                           | —                             | 24.7                          | 12.3                          |

The catalytic activity for CO oxidation was evaluated using a fixed-bed continuous flow reactor. A reaction gas mixture containing CO (0.5%) and O$_2$ (1%) diluted in He as the balance gas was fed through a catalyst (30 mg), pretreated in situ in a flow of 5% O$_2$/He at 500°C for 1 h, at a rate of 50 cm$^3$ min$^{-1}$ (Space velocity = ca. 50,000 h$^{-1}$). The activity was measured while decreasing the temperature from 500 to 40°C in steps of 20°C, and the steady-state catalytic activity was measured at each temperature. The effluent gas was analyzed with the use of an on-line gas chromatograph equipped with TCD (Shimadzu GC-8A). The catalytic activity was evaluated in terms of CO conversion to CO$_2$. 

3. Results and discussion

Figure 1 shows XRD patterns of Co($x$)–Fe$_2$O$_3$ composite oxides with different Co content. The crystal phase detected in XRD was totally different depending on the Co content. Iron oxide [Fig. 1(a)] and cobalt oxide [Fig. 1(f)] showed distinct XRD peaks indexed to $\alpha$–Fe$_2$O$_3$ and Co$_3$O$_4$ phases, respectively. When Co was added to $\alpha$–Fe$_2$O$_3$, a structure transformation to CoFe$_2$O$_4$ was observed, suggesting a substitution of Fe sites by Co. The formation of CoFe$_2$O$_4$ is theoretically completed at the Co/Fe atomic ratio of 1/2. Therefore, CoFe$_2$O$_4$ is expected to be completely formed for Co(30)–Fe$_2$O$_3$ [Fig. 1(c)]. As summarized in Table 1, a gradual increase in the lattice constant of CoFe$_2$O$_4$ was observed for Co–Fe$_2$O$_3$ with Co content lower than 30 atm%, suggesting the formation of Co$_{3-x}$Fe$_x$O$_4$ ($x \leq 1$) solid solution. On the other hand, not only CoFe$_2$O$_4$ but also Co$_3$O$_4$ are suspected of being simultaneously formed in higher Co content than 30 atm%. In fact, distinct XRD peaks due to Co$_3$O$_4$ were observed.
also observed for Co(70)–Fe2O3 [Fig. 1(e)]. However, no XRD peaks assignable to Co3O4 were detected for Co(50)–Fe2O3, suggesting the presence of Co3O4 nanoparticles with a size below the detection limit by XRD. It should also be noted that the lattice constant of CoFe2O4 was gradually decreased with an increase in the Co content from 30 to 70 atm % (Table 1). The decrease in the lattice parameter with increasing Co content was also observed by Mountapbembe Kouotou et al.\textsuperscript{20} and Le Trong et al.\textsuperscript{21} They explained this phenomenon by the replacement of Fe\textsuperscript{3+} cations in the octahedral position by Co\textsuperscript{3+} cations, indicating a gradual evolution of a normal spinel structure from an inverse spinel structure. In this study, the coordination state of Co\textsuperscript{3+} cations in the CoFe2O4 lattice is suspected of being different depending on the Co content. In other words, the dispersion state of Co species in Co(x)–Fe2O3 samples might be different.

Table 1 summarizes the BET surface area of Co(x)–Fe2O3 composite oxides with different Co content. No significant difference in the BET surface area was observed for Co–Fe2O3 composite oxide with a Co content of 0–30 atm %, although the BET surface area of Fe2O3 was slightly increased by the addition of Co. Further increase in the Co addition caused a significant decrease in the BET surface area. As can be seen in Table 1, a good correlation between the BET surface area and the crystallite size of CoFe2O4 was observed. Namely, the crystallite size of CoFe2O4 slightly decreased with an increase of the Co content from 10 to 30 atm %, and increased with a further increase in the Co content to 70 atm %. Although the crystallite size of CoFe2O4 was found to be larger than that of CoFe2O4, a relatively high BET surface area was obtained. This is probably due to the presence of micropores, which cannot be detected by N\textsubscript{2} adsorption, inside the α-Fe2O3 particles.

\textbf{Figure 2} shows the catalytic activity of Co(x)–Fe2O3 composite oxides with different Co content for CO oxidation. Fe2O3 becomes active in CO oxidation at temperatures above 200°C, and reaches complete CO conversion at 450°C. Although the addition of 10 atm % Co did not cause a change in the CO oxidation activity, a significant improvement of CO oxidation activity was achieved when 50 atm % Co was added to Fe2O3. It is noteworthy that Co(50)–Fe2O3 can effectively catalyze CO oxidation even at room temperature, where 57% CO conversion was attained. There are few reports in which quite high low-temperature activity was achieved on metal oxide–based catalysts.\textsuperscript{31} The high CO oxidation activity of Co(50)–Fe2O3 could be ascribed to the creation of new catalytically active sites by the combination of Fe2O3 and Co3O4. Unfortunately, further increase in the Co content up to 70 atm % caused a decrease in CO oxidation activity. The most active catalyst was found to be Co(50)–Fe2O3.

In order to consider the difference in the CO oxidation activity, the morphology of Co(x)–Fe2O3 samples was observed by TEM analysis. As can be seen in Fig. 3, the TEM images revealed a difference in the particle morphology depending on the Co content. Co(10)–Fe2O3 [Fig. 3(a)] and Co(50)–Fe2O3 [Fig. 3(b)] seem to consist of an aggregation of CoFe2O4 nanoparticles, which were detected by XRD (Fig. 1), with a size of ca. 10–20 nm. On the other hand, the growth of CoFe2O4 particles was observed for Co(50)–Fe2O3 [Fig. 3(c)]. This is in agreement with the results of crystallite size estimated from the XRD and BET surface area (Table 1). Although the Co content in the Co(50)–Fe2O3 sample is too much for the complete formation of CoFe2O4, the presence of particles with different morphology, which may be ascribed to the CoFe2O4 and Co3O4, was not observed [Fig. 3(c)], suggesting that Co species, which were not substituted with Fe sites, are highly dispersed in the Co(50)–Fe2O3 sample. On the other hand, as seen in Fig. 3(d), two kinds of particles with different morphology were observed for the Co(70)–Fe2O3 sample. Taking into account the fact that CoFe2O4 and Co3O4 phases were detected in the XRD pattern [Fig. 1(f)], the Co(70)–Fe2O3 sample includes the aggregation of CoFe2O4 and Co3O4 particles with a perimeter interface.

Cobalt oxide, iron oxide and cobalt-ferrite composite oxide show an $M_x$O–$M_x$O stretching band in a different wavenumber region (800–350 cm$^{-1}$),\textsuperscript{22} where $M_x$ and $M_y$ corresponds to the tetrahedral and octahedral positions, respectively. In order to confirm the formation of cobalt oxide in Co(50)–Fe2O3, FT-IR spectra of Co(x)–Fe2O3 samples were measured. As seen in Fig. 4(a), Fe2O3 gave a broad IR absorption band at 541 cm$^{-1}$ as well as a relatively sharp band at 472 cm$^{-1}$. These two bands can be attributed to vibrations of Fe–O functional groups in α-Fe2O3.\textsuperscript{22} This is in accordance with the results of XRD (Fig. 1). Two shoulder bands, assignable to γ-Fe2O3,\textsuperscript{22} were also detected.
NO to Fe$_2$O$_3$, followed by evacuation at room temperature, gave Fig. 5 were measured. As can be seen in similar IR spectrum to that for Fe$_2$O$_3$. A distinct IR band at 653 cm$^{-1}$ ascribed to the mononitrosyl species adsorbed on Fe$^{2+}$ sites was detected [Fig. 5(b)]. However, a slight shift of the IR band to a higher wavenumber was observed. This is probably because Fe$^{2+}$ sites have fewer electrons available for back-donation to the adsorbed NO by the interaction with Fe species. Similar CO oxidation activity of Fe$_2$O$_3$ and Co(10$\%$)-Fe$_2$O$_3$ (Fig. 2) would be related to the similar surface valence state of Fe species.

When the Co content was increased to 30 atm $\%$ [Co(30$\%$)-Fe$_2$O$_3$], quite different IR spectrum was observed. A weak IR band at 1773 cm$^{-1}$ as well as a shoulder band at 1839 cm$^{-1}$ were detected [Fig. 5(c)]. The latter band is in good agreement with the IR band observed as NO, which was exposed to Co$_3$O$_4$ [Fig. 5(f)]. According to the literature, the IR band at 1851 cm$^{-1}$ detected for Co$_3$O$_4$ can be assigned to the mononitrosyl species adsorbed on Co$^{2+}$ sites. Taking into account the fact that a single phase of CoFe$_2$O$_4$ is formed in Co(30$\%$)-Fe$_2$O$_3$ [Fig. 1(c)], the IR bands at 1839 and 1773 cm$^{-1}$ would be assigned to the mononitrosyl species adsorbed on Co$^{2+}$ sites and Fe$^{2+}$ sites, respectively, in CoFe$_2$O$_4$ phase. The IR bands at 1649 and 1571 cm$^{-1}$ may be due to the nitrite species adsorbed on basic sites of Co(30$\%$)-Fe$_2$O$_3$. The presence of Co$^{2+}$ species on the surface would be responsible for the higher CO oxidation activity of Co(30$\%$)-Fe$_2$O$_3$, compared with that of Co(10$\%$)-Fe$_2$O$_3$ (Fig. 2).

As can be seen in Figs. 5(d) and 5(e), the exposure of NO to Co(30$\%$)-Fe$_2$O$_3$ with higher Co content gave rise to different IR spectra from those of Co(30$\%$)-Fe$_2$O$_3$ with lower Co content, where two distinct IR bands at 1849 and 1787 cm$^{-1}$ were observed. In accordance with the case of Co(30$\%$)-Fe$_2$O$_3$, the former IR band is ascribed to the mononitrosyl species adsorbed on Co$^{2+}$ sites. On the other hand, the assignment of the latter IR band is not simple. The wavenumber for the latter band is in good agreement with that for the band due to the mononitrosyl species adsorbed on Co$^{2+}$ sites and Fe$^{2+}$ sites. However, the content of Fe$_2$O$_3$ in Co(50$\%$)-Fe$_2$O$_3$ and Co(70$\%$)-Fe$_2$O$_3$ is less than half of Fe$_2$O$_3$ itself. In addition, the BET surface area of the former two samples is smaller than that of Fe$_2$O$_3$ (Table 1). If the 1787 cm$^{-1}$ band is due to the mononitrosyl species adsorbed on Fe$^{2+}$ sites, its band intensity at 635 and 445 cm$^{-1}$, suggesting the presence of Fe$_2$O$_3$ nanoparticles, which cannot be detected by XRD. Co(30$\%$)-Fe$_2$O$_3$ showed a distinct IR band at 589 cm$^{-1}$ [Fig. 4(b)]. According to the literature, CoFe$_2$O$_4$ gives IR bands at 590 and 385 cm$^{-1}$. Although the 385 cm$^{-1}$ band could not be detected in the present study because of the use of a KBr beam splitter, the appearance of the IR band at 589 cm$^{-1}$ clearly indicates the formation of Fe$_2$O$_3$. As revealed by XRD. Co(50$\%$)-Fe$_2$O$_3$ [Fig. 4(c)] gave a very similar IR spectrum to that of Co(30$\%$)-Fe$_2$O$_3$, suggesting that Co(50$\%$)-Fe$_2$O$_3$ mainly consists of Fe$_2$O$_3$. However, as seen in Fig. 4(c), a shoulder IR band at 653 cm$^{-1}$ was observed. Li et al. measured the IR spectra of various cobalt oxides, and found that CoO gives IR bands at around 650 and 550 cm$^{-1}$. Taking into account the fact that Co(50$\%$)-Fe$_2$O$_3$ includes an excess amount of Co species for the formation of CoFe$_2$O$_4$, the shoulder IR band at 653 cm$^{-1}$ would be due to the presence of Co$^{2+}$ species unreacted with Fe$_2$O$_3$. As seen in Fig. 4(d), the IR spectrum of Co(70$\%$)-Fe$_2$O$_3$ is very similar to that of Co$_3$O$_4$, indicating the presence of Co$_3$O$_4$, although the band intensity for the former sample was lower than that for the latter one.

From the XRD, TEM and FT-IR measurements, the particle morphology of and the status of the cobalt and iron oxides in Fe$_2$O$_3$ particles. NO adsorption on Co(10$\%$)-Fe$_2$O$_3$ gave rise to a similar IR spectrum to that for Fe$_2$O$_3$. A distinct IR band at 1794 cm$^{-1}$ assignable to the mononitrosyl species adsorbed on Fe$^{2+}$ sites was detected [Fig. 5(b)]. However, a slight shift of the IR band to a higher wavenumber was observed. This is probably because Fe$^{2+}$ sites have fewer electrons available for back-donation to the adsorbed NO by the interaction with Co species. Similar CO oxidation activity of Fe$_2$O$_3$ and Co(10$\%$)-Fe$_2$O$_3$ (Fig. 2) would be related to the similar surface valence state of Fe species.

When the Co content was increased to 30 atm $\%$ [Co(30$\%$)-Fe$_2$O$_3$], quite different IR spectrum was observed. A weak IR band at 1773 cm$^{-1}$ as well as a shoulder band at 1839 cm$^{-1}$ were detected [Fig. 5(c)]. The latter band is in good agreement with the IR band observed as NO, which was exposed to Co$_3$O$_4$ [Fig. 5(f)]. According to the literature, the IR band at 1851 cm$^{-1}$ detected for Co$_3$O$_4$ can be assigned to the mononitrosyl species adsorbed on Co$^{2+}$ sites. Taking into account the fact that a single phase of CoFe$_2$O$_4$ is formed in Co(30$\%$)-Fe$_2$O$_3$ [Fig. 1(c)], the IR bands at 1839 and 1773 cm$^{-1}$ would be assigned to the mononitrosyl species adsorbed on Co$^{2+}$ sites and Fe$^{2+}$ sites, respectively, in CoFe$_2$O$_4$ phase. The IR bands at 1649 and 1571 cm$^{-1}$ may be due to the nitrite species adsorbed on basic sites of Co(30$\%$)-Fe$_2$O$_3$. The presence of Co$^{2+}$ species on the surface would be responsible for the higher CO oxidation activity of Co(30$\%$)-Fe$_2$O$_3$, compared with that of Co(10$\%$)-Fe$_2$O$_3$ (Fig. 2).

As can be seen in Figs. 5(d) and 5(e), the exposure of NO to Co(30$\%$)-Fe$_2$O$_3$ with higher Co content gave rise to different IR spectra from those of Co(30$\%$)-Fe$_2$O$_3$ with lower Co content, where two distinct IR bands at 1849 and 1787 cm$^{-1}$ were observed. In accordance with the case of Co(30$\%$)-Fe$_2$O$_3$, the former IR band is ascribed to the mononitrosyl species adsorbed on Co$^{2+}$ sites. On the other hand, the assignment of the latter IR band is not simple. The wavenumber for the latter band is in good agreement with that for the band due to the mononitrosyl species adsorbed on Co$^{2+}$ sites and Fe$^{2+}$ sites. However, the content of Fe$_2$O$_3$ in Co(50$\%$)-Fe$_2$O$_3$ and Co(70$\%$)-Fe$_2$O$_3$ is less than half of Fe$_2$O$_3$ itself. In addition, the BET surface area of the former two samples is smaller than that of Fe$_2$O$_3$ (Table 1). If the 1787 cm$^{-1}$ band is due to the mononitrosyl species adsorbed on Fe$^{2+}$ sites, its band intensity...
should be lower than that for Fe₂O₃. Therefore, this assignment would be ruled out. Topsøe et al. observed two IR bands at 1860 and 1796 cm⁻¹ when NO was adsorbed on Co₃O₄ and assigned the latter band to the asymmetric N=O stretching vibration [ν(N=O)] mode of the dinitrosyl species adsorbed on Co²⁺ sites. Therefore, the IR band at 1787 cm⁻¹ observed in this study (Fig. 5) can be ascribed to the overlapping peak due to ν(N=O) of the dinitrosyl species adsorbed on Co²⁺ sites and the mononitrosyl species adsorbed on Fe²⁺ sites. Topsøe et al. also observed that the relative intensity of the 1796 cm⁻¹ band toward that of the 1860 cm⁻¹ band clearly increased with decreasing Co content. Since the IR spectrum observed for 2% Co/Al₂O₃ was very similar to that for CoAl₂O₄, they explained the relatively strong intensity of the 1796 cm⁻¹ band by the NO adsorption on quasi-tetrahedrally coordinated Co²⁺ sites. As can be seen in Fig. 5, the relative intensity of the 1787 cm⁻¹ band for Co(50)–Fe₂O₃ is stronger than that for Co(70)–Fe₂O₃. Therefore, Co(50)–Fe₂O₃ is suspected to include relatively more quasi-tetrahedrally coordinated Co²⁺ sites on the surface. Since no XRD peaks due to Co₂O₃ were detected for Co(50)–Fe₂O₃ (Fig. 1(e)), the remaining Co²⁺ species, which were not substituted with Fe²⁺ sites to form CoFe₂O₄, were highly dispersed on the catalyst surface. In the case of Co(70)–Fe₂O₃, the presence of Co²⁺ species in Co₂O₃ particles because of the quite high Co content. The presence of quasi-tetrahedrally coordinated Co²⁺ sites would be responsible for the high CO oxidation activity of Co(50)–Fe₂O₃ (Fig. 2).

Since the participation of surface and lattice oxygen in CO oxidation over metal oxide catalysts was proposed, the reactivity of oxygen species in Co(x)–Fe₂O₃ composite oxides was evaluated by H₂–TPR. Figure 6(A) shows the H₂–TPR profiles of Co(x)–Fe₂O₃ samples in a wide temperature range. Fe₂O₃ gave a strong H₂ consumption peak at 329°C, which is ascribed to the reduction of Fe₂O₃ to FeO. Co₁₀(10)–Fe₂O₃ gave a similar H₂–TPR profile to that of Fe₂O₃, indicating that Co₁₀(10)–Fe₂O₃ mainly consists of Fe₂O₃. Since no XRD peaks due to Fe₂O₃ were observed (Fig. 1(b)), Fe₂O₃ nanoparticles are suspected to be deposited on the surface of CoFe₂O₄ particles. This is in agreement with the results of IR spectra for NO adspecies (Fig. 5). As can be seen in Fig. 6(A-c), a distinct H₂ consumption peak was not observed in the H₂–TPR profile of Co(30)–Fe₂O₃, suggesting a slow reduction of CoFe₂O₄ at the temperatures below 500°C. The H₂–TPR profiles of Co(50)–Fe₂O₃ and Co(70)–Fe₂O₃ with higher Co content were found to be very similar to that of Co₂O₃. Since H₂ consumption peaks became stronger with increasing Co content, Co(70)–Fe₂O₃ consists of a relatively large amount of Co₃O₄ particles deposited on the surface of CoAl₂O₄.

FT-IR spectroscopy following NO adsorption revealed that the surface valence state of Co(x)–Fe₂O₃ is different depending on the Co content, leading us to the consideration that the reactivity of oxygen species in the lower temperature region must be different. Figure 6(B) shows the H₂–TPR profiles extended in the low temperature region. Co(10)–Fe₂O₃ did not show any peaks at temperatures below 150°C. In accordance with the light-off curve for CO oxidation (Fig. 2), Co(10)–Fe₂O₃ can effectively catalyze CO oxidation at temperatures above 150°C. It is of interest that the H₂ consumption of Co(30)–Fe₂O₃, Co(50)–Fe₂O₃ and Co(70)–Fe₂O₃ was initiated from 70°C, indicating the presence of highly active oxygen species. Among them, the amount of H₂ consumption from Co(30)–Fe₂O₃ was the smallest, while the largest amount of H₂ consumption was observed for Co(50)–Fe₂O₃. This is in agreement with the order of CO oxidation activity: Co(30)–Fe₂O₃ < Co(70)–Fe₂O₃ < Co(50)–Fe₂O₃. The oxygen species, which mainly present on the surface of Fe₂O₃, would participate in the CO oxidation reaction. A relatively large amount of active oxygen species on the surface of Co(50)–Fe₂O₃ would be related to the presence of quasi-tetrahedrally coordinated Co²⁺ sites.

4. Conclusions

Co–Fe₂O₃ composite oxides with different Co content were prepared using the hydrothermal method. XRD revealed the formation of a single phase of CoFe₂O₄ for Co(x)–Fe₂O₃ composite oxides with x = 10–50 at%. The presence of two phases of CoFe₂O₄ and Co₃O₄ was recognized for Co(70)–Fe₂O₃ with higher Co content. From TEM observation, the Co(70)–Fe₂O₃ sample was found to include the aggregation of CoFe₂O₄ and Co₃O₄ particles with a perimeter interface. On the other hand, FT-IR absorption spectra of the Co–Fe₂O₃ composite oxides suggested that Co species, which were not substituted with Fe sites, are highly dispersed in the Co(50)–Fe₂O₃ sample. The highest CO oxidation activity was achieved when 50 at% Co was added to Fe₂O₃. CO conversion on Co(50)–Fe₂O₃ was as high as 57% at room temperature. FT-IR spectroscopy following NO adsorption revealed that the surface valence state of Co(x)–Fe₂O₃ surface is different depending on the Co content. No significant difference in the surface valence state of Fe species was observed for Fe₂O₃ and Co(10)–Fe₂O₃ with a low Co content. On the other hand, Co²⁺ sites are predominantly exposed on the surface of Co–Fe₂O₃ with a higher Co content. It is of interest that Co(50)–Fe₂O₃ includes a relatively high amount of quasi-tetrahedrally coordinated Co²⁺ sites on the surface, while Co(70)–Fe₂O₃ includes mainly octahedrally coordinated Co²⁺ sites. H₂–TPR measurements revealed that the reactivity of oxygen species in the lower temperature region is different depending on the Co content. H₂ consumption of Co(30)–Fe₂O₃, Co(50)–Fe₂O₃ and Co(70)–Fe₂O₃ was found to initiate from 70°C, indicating the presence of highly active oxygen species. Among them, Co(50)–Fe₂O₃ had the highest H₂ consumption. We concluded that the surface oxygen species of which the formation is related to the presence of quasi-tetrahedrally coordinated Co²⁺ sites can participate in the CO oxidation reaction on Co–Fe₂O₃.


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