Enhancement of NO-elimination activity of Co-silicate catalyst by high-temperature calcination in steam-containing air

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H–Co-silicate having an MFI structure (CoMFI), calcined in steam-containing air at 800 °C (CoMFI-800S), was characterized by XRD and diffuse reflectance electron absorption (EA). The calcination educed some of the Co ions from the CoMFI framework to make small clusters nearby. The CoMFI-800S performance in NO elimination in the presence of excess O_2 was compared with that of Co supported on siliceous MFI zeolite ([Co]SiMFI), Co supported on H–Co-silicate ([Co]CoMFI), and a physical mixture of CoMFI and [Co]SiMFI (Co + [Co]). The educed Co ions enhanced NO elimination due to the uniform and isolated dispersion of oxidized Co clusters.

Keywords: Co-silicate, high-temperature calcination, steam, supported Co catalyst, non-framework Co, NO elimination

1. Introduction

Several years ago, it was found that NO could be reduced to N_2 on a catalyst by the addition of a low concentration of an appropriate hydrocarbon or methanol, even in the presence of O_2 [1–3]. Although numerous studies have since been carried out, catalyst durability is insufficient at high temperatures, especially in the presence of steam.

Copper-ion-exchanged H-ZSM-5 (Cu/H-ZSM-5) is well known as a highly active catalyst for the de-NOx reaction under excess-O_2 conditions [4,5]; however, as is often pointed out, this catalyst easily deteriorates under practical reaction conditions [6–8].

In contrast, Armor et al. [9] reported that the activity of Co-ion-exchanged H-ZSM-5 (Co/H-ZSM-5) is stable, but the reason for this stability has not been elucidated. Our previous studies [10–12] emphasized that the thermal stability of a protonated Cu-silicate having an MFI structure (CuMFI) was apparently higher than that of Cu/H-ZSM-5, although the activity of the former was lower than that of the latter. Unique and excellent performance of protonated Co-incorporated silicate having an MFI structure (CoMFI) has also been reported as the most appropriate catalyst for eliminating NO at around 400 °C in the presence of easily combustible hydrocarbons such as propylene, n-octane (n-C_8H_{18}), and cetane (n-$C_{16}H_{34}$) [10,13]. It is also worth noting that the performance of the catalyst in the elimination of NO is not suppressed in the presence of water vapor up to 10 vol% or SO_2 up to 200 ppm [14]. High-temperature calcination of CoMFI in air flow with or without steam did not decrease its BET surface area or the NO-elimination performance, while the same treatment of metal-ion-exchanged H-ZSM-5 and other metallosilicates having an MFI structure significantly decreased the surface area and catalytic performance [15]. Moreover, when CoMFI was treated carefully at 800 °C in a 10 vol% steam-containing air flow, its catalytic activity for NO elimination was rather enhanced [16].

In this paper, to elucidate the reason for the enhanced catalytic activity of CoMFI by calcination, CoMFI and various Co-containing catalysts were characterized by X-ray powder diffraction (XRD) and diffuse reflectance electron absorption spectroscopy (EA). The performances of these catalysts in NO elimination reaction were compared and the role of the Co species educed from the CoMFI framework by calcination was discussed.

2. Experimental

2.1. Catalyst preparation

Co-silicate was prepared by the rapid crystallization method [17]. The charged Si/Co atomic ratio of Co-silicate was adjusted to 40. As-synthesized crystals, washed, dried, and heated at 540 °C for 3.5 h in air to remove the organic template, were then ion-exchanged twice with 1 N NH_4NO_3 aqueous solution at 80 °C for 1 h, while being stirred with a magnetic stirrer, washed, and dried, followed by heating again at 540 °C for 3.5 h in air to convert the ammonium form to the protonated form. They were then tabletted, crushed, and sieved by 12–24 mesh. The Co content in this catalyst was 0.4 wt%.

CoMFI was heated at a constant rate of 2.5 $^{\circ}C\,min^{-1}$ up to 800 °C, and this temperature was maintained for 2 h in a stream of air containing 10 vol% of steam. This catalyst is designated CoMFI-800S.

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Siliceous MFI zeolite was also prepared by the same rapid crystallization method, and calcined at 540 °C for 3.5 h in air to remove template. This is designated SiMFI. By an incipient impregnation method using $Co(NO_3)_2$, 0.50 wt% Co was supported on SiMFI. This catalyst, designated [Co]SiMFI, was used as a reference catalyst containing only cobalt-oxide clusters on the surface of MFI crystals.

A physical mixture of CoMFI and [Co]SiMFI with a weight ratio of 5 to 1 was prepared, and is designated Co + [Co], containing both Co ions in the framework sites and cobalt-oxide clusters on the surface of MFI crystals.

By the incipient impregnation method, 0.08 wt% Co was supported on CoMFI. This catalyst is designated [Co]CoMFI, also containing two types of Co species; however, in this catalyst, the distance between Co ions in the framework sites and cobalt-oxide clusters, however, is shorter than in Co + [Co].

2.2. Characterization

The metal content was analyzed on an atomic emission spectrometer with inductively coupled plasma source (ICP; Shimadzu ICPS-1000 III). The BET surface area was measured on a Shimadzu Flow Sorb II 2300 sorptograph. The XRD patterns were recorded on an X-ray diffractometer, Shimadzu XD-D1, using Cu Kα radiation and a carbon monochromator. The EA spectra were recorded on a Shimadzu MPS-2000 spectrometer equipped with a multipurpose reflectometry attachment, RTA-2000, with reflected beams gathered by an integrating sphere of 50 mm inner diameter, with $BaSO_4$ as a reflectance standard. To examine the effect of exposure to ammonia on EA spectra, the samples were previously exposed to the saturated vapor of 28 wt% aqueous ammonia solution at 60 °C for 10 min.

2.3. Reaction

Performance in the elimination of NO was examined using an ordinary flow-type reactor under atmospheric pressure, by lowering temperature from 600 to 200 °C. The reaction gas, composed of 1,000 ppm NO, 1,000 ppm n-C_8H_{18}, and 10.0% O_2 with N_2 balance gas, was allowed to flow at a space velocity (SV) of 30,000 h^{-1}. Reaction gas and products were analyzed by a chemiluminescence NOx analyzer Shimadzu NOA-305A for NO, an infrared gas analyzer Shimadzu CGT-7000 for CO and CO_2 and a gas chromatograph Shimadzu GC-8A, with MS-5A and Porapack Q columns equipped with integrators, for other products.

3. Results and discussion

3.1. Environment of Co in catalyst

As shown in figure 1, the calcination of CoMFI in steam-containing air flow at 800 °C did not alter the XRD pattern, and the calcined sample (CoMFI-800S) had a BET-surface area similar to that of CoMFI [16]. These results indicate that the MFI structure was not destroyed by this treatment.

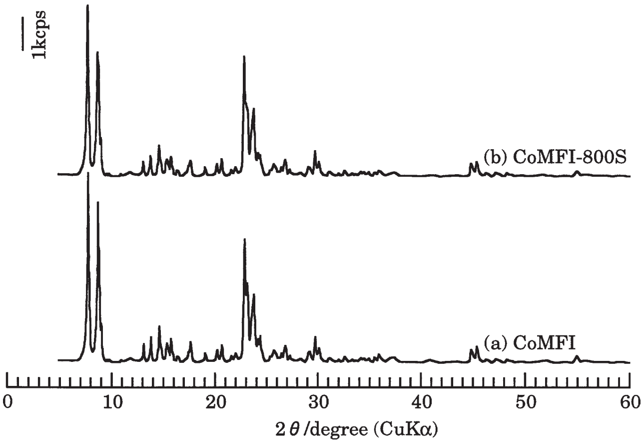

Figure 1. Effect of high-temperature calcination in steam-containing air on X-ray powder diffraction patterns of H–Co-silicates calcined under different conditions. (a) H–Co-silicate calcined at 540 °C for 3.5 h in air (CoMFI); (b) H–Co-silicate calcined at 800 °C for 2 h in 10% steam-containing air (CoMFI-800S).

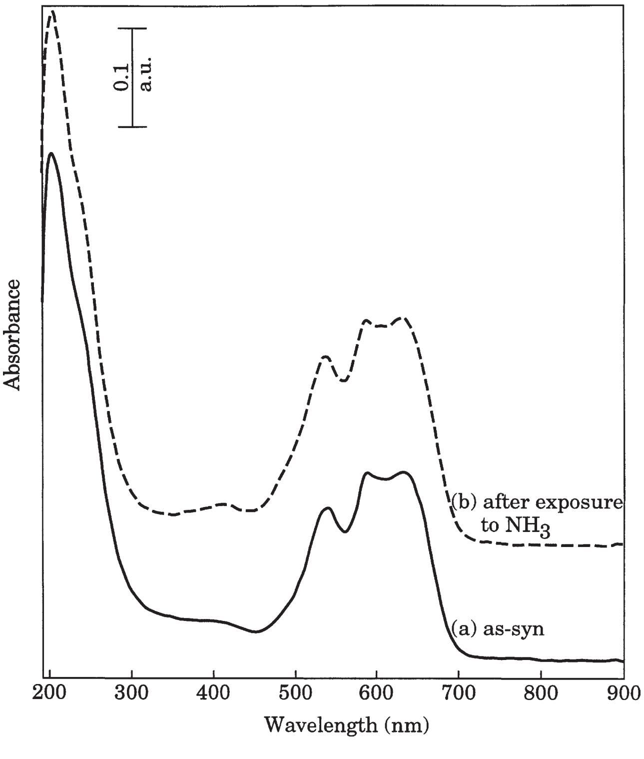

Figure 2. EA spectra for as-synthesized Co-silicate before (a) and after (b) exposure to the ammonia vapor.

Czarnetzki et al. [18] reported that framework and non-framework Co in CoAPO molecular sieves could be monitored by EA spectra. To investigate the environment of Co in CoMFI, EA spectra were measured. As shown in figure 2, as-synthesized Co-silicate has three intense absorption bands between 500 and 650 nm and a weak band around 400 nm. The former bands are assigned to the typical high-spin (d^7) Co(II) species in a tetrahedral crystal

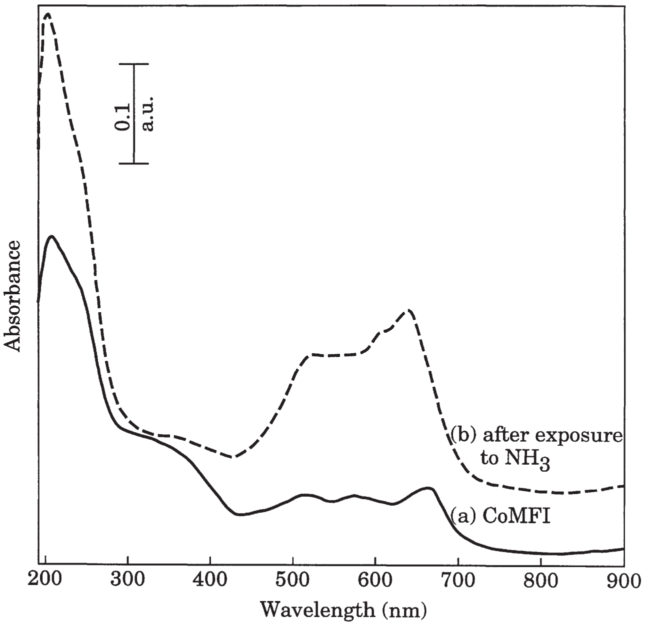

Figure 3. EA spectra for H–Co-silicate calcined at 540 °C for 3.5 h in air (CoMFI) before (a) and after (b) exposure to the ammonia vapor.

field [19], the latter band to high-spin Co(III) [20] in a tetrahedral crystal field. The EA spectrum of the as-synthesized Co-silicate was not altered by exposure to ammonia vapor, because the pore channels of the as-synthesized crystals are filled up with the organic template molecules and bound water molecules, making the Co ions in the framework sites inaccessible to the ammonia molecules.

The EA spectrum for CoMFI, shown in figure 3, differs from that for as-synthesized Co-silicate. The intensities of absorption bands between 500 and 650 nm due to the tetrahedral Co(II) decreased considerably, whereas the intensity of the absorption band around 350 nm due to the tetrahedral Co(III) slightly increased [21]. During the two calcination processes and the ion-exchange treatment, a major portion of tetrahedral Co(II) was removed from the framework site, and Co(II) was partly oxidized to Co(III). Oxidation of Co(II) species into Co(III) species during the calcination for CoAPSO-34 and CoAPO-34 was previously reported by Iton et al. [20].

Ballhausen et al. [22] reported that the EA spectra of Co(II) species, coordinated with H_2O, were intensified by substituting H_2O for NH_3. The EA spectrum of CoMFI after exposure to ammonia vapor is also shown in figure 3. The absorption bands due to the tetrahedral Co(II) significantly increased. Through the removal of the organic template, micropores are generated and ammonia molecules can migrate in the pore channels and coordinate with the tetrahedral Co(II) located in the framework.

Figure 4 shows EA spectra for CoMFI-800S before/after exposure to ammonia vapor. After calcination, absorption bands between 500 and 650 nm due to the tetrahedral Co(II) become flat and featureless, while the absorption band around 350 nm due to the tetrahedral Co(III) is broad. These flat absorption bands are due to the charge transfer between Co(II) and Co(III); this result suggests the formation of Co_3O_4. A considerable portion of the Co(II) located in the framework sites is educed from the framework, yielding clusters of cobalt oxide. After ammonia vapor treatment, the spectra due to the tetrahedral Co(II) appear, indicating that a small amount of Co(II) is still incorporated in the MFI structure with tetrahedral coordination even after calcination at 800 °C.

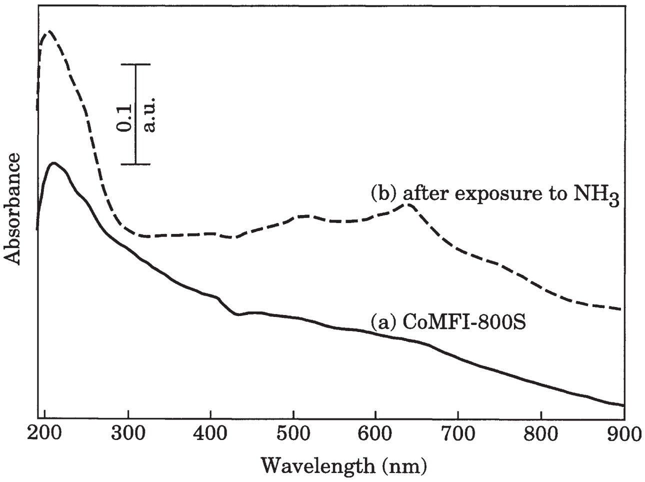

Figure 4. EA spectra for H–Co-silicate calcined at 800 °C for 2 h in 10 vol% steam-containing air (CoMFI-800S) before (a) and after (b) exposure to the ammonia vapor.

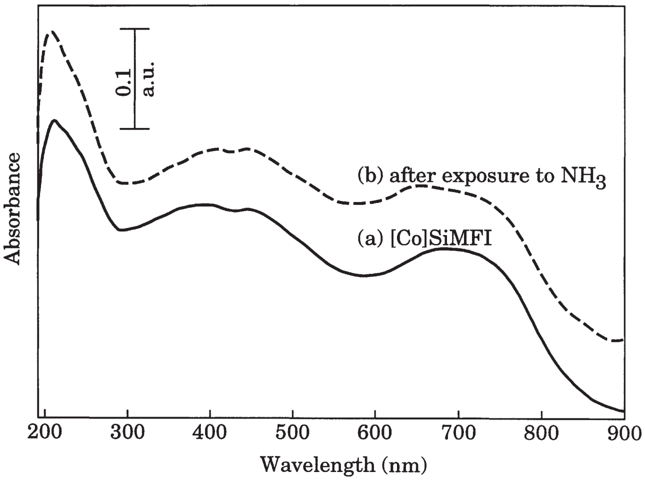

Figure 5. EA spectra for Co-supported siliceous MFI zeolite ([Co]SiMFI) before (a) and after (b) exposure to the ammonia vapor.

To elucidate the environment of Co in CoMFI-800S, EA spectra for the three reference catalysts ([Co]SiMFI, Co + [Co], and [Co]CoMFI) were measured before and after exposure to ammonia vapor; they are shown in figures 5–7, respectively. The [Co]SiMFI was gray, and its EA spectra did not change before or after exposure to the ammonia vapor, as shown in figure 5, indicating that the Co in [Co]SiMFI is easily oxidized to cobalt-oxide clusters [18]. In figures 6 and 7, though all absorption bands become flat, they have tetrahedral Co(II) and Co(III). EA spectra for Co + [Co] and [Co]CoMFI are similar to that for

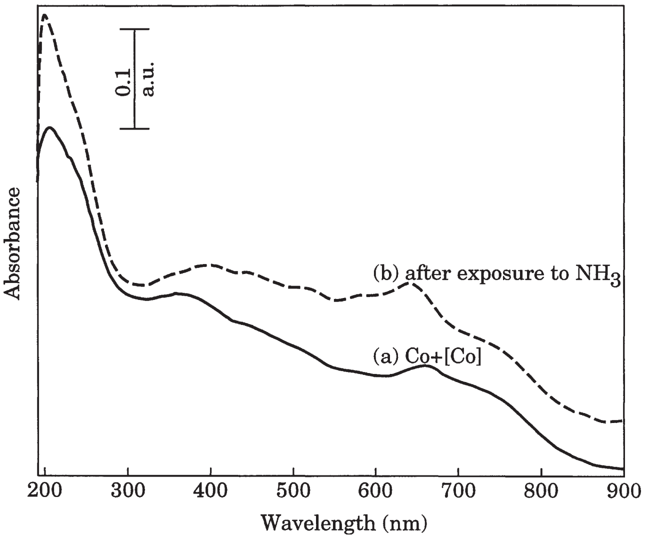

Figure 6. EA spectra for a mixture of CoMFI and [Co]SiMFI (Co + [Co]) before (a) and after (b) exposure to the ammonia vapor.

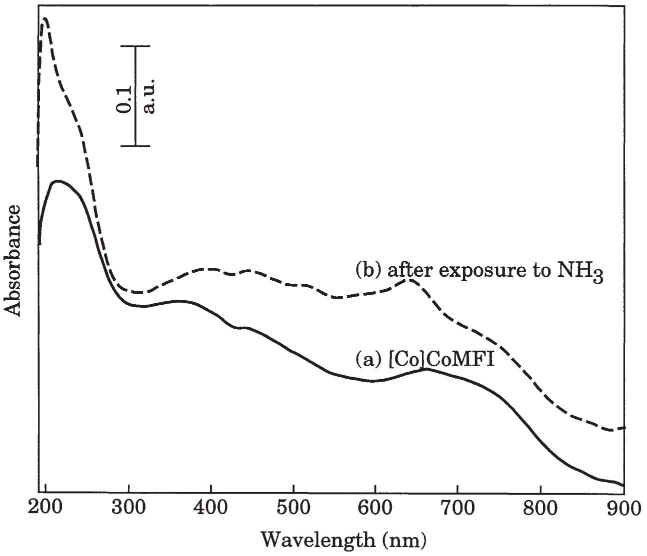

Figure 7. EA spectra for Co-supported H–Co-silicate ([Co]CoMFI) before (a) and after (b) exposure to the ammonia vapor.

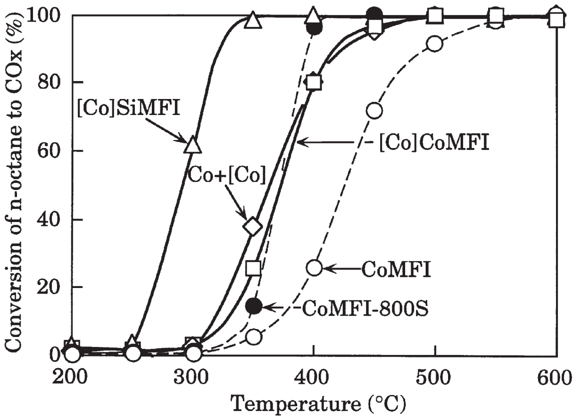

Figure 8. Effect of reaction temperature on the conversion of n-octane to COx on various Co-involving catalysts. (△) Co-supported siliceous MFI zeolite ([Co]SiMFI), (◇) physical mixture of CoMFI and [Co]SiMFI (Co + [Co]), (□) Co-supported H–Co-silicate ([Co]CoMFI), (○) H–Co-silicate (CoMFI), (●) H–Co-silicate calcined at 800 °C for 2 h in 10 vol% steam-containing air (CoMFI-800S). Feed gas: NO 1,000 ppm, n-octane 1,000 ppm, O_2 10.0%, N_2 balance, SV 30,000 h^{-1}.

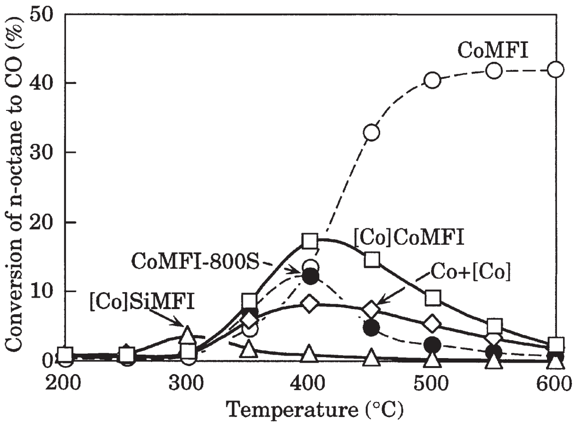

Figure 9. Effect of reaction temperature on the conversion of n-octane to CO on various Co-involving catalysts. Captions are the same as those shown in figure 8.

CoMFI-800S, shown in figure 4. This means that CoMFI-800S includes tetrahedral Co(II) and tetrahedral Co(III) in the framework and cobalt-oxides clusters.

3.2. Performance of Co-containing catalysts

To investigate the catalytic properties of Co species in various Co-containing catalysts, NO-elimination reaction was carried out on these catalysts in the presence of n-octane. The conversion of n-octane to COx and to CO, and that of NO to N_2 are shown in figures 8–10, respectively. As shown in figure 8, the n-octane combustion activity of CoMFI with tetrahedral Co(II) was the lowest among the catalysts tested, while the activity of [Co]SiMFI with cobalt-oxide clusters was the highest. The combustion activities of Co + [Co], [Co]CoMFI, and CoMFI-800S, having both framework tetrahedral Co(II) and cobalt-oxide clusters, are between those of [Co]SiMFI and CoMFI. This indicates that cobalt-oxide clusters have high activity, and tetrahedral Co has mild activity for n-octane combustion. Therefore, CO is formed on CoMFI with tetrahedral Co(II), even above 400 °C, in significantly larger amounts than on cobalt-oxide-containing catalyst, as shown in figure 9, while CO_2 is formed on cobalt-oxide-containing catalysts. Reflecting this property, the conversion of NO to N_2 and of n-octane on CoMFI increases with increase of temperature to 450 °C. Even above 450 °C, the conversion of NO on CoMFI is still high. The window of temperature, at which the conversion of n-octane is between 80 and 95%, is ca. 140 °C for CoMFI and only 20 °C for CoMFI-800S.

However, the maximum conversion of NO on CoMFI-800S is higher than that of CoMFI, as shown in figure 10 and table 1, and CoMFI-800S is active especially at lower temperature. To elucidate the reason for this high catalytic activity of CoMFI-800S, the reference catalyst, [Co]SiMFI

Table 1
The catalytic performance of n-octane combustion and maximum conversion of NO on various catalysts involving Co.

Catalyst		Temperature (°C) at which the conversion of n-octane to COx became >0, 50 and 100%	Maximum conversion of NO (%) (at the corresponding temperature (°C))
CoMFI	H–Co-silicate	300, 426, 600	32 (450)
CoMFI-800S	Calcined CoMFI	300, 371, 450	40 (375)
[Co]SiMFI	Co-supported siliceous MFI zeolite	250, 292, 400	13 (300)
Co + [Co]	Physycal mixture of CoMFI and [Co]SiMFI	300, 364, 500	22 (360)
[Co]CoMFI	Co-supported CoMFI	300, 373, 500	28 (375)

NO 1,000 ppm, n-octane 1,000 ppm, O_2 10.0%, N_2 balance, SV 30,000 h^{-1}.

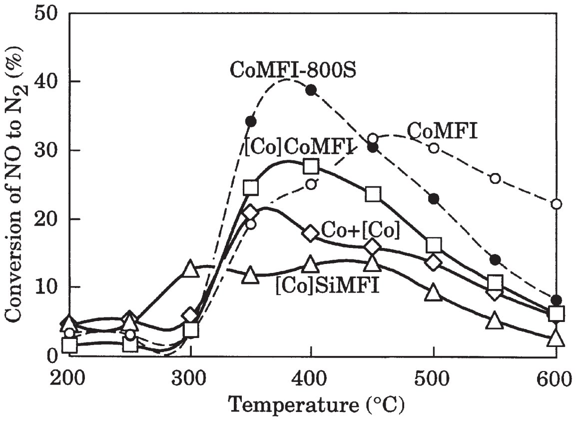

Figure 10. Effect of temperature on the conversion of NO to N_2 on various Co-involving catalysts. Captions are the same as those shown in figure 8.

with cobalt-oxide clusters, was used for the conversion of NO. As expected, the activity of [Co]SiMFI for n-octane combustion is high, and n-octane is converted to CO_2 above the lowest temperature; however, NO conversion did not exceed 13% and decreased above 450 °C. [Co]SiMFI was mixed with CoMFI at a ratio of 1 to 5, and a prescribed amount of Co (0.08 wt%) was loaded on CoMFI. They were used as catalyst for the elimination of NO for comparison with CoMFI-800S. As shown in figure 7 and table 1, the temperature dependence of the conversion of n-octane on CoMFI-800S was similar to those on both Co + [Co] and [Co]CoMFI. The conversion of NO to N_2 on CoMFI-800S was greater than on either Co + [Co] or [Co]CoMFI. CoMFI-800S, Co + [Co] and [Co]CoMFI are expected to have cobalt-oxide clusters and tetrahedral Co(II), the distance between cobalt-oxide clusters and tetrahedral Co(II) being as follows:

$$\text{Co} + [\text{Co}] > [\text{Co}]\text{CoMFI} > \text{CoMFI-800S}.$$

Since cobalt-oxide clusters are the active site for n-octane combustion, and tetrahedral Co(II) is the active site for NO decomposition, the distance between cobalt-oxide clusters and tetrahedral Co(II) is the important factor. CoMFI-800S is the most suitable because cobalt-oxide clusters exist close to tetrahedral Co(II).

All of those results indicate that the effect of high-temperature calcination on CoMFI-800S is ascribed to the activity of the educed cobalt-oxide clusters, in addition to the intrinsic activity attributable to the Co incorporated into the framework. It is, therefore, concluded in light of the proposed mechanism [13,23,24] that a small amount of educed Co enhances the combustion activity to a sufficient extent, and contributes to the decomposition of NO.

4. Conclusions

The environment of Co contained in H–Co-silicate was clarified by EA spectra for Co-silicates and three kinds of reference catalysts containing framework and/or non-framework Co. Both tetrahedral Co(II) and Co(III) in the framework and highly dispersed and isolated cobalt-oxide clusters are present in H–Co-silicate calcined with steam. The catalytic activity of NO-elimination reaction was improved by enhancing n-octane combustion on Co components educed from the framework of H–Co-silicate by the calcination. This enhancement was ascribed to the combustion activity of the cobalt-oxide clusters educed from the framework of CoMFI by calcination.

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