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Gallosilicate-Based Catalysts for NO_x-SCR with CH_4

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Ga-incorporated H-MFI (GaMFI) metallosilicate catalysts show robust activity for selective catalytic reduction of NO_x (NO_x-SCR) with CH_4, although the reactivity of NO–CH_4 is very low in the absence of O_2. Over these catalysts, NO_x–CH_4 reaction proceeds selectively in the presence of O_2. In contrast, FeMFI shows high activity for NO–CH_4 reaction without O_2, although no reactivity is shown in the presence of O_2. In addition, transition-metal ion modification on FeMFI does not enhance NO_x-SCR activity. From the results of XRD and XAFS characterization at Ga and Si K-edges, active Ga species are incorporated in H-MFI frameworks with T_d symmetry. Local structure around Ga is very stable but distorted Si–O_4 local structure can be formed after NO_x-SCR reaction with CH_4.

Zeolites are well known as microporous materials, and have been applied widely to several engineering processes because of surface activity resulting from acidity. Zeolites are open framework aluminosilicates consisting of SiO_4 and AlO_4, interconnected via oxygen atoms, and both Si and Al are present with T_d symmetry in the framework. Distortion of T_d sites (SiO_4 and AlO_4) is often brought about by application of several thermal processes or reactions. MFI zeolites are typical catalysts with unique activity for several useful reactions. In particular, Cu^{2+} ion-exchanged H-MFI shows high deNO_x activity with hydrocarbons.[1,2] For ion-exchanged zeolite catalysts, significant problems due to hydrothermal stability cannot be avoided in the case of modified MFI. On the other hand, metallosilicates are an appropriate material because active transition-metal ions are incorporated onto the framework.[3] For example, Fe^{3+}-substituted MOR zeolites show high NO-SCR activity for methane.[4] But deactivation during the reaction is a major issue. We synthesized Fe- and Ga-MFI with various metal ratios by hydrothermal synthesis. Fe^{3+}- and Ga^{3+}-cosubstituted MFI (FeGaMFI) can be obtained. These materials show unique reactivity for NO_x-SCR.[5] FeMFI with high Fe ratio shows high NO–CH_4 reactivity, while no activity for NO_x-SCR in the presence of O_2. In contrast, GaO_x is an appropriate component for NO_x-SCR. It has been reported that Ga_2O_3–Al_2O_3 catalyst systems show high NO_x-SCR activity.[6] Ga ion-exchanged H-MFI is also a widely-known catalyst for NO_x-SCR with methane, as reported by Kikuchi et al.[7] and Inui et al.[8] Ga species on H-MFI show high and selective activity for NO_x-SCR, but Ga modification brings about low acidity of H-MFI support because of coverage of non-framework Ga ions on the strong acid sites.[9] The NO_x-SCR reactivity is likely to relate to the formation rate of NO_2, and thus the acidity of Ga-modified H-MFI is important to oxidize NO to NO_2. In order to design useful and robust NO_x-SCR catalysts, Ga-incorporated MFI metallosilicates (gallosilicates: GaMFI) are attractive because of stronger acidity than Ga ion-exchanged MFI.[9,10] Therefore, both the strong acidity and structural stability of active Ga sites will affect the high NO_x-SCR activity over GaMFI catalysts.

In this study, Ga-incorporated MFI metallosilicates with various Ga ratios were synthesized. NO_x-SCR reactivity over the GaMFI catalyst under lean O_2 atmosphere is evaluated, and the role of Ga ions is studied. To characterize the active species and/or intermediates after the reaction, ESR and TPD (thermally programmed desorption) studies are introduced. In this article, the relationship between substituted Ga^{3+} species on H-MFI and catalytic activity for NO_x-SCR with CH_4 is investigated. In order to clarify the local structure of substituted Ga species and evaluate their stability over Fe- and/or Ga-substituted MFI metallosilicates, Ga and Si K-edge XAFS (X-ray absorption fine structure) spectroscopy is applied to characterize the local symmetry of both atoms.

Experimental

Synthesis of Metallosilicates. The GaMFI and FeMFI metallosilicates were prepared by a method described in a separate paper.[3] In brief, GaMFI with several $Si/(Ga + Al)_2$ ratios were prepared from aluminum chloride, iron(II) sulfate, pentahydrated gallium nitrate, sodium silicate, and TPABr (as a template for MFI) mixed solution. They were stirred for ca. 3 h to form a gel. From the gels, MFI metallosilicates were synthesized hydrothermally at 443 K for 7 days using a stainless autoclave. After the synthesis, obtained gel was dried overnight and calcined at 873 K for 3 h. In this article, the materials are denoted as Ga*N*MFI(*R*) in which *N* and *R* represent the molar ratio of $Ga/(Ga + Al) \times 100(\%)$ and total Ga ratio due to $Si/(Ga + Al)_2$, respectively.

Evaluation of NO_x-SCR Activity. The NO_x-SCR reaction was carried out by using a fixed bed reactor at atmospheric pressure. Before each reaction, the catalyst (0.250 g) was pretreated under O_2(10%)–He flow of 30 mL min^{-1} for 1 h, and then the reactor was purged by He flow for 5 min to remove O_2. A reactant gas consisting of NO(5000 ppm)–CH_4(2600 ppm)–O_2(0.0–2.0%)–Ne(10%)–He(base) was fed into the reactor at 873 K for steady-state reaction. In the case of temperature-programmed reaction, the same reactant gas was fed into the reactor at 473 K for 1 h, and then

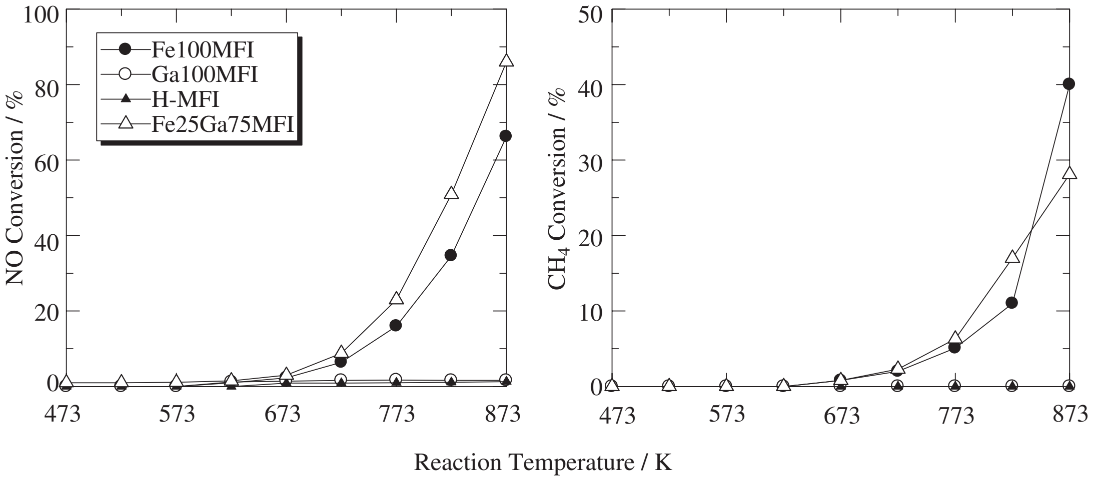

Figure 1. Reactivity of NO and CH_4 in a temperature-programmed NO–CH_4 reaction over Fe- and Ga-substituted MFI ($Si/(Fe_2 + Ga_2) = 72$).

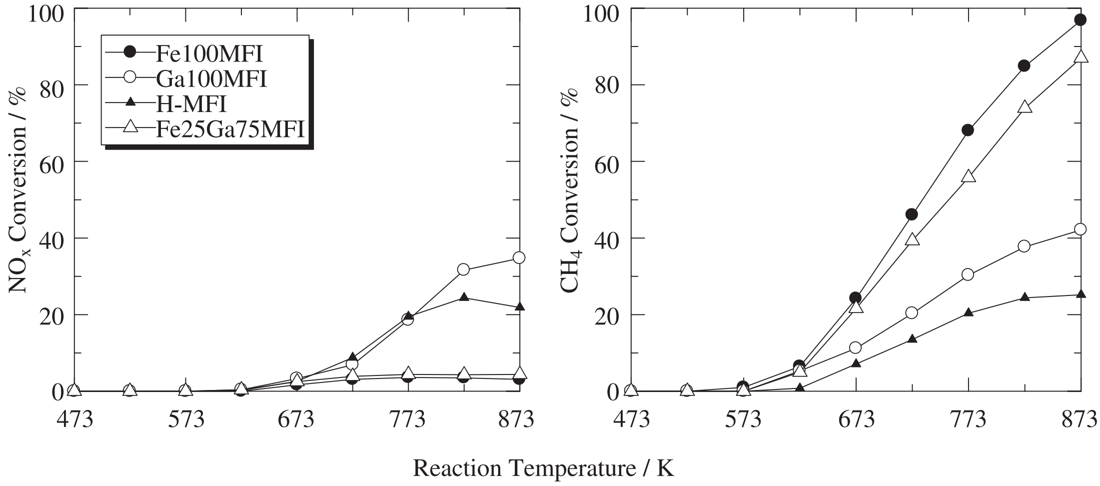

Figure 2. Reactivity of NO_x and CH_4 in temperature-programmed NO–O_2–CH_4 reaction over Fe- and Ga-substituted MFI ($Si/(Fe_2 + Ga_2) = 72$).

reaction temperature was elevated periodically for step-by-step reaction up to 873 K at a programmed rate of 5 K min^{-1}. Products were analyzed by online TCD-GC (Shimadzu GC-14B equipped with MS13X and Porapack-Q columns at 318 K) and FT-IR (JASCO FT/IR-420, for analyzing the NO/NO_x and NO_2/NO_x ratios).

Characterization of Active Species. Crystallinity of the bulk phase of the whole catalysts before and after the catalytic reaction was evaluated by powder X-ray diffraction (Rigaku, RINT2300). In brief, only diffraction peaks due to MFI structure were observed. ESR signal (JEOL JES-RE2X) was measured at 77 K or room temperature using 100 KHz X-band mode and 0.63 mT modulation width.

Al K-edge XANES spectra were obtained in the BL-1A station at the UVSOR-IMS, Okazaki, Japan (with ring energy of 750 MeV and stored current of 180–320 mA). Each sample was mounted on carbon tape and then attached to a beryllium–copper dynode as the first stage of the electron multiplier placed in a vacuum chamber. After the chamber was evacuated, the spectrum was measured in the total electron yield mode at room temperature, using a KTP ($KTiOPO_4$) double-crystal monochromator ($d = 0.5477$ nm). Ga K-edge XAFS spectra were obtained in BL-7C of KEK-PF, Tsukuba, Japan (with 2.5 GeV of ring energy and 200–350 mA of stored current). The ionization chambers filled with Ar(15%)–N_2 (as I_0) and Ar (as I) gases were used as transmitted beam detectors, and the samples were set between these detectors. The photon source was monochromatized by means of a Si(111) double-crystal monochromator ($d = 0.313551$ nm), and the spectrum was obtained by transmission mode. A channel-cut chamber line and a 1 mm slit were used for the elimination of harmonics. For computational analyses of XAFS spectra at Al and Ga K-edges, REX2000 program (Rigaku Co.)[11] was used.

Results and Discussion

Evaluation of NO_x-SCR Activity. The catalytic reactivity over typical catalysts (FeMFI, FeGaMFI, GaMFI, and H-MFI) is shown in Figure 1 (NO–CH_4 reaction without O_2) and Figure 2 (NO_x–CH_4 reaction with 1% O_2). In the absence of O_2 (Figure 1), Fe100MFI and Fe25Ga75MFI show catalytic activity above 723 K, although Ga100MFI shows no activity. In the presence of 1% O_2 (Figure 2), low NO_x and high CH_4 conversion are shown over Fe100MFI and Fe25Ga25MFI. These results show high CH_4 combustion with O_2, independent

Table 1. NO_x-SCR Activity with CH_4 in the Absence/Presence of O_2 over Various Metallosilicates (at 873 K under Steady-State Reaction Conditions)

Catalyst	O_2 absent		O_2(10000ppm) present	
	NO conv./%	CH_4 conv./%	NO_x conv./%	CH_4 conv./%
Fe100MFI(72)	52.7	19.7	4.0	93.8
Fe75MFI(72)	54.8	18.9	4.0	94.5
Fe50MFI(72)	29.7	12.6	4.0	94.2
Fe25MFI(72)	9.2	2.4	3.4	86.3
Fe/H-MFI[a]	10.2	3.2	9.3	67.0
Fe-MFI[b]	4.2	1.2	7.0	31.3
Ga100MFI(72)	1.6	0.0	58.1	58.0
Ga75MFI(72)	1.6	0.3	40.1	33.6
Ga50MFI(72)	1.7	0.0	34.7	43.1
Ga25MFI(72)	1.4	0.0	31.7	41.0
Ga/H-MFI[c]	1.5	0.0	24.8	37.0
Fe75Ga25MFI(72)	36.8	13.1	5.7	89.3
Fe50Ga50MFI(72)	35.6	14.0	5.4	88.8
Fe25Ga75MFI(72)	76.0	26.2	3.4	97.3
H-MFI	1.3	0.0	23.3	24.1

a) Fe-impregnated (2.05 wt %). b) Fe ion-exchanged. c) Ga-impregnated (0.5 wt %).

of NO. In contrast, Ga100MFI and H-MFI show high NO_x-SCR activity above 673 K. Ga100MFI shows the highest NO conversion at 873 K with lower CH_4 conversion than that of Fe100MFI or Fe25Ga75MFI. Thus, Fe sites on Fe100MFI and Fe25Ga75MFI preferentially promote CH_4–O_2 reaction even in the presence of Ga sites.

Table 1 shows NO_x-SCR reactivity in a steady-state reaction at 873 K, with CH_4 in the presence of 10000 ppm O_2 over various metallosilicates. For FeMFI, NO_x conversion is low although CH_4 conversion is very high in the presence of O_2. It indicates that in the presence of oxygen CH_4 combustion proceeds more rapidly than oxidation via NO_x. In contrast, Ga-substituted MFI (GaMFI) catalysts show high NO_x conversion in the presence of O_2 and low conversion in the absence of O_2. This shows that GaMFI exhibits selective reactivity for NO_x (largely NO_2) with CH_4, rather than CH_4 with O_2. On the other hand, like FeMFI, Fe–Ga co-substituted MFI catalysts (Fe75Ga25MFI, Fe50Ga50MFI, and Fe25Ga75MFI) show low NO_x-SCR activity. From this it is concluded that CH_4 combustion at Fe sites proceeds in preference to NO_x-SCR at Ga sites over FeGaMFI catalysts. For all the Fe/Ga ratios in FeGaMFI, this can be seen. It has been reported by Pérez-Ramírez et al.[12,13] that enhancement of both redox activity (on Fe^{3+}) and total acidity can be achieved by co-substitution of Ga ions onto FeMFI. The main origin may be the charge valances of Fe^{3+} and Ga^{3+} ions on the MFI framework. It is suggested in our study that Fe–Ga co-substitution affects the enhancement of redox activity of Fe^{3+} sites, and the activity of Ga sites is depressed apparently at the same time.

For GaMFI, high Ga content brings about high NO_x-SCR activity (Table 2). It suggests that substituted Ga ions on the MFI framework are the active species for NO_x-SCR. In addition, substituted Ga ions show higher activity than those modified by impregnation or ion-exchange, shown in Table 2. These results suggest that stabilization of Ga ions in the framework gives high conversion and selective activity for NO_x removal. One typical differences between Ga-substituted and modified MFI is the acidity, as revealed by Choudhary et al.,[9,10] and GaMFI gallosilicates possess strong acidity. It is suggested that the acid sites (Ga^{3+}) can oxidize NO to NO_2 as an adsorbed species, and the NO_2 species can react with CH_4 selectively even in the presence of O_2.

Table 2. NO_x-SCR Activity with CH_4 in the Absence/Presence of O_2 over Various Gallosilicates (at 873 K under Steady-State Reaction Conditions)

Catalyst[a]	O_2 absent		O_2(10000ppm) present	
	NO conv./%	CH_4 conv./%	NO_x conv./%	CH_4 conv./%
Ga100MFI(288)	2.5	0.4	24.6	56.1
Ga100MFI(144)	1.4	0.0	41.0	34.9
Ga100MFI(100)	1.2	0.0	58.8	30.6
Ga100MFI(72)	1.6	0.0	58.1	58.0
Ga100MFI(40)	1.1	0.0	12.4	11.6
Ga/H-MFI(72)[b]	3.5	0.6	27.7	32.7
H-MFI(72)	2.0	0.3	15.5	35.5

a) Catalysts are denoted as "Ga*N*MFI(*R*)," $N = $ Ga [mol %], $R = $ silica/gallia ratio. b) Ga-impregnated (0.5 wt %).

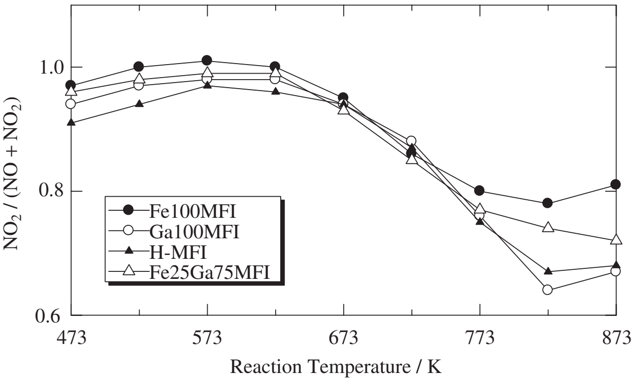

Figure 3. NO_2 ratio (NO_2/(NO + NO_2)) in the products during a temperature-programmed reaction over Fe- and Ga-substituted H-MFI (Si/(Fe_2 + Ga_2) = 100). The ratio is obtained by means of online FT-IR analysis.

In the steady-state NO_x-SCR reaction over GaMFI, durable activity is shown and deactivation is not observed. Ga100MFI in $Si/Ga_2 = 100$ shows the maximum reactivity for NO_x-SCR with CH_4 (Table 2). These results suggest the relation between dispersed Ga species in the MFI framework and formation of Ga sites highly active for NO_x-SCR. In addition, gas-phase NO_x (mainly NO_2) needs to react with CH_4 on GaMFI because of the low activity for NO–CH_4 reaction (in the absence of O_2). For this reason, NO_2 ratio (=NO_2/(NO + NO_2)) was monitored by means of FT-IR analysis in the temperature-programmed reaction. Under these conditions, NO_x–CH_4 reaction proceeds above 673 K in all the catalysts. As shown in

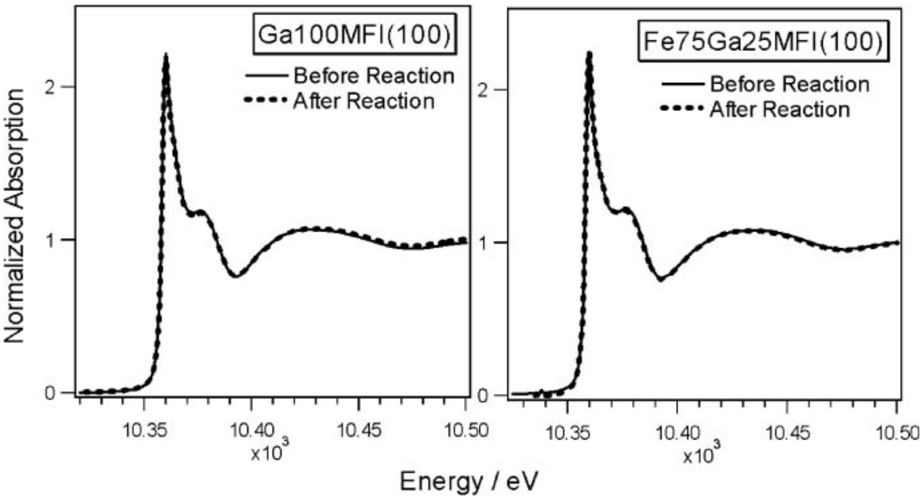

Figure 4. Ga K-edge XANES of Ga100MFI(100) and Fe75Ga25MFI(100) catalysts before and after NO_x-SCR.

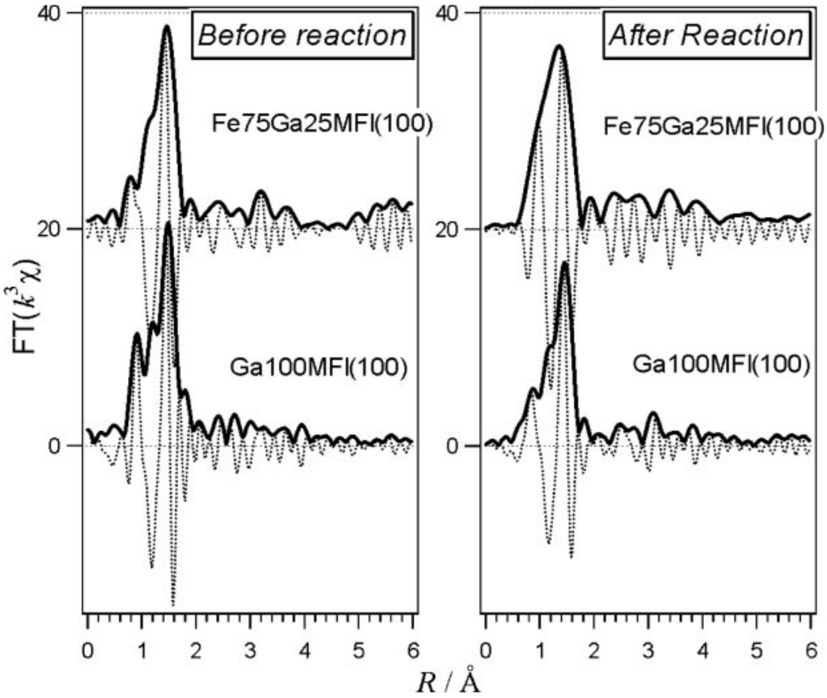

Figure 5. Ga K-edge FT-EXAFS of Ga100MFI(100) and Fe75Ga25MFI(100) catalysts before and after NO-SCR (without O_2).

Figure 3, NO_2 concentration decreases above 673 K, and the minimum NO_2 ratio is shown in the case of GaMFI at 823 K. This indicates the reduction of NO_2 (not NO) with CH_4 preferentially.

Characterization of the Catalysts. Figure 4 shows Ga K-edge XANES spectra of Ga100MFI(100) and Fe75Ga25MFI(100) catalysts before and after NO_x-SCR. In both cases, the XANES spectra are quite similar, indicating that no structural change occurs during the reaction. In addition, their spectra are assigned as. T_d-symmetric Ga species.[14,15] Because the XANES of GaMFI is different from Ga-modified (non-incorporated) H-MFI,[16] it is concluded that substituted Ga^{3+} ions exist on the MFI framework. The Ga^{3+} sites on the MFI framework act as highly stabile NO_x-SCR active species. The results of FT-EXAFS analyses are shown in Figure 5. For GaMFI and GaFeMFI before and after NO-SCR, only the first shell due to Ga–O at ca. 1.6 Å can be seen definitely. The second shell due to Ga–O–Ga (in the range of 2.6–3.3 Å) is hardly seen, which indicates the presence of dispersed Ga ions in MFI. These results indicate that the Ga^{3+} species on the MFI framework is very stable against the NO_x-SCR reaction.

On the other hand, Si K-edge XANES spectra show structural changes around Si ions before and after the reaction. At the Si K-edge in Figure 6, 1s–4p electron transition in Si is reflected in the white line XANES spectra, and the intensity of the white line spectrum relates to the mean symmetry of Si atoms. For example, quartz-SiO_2 occupies T_d symmetric tetrahedra (SiO_4 cluster). In this case, strong intensity of the white line peak (Figure 6) can be seen. In the case of silica gel occupying slightly distorted tetrahedra, the white line

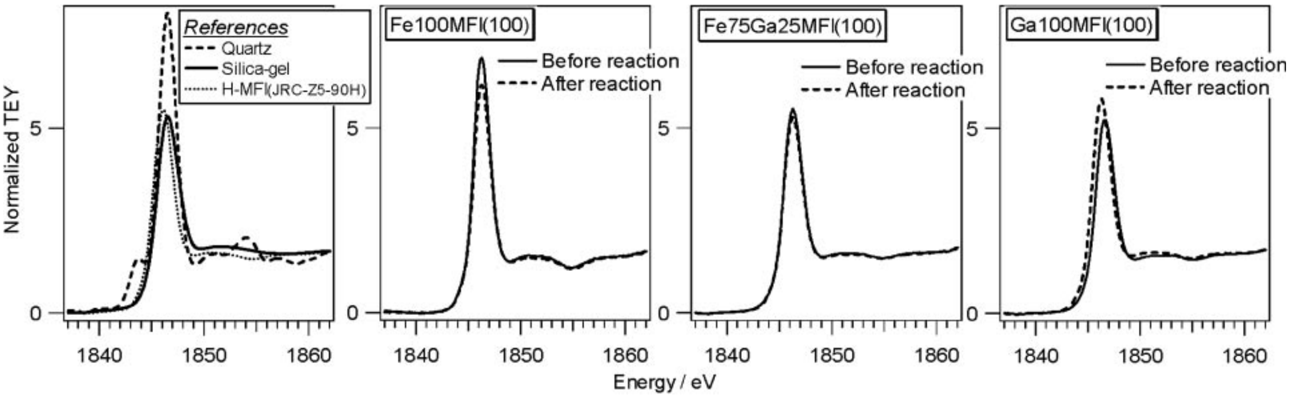

Figure 6. Si K-edge XANES of reference Si compounds, Fe100MFI(100), Fe75Ga25MFI(100), and Ga100MFI(100) catalysts before and after NO$_x$-SCR.

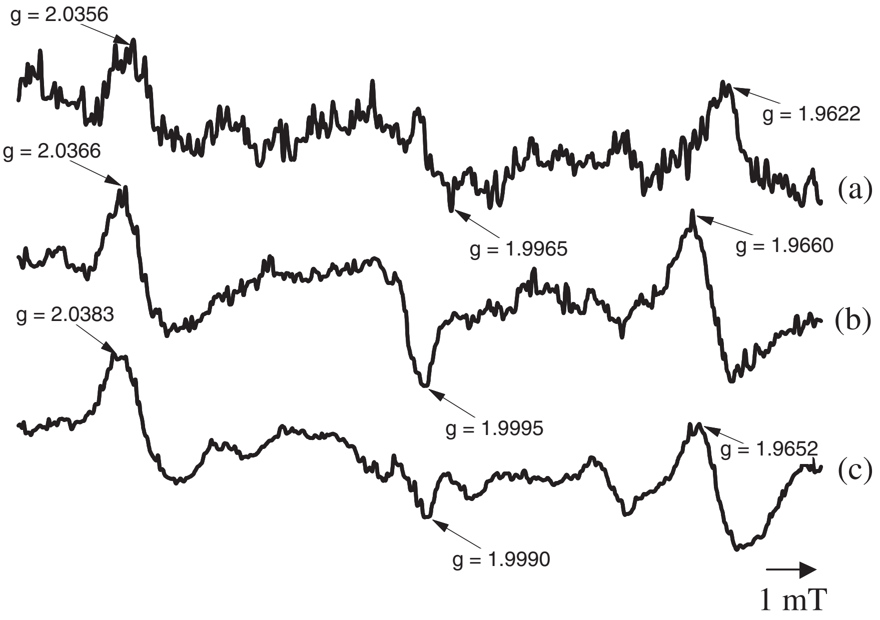

Figure 7. ESR signals of Ga100MFI(100) catalysts: (a) pretreated with O_2(10%)–He at 873 K, (b) after NO(0.5%)–CH_4(0.26%)–He treatment at 873 K, and (c) after NO(0.5%)–O_2(1.0%)–CH_4(0.26%)–He treatment at 873 K.

is broader and less intense than that of quartz. From this information, local structure around Si atoms can be evaluated. For FeMFI, the white line due to SiO_4 tetrahedra in the MFI framework can clearly be seen. The intensity of the peak is larger than that of bare H-MFI (consisting of SiO_2–Al_2O_3), indicating the formation of highly symmetric T_d sites. In contrast, the intensity in Ga-substituted MFI is slightly smaller than that of H-MFI, as well as that of FeGaMFI. These results suggest that Fe substitution brings about structural changes of the framework, and Ga co-substitution inhibit the structural change. It is likely that Fe sites in FeMFI are less stable than Ga sites in the structure. After NO$_x$-SCR, the intensity in FeMFI becomes smaller. It suggests a structural change due to separation of Fe site by hydration. The Ga site is largely stable under the reaction conditions. It can be expected that the local Si structure of FeGa co-substituted MFI is very stable during the NO–CH_4 reaction (without O_2) because of the structural stability of the active Fe and Ga sites. In the case of GaMFI, mainly distorted tetrahedra exist before NO$_x$-SCR. After the reaction, SiO_4 symmetry is increased. This suggests the reconstruction of SiO_4 local structure, while the crystallinity of bulk MFI phase is not changed by the reaction. These results suggest that structural change in the MFI framework is not brought about by active Ga species but by inactive Si sites. This may relate to the stability of Ga ions possessing durable NO$_x$-SCR reactivity.

Figure 7 shows ESR signals over Ga100MFI(100) after NO$_x$-SCR in the absence and presence of O_2. No signal due to Ga^{3+} or other catalytic components can be seen. After NO–CH_4 reaction in the absence O_2, adsorbed NO and NO_2 species can be observed at $g = 1.9660$, 2.0366 (mainly due to $g_\perp$ of NO[17,18]), and $g = 1.9995$ (overlapping with $g_\perp$ of NO and NO_2[17,19]), respectively. This indicates that oxidation of NO proceeds to form adsorbed NO_2 by interaction with lattice oxygen in GaMFI. In this case, low NO$_x$-SCR reactivity is observed. After NO$_x$-SCR reaction in the presence of O_2, their signals also can be seen. After NO_x-SCR reaction (with O_2), the signal intensity at $g = 1.9990$ (due to adsorbed NO and NO_2) is lower than that after NO-SCR (without O_2), although intensity of the signals at $g = 1.9660$, 2.0366 (due to NO) is almost similar. This result indicates that NO_2 species decreased by addition of O_2 with NO–CH_4. These results suggest that adsorbed NO_2 can react easily with CH_4 in NO_x-SCR reaction.

Conclusion

H-MFI metallosilicate catalysts incorporating Ga (GaMFI) show robust activity for selective catalytic reduction of NO_x (NO_x-SCR) with methane, although NO–CH_4 reactivity is very low in the absence of O_2. On these catalysts, NO_x-CH_4 reaction proceeds selectively in the presence of O_2. On the other hand, FeMFI shows high activity for NO–CH_4 reaction; however, almost no reactivity is shown in the presence of O_2. In contrast, Ga100MFI(100) shows the highest NO_x-SCR activity in the presence of O_2(1%), and almost no activity is shown in the absence of O_2. NO_2 forms easily in the presence of NO and O_2 under the reaction conditions and the NO_2- and NO-signals on GaMFI can be detected by ESR. Thus, selective reactivity between NO_x and CH_4 is a key role for NO_x-SCR on Ga species on GaMFI. Active Ga species are incorporated in H-MFI frameworks with T_d symmetry. Local structure around Ga is very stable but distorted Si–O_4 local structure can be formed after the NO_x-SCR reaction with CH_4. It is concluded that the origin of high activity for NO_x-SCR over GaMFI is a result of the structural stability of Ga^{3+} sites and flexibility of Si sites on the MFI framework.

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