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Direct decomposition of nitrogen monoxide over Cu-MFI containing rare-earth elements: Sm and Gd as promoter

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Abstract

The decomposition activities of nitrogen monoxide (NO) were investigated for the copper ion-exchanged ZSM-5 zeolites (Cu-MFI) containing the rare-earth elements: La, Ce, Pr, Nd, Sm, and Gd. It was found that Sm and Gd acted as promoter for NO decomposition over Cu-MFI with 60–70% of the exchange level of copper ion, while the addition of the other rare-earth elements to Cu-MFI showed no positive effect on NO decomposition activity. The introduction of Sm and Gd to Cu-MFI had little influence on the effectiveness of each copper ion for NO adsorption in the MFI zeolite. The presence of Sm and Gd stabilized Cu^+ as an active center.

Keywords: Cu-ZSM-5; NO decomposition; Rare-earth metal; Samarium; Gadolinium; Temperature-programmed reduction

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1. Introduction

The removal of NO is one of the important subjects among the global environmental problems. Two catalytic systems are commercially available; one is noble metal-based three-way catalysts for the purification of automobile emissions and the other is the vanadium catalysts for the control of stationary emissions by selective catalytic reduction with NH_3 [1]. Since the end of the last century, new catalytic technologies for emission control have been developed such as selective catalytic reduction with hydrocarbon and NOx storage-reduction [2]. On the other hand, the catalytic decomposition of NO is continuously studied because it is the most ideal reaction among the catalytic methods for removing NO from engine exhaust gases.

Iwamoto et al. [3,4] first demonstrated that Cu-MFI having $Cu^{2+}/Al > 0.5$, which has been called "overexchanged Cu-MFI", shows very high decomposition activity. Although the discovery of exceptionally high activity of the Cu-MFI zeolite for NO decomposition is undoubtedly a milestone in the field of catalytic deNOx technology, the activity of Cu-MFI is not yet sufficient in practice. The modification of Cu-MFI has been studied in order to achieve a higher performance in NO decomposition. Kagawa et al. [5] tested a large number of additives to enhance the activity of Cu-MFI. They found the important fact that the Cu-MFI zeolites containing Ba, Sr, Co, Ni, or Pt show roughly the same activity as overexchanged Cu-MFI, although the Cu ion-exchange level of the former Cu-MFI was more than 50% lower than that of the latter one. This suggests that the number of active sites or the turnover frequencies of active site can be controlled by the addition of metal ions. Following the same line, the effects of rare-earth elements on the activity of Cu-MFI were investigated. Zhang and Flytzani-Stephanopoulos [6] reported that cerium addition to Cu-MFI promotes the activity for the NO decomposition in wet gas streams in the range 673–873 K. Pârvulescu et al. [7,8] have vigorously studied the influence of samarium addition on the decomposition activity of Cu-MFI.

The first aim of the present study was to investigate systematically the effect of the introduction of rare-earth elements: La, Ce, Pr, Nd, Sm, and Gd, on the activity of Cu-MFI with copper content smaller than that corresponding to the exchange capacity. Influences on the activity of overexchanged Cu-MFI were not examined in the present study because the state of copper ion has been very complicated in overexchanged Cu-MFI. The second aim was to investigate how the rare-earth elements in Cu-MFI influence on the reduction behavior of copper ion.

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2. Experimental

Sodium ion-exchanged ZSM-5 zeolite (Na-MFI) with Si/Al = 11.9 was supplied from Tosoh Co. Cu-MFI zeolites containing rare-earth metal ions were prepared by the successive ion-exchange with an aqueous solution of rare-earth metal nitrate and then with an aqueous cupric acetate solution unless otherwise stated. The exchange levels of copper ion, rare-earth metal ion, and sodium ion were determined by the induced coupled plasma (ICP) method after the sample was dissolved in hydrofluoric acid solution. The exchange levels of metal ions were calculated by the assumption that the valences of copper ion, rare-earth metal ion, and sodium ion were +2, +3, and +1, respectively. Hereafter, the sample is abbreviated as Cu(x)Ln(y)Na(z)-MFI, where x, y, and z indicate the exchange levels of each metal ion.

The NO decomposition reaction was carried out in a conventional fixed-bed flow reactor as described elsewhere [4]. The zeolite catalyst (0.5 g) placed in the flow reactor made of quartz tube was activated at 773 K for 4 h under a He stream prior to the NO decomposition reaction. The reaction gas (2.18 vol.% of NO in He) was fed at a rare of 30 $cm^3\ min^{-1}$. The reaction temperature was increased stepwise from 573 to 973 K, and the reaction was carried out at each temperature until the conversion reached a constant value. The gas composition was analyzed by gas chromatography (Shimazu, GC-8AIT) using Molecular Sieve 5A column for detecting NO, N_2, and O_2. Although the formation of N_2O and NO_2 as by-products is expected in the effluent gas, we did not analyze them quantitatively because it was reported that N_2O was not formed above 673 K over Cu-MFI and NO_2 was formed both on the Cu-MFI and in the homogeneous phase through the reaction of NO and the O_2 that is produced [2,3]. Therefore, in the present study, the activity was evaluated by the conversion of NO into N_2 ($(2[N_2]_{out}/[NO]_{in}) \times 100$).

NO-TPD measurements were carried out to determine the amount of NO adsorbed on zeolite catalysts [9]. The TPD profiles were measured with the same apparatus as was used for the flow reaction. After the catalyst was activated at 773 K for 4 h in a He stream, the catalyst was cooled down to 303 K and then exposed to the gas containing NO (2.18 vol.% of NO in He) for 1 h. Subsequently, the gas was changed to pure helium with a rate of 30 $cm^3\ min^{-1}$ and the measurement started with a heating rate of 2 K min^{-1}. The amount of NO desorbed was analyzed by a gas chromatography.

The reduction behavior of copper ion exchanged into zeolite was investigated by H_2-TPR techniques. Prior to H_2-TPR measurement, the catalysts were activated at 773 K for 4 h in an Ar stream and then cooled down to 303 K. H_2-TPR was carried out by flowing 5 vol.% H_2/Ar (30 $cm^3\ min^{-1}$) in the temperature range 303–773 K. The sample temperature increased with a rate of 2 K min^{-1} and the amount of H_2 consumed was measured by a gas chromatograph.

3. Results and discussion

3.1. Activities of Cu(x)Ln(y)Na(z)-MFI catalysts

The effect of the order of the ion exchange procedures on the activity for NO decomposition was first investigated for samarium-containing Cu-MFI catalysts. Sm(6)Na(80)-MFI was inactive in NO decomposition, indicating that the copper ions are the active species. Fig. 1 shows the catalytic activities of samarium-containing Cu-MFI catalysts prepared by the different ion exchange procedures. Three types of ion-exchange methods were attempted to introduce samarium into Cu-MFI. As can be seen in Fig. 1, the decomposition activity of Cu(73)Sm(10)Na(11)-MFI prepared by the successive ion-exchange method with an aqueous solution of samarium nitrate and then with an aqueous cupric acetate solution was higher than that of Sm(5)Cu(71)Na(9)-MFI prepared in the reverse sequence.

The decomposition activity of Cu(63)Sm(29)Na(14)-MFI catalyst prepared by the simultaneous ion-exchange method with a mixed aqueous solution, reported by Pârvulescu et al. [7], is also shown in this figure. The decomposition activity of the Cu(63)Sm(29)Na(14)-MFI catalyst was a little lower than that of the Cu(73)Sm(10)Na(11)-MFI catalyst. However, considering that the copper content in Cu(63)Sm(29)Na(14)-MFI was lower than that of the Cu(73)Sm(10)Na(11)-MFI, the simultaneous ion-exchange may be effective for improving the catalytic activity. Since the catalysts prepared by two-step exchange, a first exchange with rare-earth elements followed by a second exchange with copper ion, showed the highest decomposition activity, here-in-after the Cu-MFI catalysts containing rare-earth elements were prepared by this two-step exchange.

The catalytic activities of the Cu(x)Ln(y)Na(z)-MFI are summarized in Table 1. As a reference, the activity of Cu(84)Na(14)-MFI with a comparable ion-exchange level of

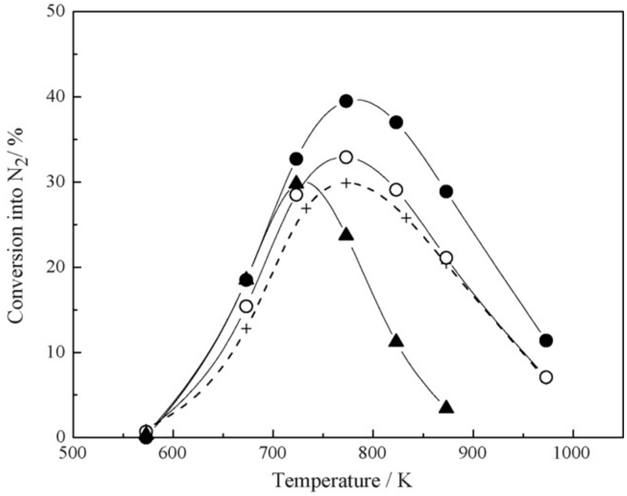

Fig. 1. Decomposition activity of the catalysts prepared by the different procedures. (●) Cu(73)Sm(10)Na(11)-MFI; (▲) Sm(5)Cu(71)Na(9)-MFI; (○) Cu(63)Sm(29)Na(14)-MFI; (+)Cu(73)Na(23)-MFI. NO = 2.18% and W/F = 2.0 g s cm^{-3}.

Table 1
NO decomposition activities over Cu(*x*)Ln(*y*)Na(*z*)-MFI catalysts

Catalyst	Conversion into N_2 (%)				
	573 K	673 K	773 K	873 K	973 K
Cu(84)Na(14)-MFI	1	20	47	37	13
Cu(85)La(10)Na(7)-MFI	1	19	46	40	19
Cu(73)Ce(13)Na(10)-MFI	1	24	46	34	10
Cu(83)Pr(9)Na(10)-MFI	1	22	47	40	16
Cu(82)Nd(8)Na(6)-MFI	1	22	44	30	10
Cu(84)Sm(7)Na(8)-MFI	0	25	53	42	21
Cu(85)Gd(10)Na(7)-MFI	1	23	51	43	22

copper ion is also shown in this table. No deterioration of the catalysts listed in Table 1 was observed even after 5 h of continuous service. Maximal activity was observed at 773 K for the Cu-MFI catalysts with and without rare-earth elements. It has been reported that the optimum temperature depends on the catalyst used and the partial pressure of NO in the feed [9]. Several reasons have been proposed for the temperature dependence, but the most important factor is likely the desorption temperature of the adsorbed/produced oxygen [9]. The fact that optimum temperature was independent on the kind of rare-earth elements introduced suggests that the rare-earth elements had little influence on the desorption ability of oxygen from the catalysts. Among the rare-earth elements tested in the present study, samarium and gadolinium promoted the decomposition activity of CuNa-MFI, although the catalysts were not exactly identical with respect to the exchange levels of copper- and rare-earth metal-ions. A similar result was reported by Pârvulescu et al. [7,8], who demonstrated that samarium promoted the activity of CuNa-MFI in NO decomposition. Hereafter, the CuNa-MFI catalysts with samarium and gadolinium were investigated in more detail.

Fig. 2 shows the temperature dependences of the catalytic activities of Cu(*x*)Sm(*y*)Na(*z*)-MFI and Cu(*x*)Gd(*y*)Na(*z*)-MFI catalysts. The catalytic activity increased with the increase in Cu ion-exchange level. The co-cation effect depended significantly on Cu ion-exchange level. Fig. 3 shows the specific activity of Cu(*x*)Sm(*y*)Na(*z*)-MFI and Cu(*x*)Gd(*y*)-Na(*z*)-MFI catalysts as a function of Cu ion-exchange level, where the specific activity was defined as the ratio of the activity of Cu(*x*)Ln(*y*)Na(*z*)-MFI to that of Cu(*x*)Na(*z*′)-MFI with the same Cu ion-exchange level. The specific activities increased with Cu ion-exchange level, reached a maximum around 60–70% of exchange level, and then decreased with further increase in the exchange level. In addition, as can be seen in Fig. 3, it was demonstrated that a strong co-cation effect enhancing the activity was significant at lower temperature. Kagawa et al. [5] reported that the co-cation effect disappeared above 723 K when alkaline metal ion, alkaline earth metal ion, and transition metal ion were used as co-cations.

3.2. NO-TPD measurement of Cu(x)Ln(y)Na(z)-MFI catalysts

It was reported that the number of copper ions accessible to a NO molecule can be estimated by means of NO-TPD measurement [9]. Fig. 4 shows NO-TPD profiles of Cu(84)Sm(7)Na(8)-MFI, Cu(85)Gd(10)Na(7)-MFI, and Cu(85)Na(15)-MFI catalysts. No desorption peak was observed on samarium- and gadolinium-exchanged MFI zeolites without copper ion, indicating that the NO adsorption is associated with copper ion. The NO-TPD profiles of the three catalysts were essentially the same for each sample with the overlapped peaks around 300–530 K and a small peak centered at 650 K. The desorption peaks observed at lower temperature result from the NO^+ species irreversively adsorbed on copper ion, while the small peak observed at higher temperature originates from the decomposition of nitrate, nitrite, or NO_2^+ because oxygen desorption was also observed at the same temperature [10]. Similar TPD profiles have been reported by Iwamoto et al. [9,10], Li and Armor [11], Eränen et al. [12], and Hierl et al. [13]

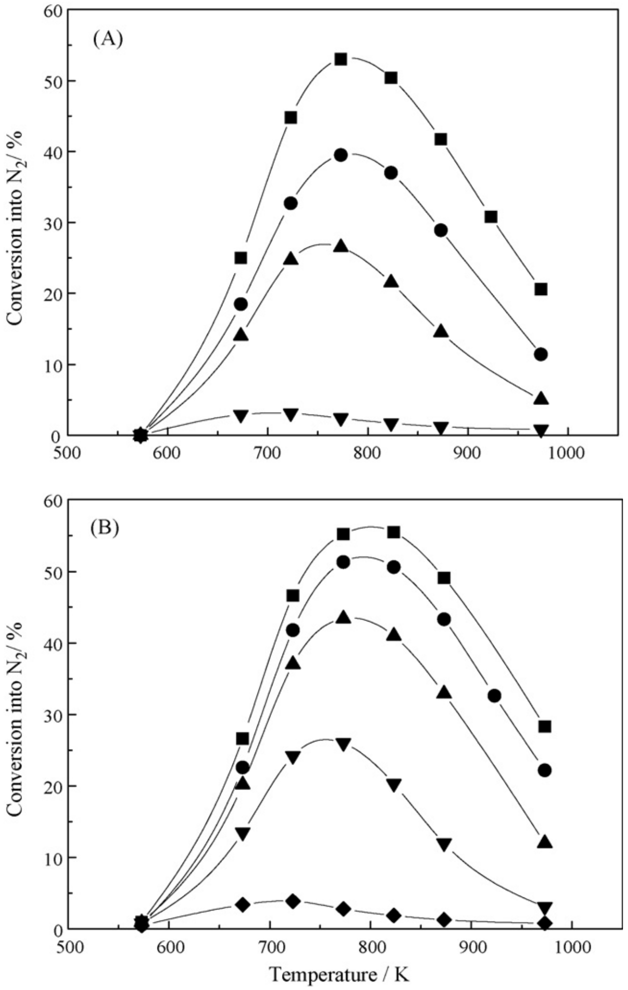

Fig. 2. NO decomposition activities of (A) Cu(*x*)Sm(*y*)Na(*z*)-MFI and (B) Cu(*x*)Gd(*y*)Na(*z*)-MFI catalysts. NO = 2.18% and W/F = 2.0 g s cm^{-3}. (A) (■) Cu(84)Sm(7)Na(8)-MFI, (●) Cu(73)Sm(10)Na(11)-MFI, (▲) Cu(56)Sm(13)Na(23)-MFI, and (▼) Cu(29)Sm(29)Na(49)-MFI. (B) (■) Cu(96)Gd(7)Na(3)-MFI, (●) Cu(85)Gd(10)Na(7)-MFI, (▲) Cu(79)Gd(5)Na(10)-MFI, (▼) Cu(60)Gd(4)Na(25)-MFI, and (◆) Cu(30)Gd(6)Na(53)-MFI.

Based on the amounts of NO desorbed, the NO/Cu molar ratios were calculated to be 0.85, 1.05, and 0.91 for

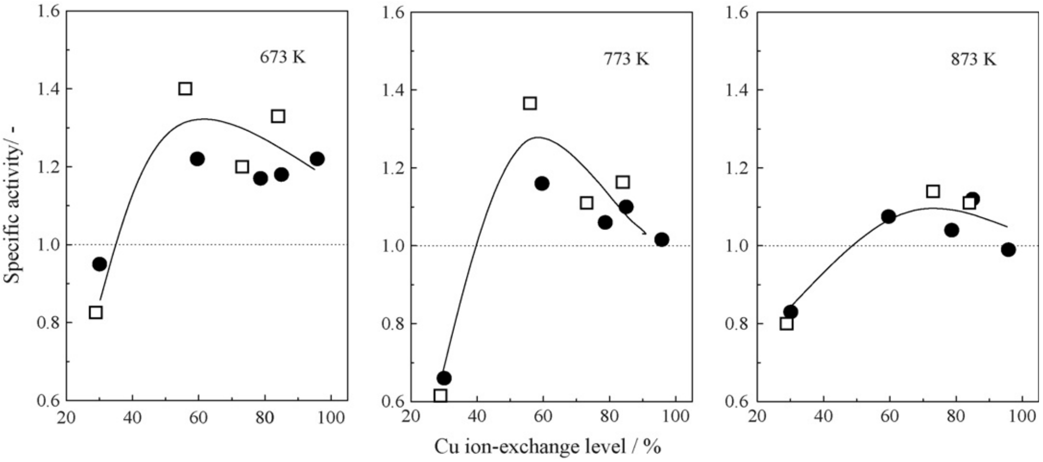

Fig. 3. Specific activities of (●) Cu(*x*)Sm(*y*)Na(*z*)-MFI and (□) Cu(*x*)Gd(*y*)Na(*z*)-MFI catalysts as a function of Cu ion-exchange level at 673, 773, and 873 K. NO = 2.18% and W/F = 2.0 g s cm^{-3}.

Cu(84)Sm(7)Na(8)-MFI, Cu(85)Gd(10)Na(7)-MFI, and Cu(85)Na(15)-MFI, respectively. The molar ratio NO/Cu was almost unity for all the catalysts. It follows that the introduction of the rare-earth elements to CuNa-MFI had little influence on the effectiveness of each copper ion for NO adsorption in the MFI zeolite.

3.3. H_2-TPR measurements of Cu(x)Ln(y)Na(z)-MFI catalysts

In order to examine the reduction property of copper ion exchanged into MFI zeolites, H_2-TPR measurements were carried out in the temperature range 303–773 K. Fig. 5 shows the H_2-TPR profiles of Cu(60)Na(40)-MFI, Cu(66)Sm(13)Na(12)-MFI, and Cu(60)Gd(12)Na(20)-MFI catalysts. The catalysts were pretreated by flowing Ar at 773 K for 4 h. No more reduction peak was observed even upon heating up to 973 K, suggesting that the reduction of copper in MFI zeolite was complete after H_2-TPR. The H_2-TPR profile of the Cu(60)Na(40)-MFI catalyst, as shown in Fig. 5(a), was characterized by the appearance of two reduction peaks, α and β, around 440 and 600 K, respectively. Similar profiles were reported by Sachtler and co-workers [14,15], Abreu et al. [16], and Schmal et al. [17] The amounts of H_2 consumed during TPR measurement are summarized in Table 2.

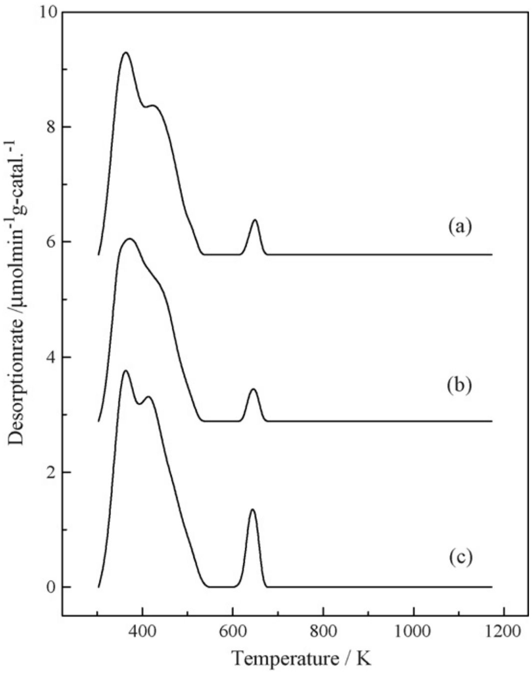

Fig. 4. NO-TPD profiles of (a) Cu(84)Na(15)-MFI, (b) Cu(84)Sm(7)Na(8)-MFI, and (c) Cu(85)Gd(10)Na(7)-MFI catalysts.

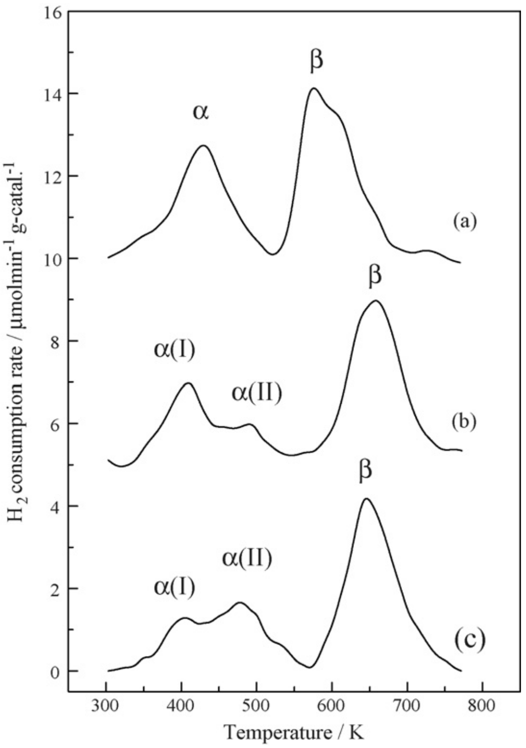

Fig. 5. H_2-TPR profiles of (a) Cu(60)Na(40)-MFI, (b) Cu(66)Sm(13)Na(12)-MFI, and (c) Cu(60)Gd(12)Na(20)-MFI catalysts pretreated by flowing an Ar stream at 773 K for 4 h.

Table 2
Amounts of H_2 consumed in H_2-TPR measurements

Catalyst	Copper content[a] (μmol g catal.$^{-1}$)	Amount of H_2 consumed (μmol g catal.$^{-1}$)	
		α	β
Cu(60)Na(40)-MFI	356	126	184
Cu(66)Sm(13)Na(12)-MFI	392	104 (α(I): 75, α(II) 29)	200
Cu(60)Gd(12)Na(20)-MFI	356	108 (α(I): 41, α(II) 67)	172

[a] Determined by ICP analysis.

According to Ref. [14], the α peak was assigned to the reduction of the aggregated CuO to Cu^0 and the Cu^{2+} to Cu^+ located at an exchangeable position, while the α peak was assigned to the reduction of Cu^+ to Cu^0. Thus, the following reduction processes with H_2 are discerned:

$$CuO + H_2 = Cu^0 + H_2O \quad (\alpha\ \text{peak}) \tag{1}$$

$$Cu^{2+} + 0.5H_2 = Cu^+ + H^+ \quad (\alpha\ \text{peak}) \tag{2}$$

$$Cu^+ + 0.5H_2 = Cu^0 + H^+ \quad (\beta\ \text{peak}) \tag{3}$$

It is considered that the β peak involves the reduction of Cu^+ ions produced not only through the reduction process (2), but also by the thermal reduction of copper ion with the extra-lattice oxygen (ELO) [18] such as $[Cu–O–Cu]^{2+}$ and $Cu^{2+}O^-$ because the catalysts were pretreated in Ar at 773 K before TPR measurement. It should be noted that the molar ratio of H_2 consumption originated from the β peak to the copper content was ca. 0.5, i.e., the reduction process (3) was stoichiometrically observed in the H_2-TPR study. This suggests that the direct reduction from CuO to metallic copper (reduction process (1)) did not contribute to the appearance of the α peak. Thus, the α peak mainly originated from the reduction of Cu^{2+} located at an exchangeable position, which could not be reduced by the pretreatment in Ar at 773 K.

The TPR profiles of Cu-MFI containing Sm and Gd elements are illustrated in Fig. 5(b) and (c), respectively. The TPR profiles of Cu-MFI containing rare-earth element were a little different from that of Cu(60)Na(40)-MFI. When the rare-earth element was introduced to Cu-MFI, two reduction peaks, α(I) and α(II), were observed in the temperature range 350–550 K. These peaks could be assigned to the reduction of Cu^{2+} to Cu^+, probably located at a different exchangeable site. As can be seen in Table 2, the total H_2 consumption of α(I) and α(II) peaks was smaller than that of the α peak for Cu(60)Na(40)-MFI. This indicates that the introduction of the rare-earth element to Cu-MFI reduces the number of Cu^{2+} ions which cannot be reduced by the pretreatment at high temperature.

The molar ratio of H_2 consumption originated from the β peak to the copper content was ca. 0.5, indicating that the stoichiometric reduction process (3) was maintained even by the introduction of the rare-earth element. However, the temperature at the peak maximum of the β peak was shifted to higher temperature when rare-earth element was introduced to Cu-MFI. This suggests that the introduction of rare-earth element stabilizes Cu^+ ion, compared with Cu-MFI. A similar conclusion was reported by Grange and co-workers, who confirmed by XPS studies that the presence of Sm stabilizes $Cu^+–O–Cu^{2+}$ as active species. In addition, it should noted that the atomic ratio Ln/Cu is much lower than 1. This suggests that one single Ln ion can modify the reduction properties of several Cu ions.

In previous publications [4,19–24], considerable evidences have been provided to indicate that Cu^+ species participate in the reaction and that the NO decomposition is a redox process. In addition, it was proposed that the NO decomposition reaction is closely related with the extra-lattice oxygen (ELO) species: a unique dimeric Cu species with the ELO such as $Cu^{2+}–O^{2-}–Cu^{2+}$, $Cu^+–O^{2-}–Cu^{2+}$, and $Cu^+\cdots Cu^{2+}O^-$, which is stabilized by the zeolite framework [4,14,25–31], and an isolated Cu^{2+} sites associated with the ELO such as $Cu^{2+}O^-$ or $Cu^{2+}O^{2-}$ [32–34]. The geometrical structure of copper ion interacting with introduced rare-earth element is unclear from the present study; however, the present study suggests that the addition of rare-earth element to Cu-MFI stabilizes Cu^+ ions as an active center, leading to an enhanced decomposition activity of Cu-MFI, although further studies are necessary.

4. Conclusion

The catalytic activities of NO decomposition were investigated for Cu-MFI catalysts containing several rare-earth elements. The following aspects were obtained from the present study.

(1) The decomposition activity of the catalysts prepared by the successive ion-exchange method with rare-earth element and then with copper was higher than that of the catalysts prepared in the reverse sequence.
(2) The maximal activity of Cu(x)Ln(y)Na(z)-MFI was obtained at 773 K, regardless of the kind of rare-earth element. The order of activity was Sm, Gd > Pr, none, La, Ce > Nd (773 K). When the exchange level of copper ion was 60–80%, the addition of Sm or Gd into Cu-MFI was effective for the improvement of activity.
(3) The introduction of the rare-earth elements to CuNa-MFI had little influence on the effectiveness of each copper ion for NO adsorption in the MFI zeolite; however, it reduced the number of Cu^{2+} ions which cannot be reduced by the pretreatment at high temperature and stabilized Cu^+ ions as an active center.

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