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Selective Reduction of Nitric Oxide with Methane on Gallium and Indium Containing H-ZSM-5 Catalysts: Formation of Active Sites by Solid-State Ion Exchange

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H-ZSM-5 catalysts containing Ga and In were prepared by the ion-exchange method and by physically mixing H-ZSM-5 and Ga_2O_3 or In_2O_3, and they were used in the NO reduction with methane to determine the active species of these metals, particularly of In, for this reaction. Ga-loaded H-ZSM-5 prepared by the ion-exchange method gave a higher catalytic activity than the physical mixture of Ga_2O_3 and H-ZSM-5, of which the catalytic activity was comparable to that of H-ZSM-5. On the contrary, both ion-exchange and physical mixing methods yielded equally high catalytic activities of In-loaded H-ZSM-5. The reduction of NO on these catalysts proceeds consecutively by way of oxidation of NO to NO_2 and reduction of NO_2 with CH_4 to N_2. With increasing heat treatment temperature, the catalytic activity of the mixture of In_2O_3 and H-ZSM-5 for the reduction of NO_2 increased, while that for NO oxidation decreased. An IR study of OH groups on this catalyst indicated that the solid-state exchange reaction occurred between In_2O_3 and H-ZSM-5 leading to the increase in the number of indium cation sites and consequently the catalytic activity for NO_2 reduction. © 1996 Academic Press, Inc.

INTRODUCTION

As emission of nitrogen oxides (NO_x) from vehicles and stationary sources causes serious impacts on terrestrial ecosystems (acid rain, air pollution, greenhouse effect, etc.) (1), emergent improvement of the exhaust is required. Catalysis has played, and will continue to play, important roles in reducing the pollutants. At present, automotive exhausts are cleaned up solely by use of the three-way catalyst, on which NO_x is effectively reduced by carbon monoxide and unburned hydrocarbons coexisting in the exhausts. This catalytic process, however, cannot be applied to the lean-burn combustion exhaust due to the presence of excess oxygen. In the case of stationary sources, the combustion is carried out with excess oxygen, so that the removal of NO_x requires a selective reductant such as NH_3, which is, however, a harmful reagent.

Since the reports by Iwamoto *et al.* (2) and Held *et al.* (3), selective catalytic reduction (SCR) of NO_x with unburned hydrocarbons (HC) found in the emission exhaust has attracted a lot of attention (4–8). A remarkable feature of the HC-SCR, as has been pointed out, is that oxygen is indispensable for this reaction. The reductant used for this reaction should selectively be oxidized by NO_x with a minor consumption by combustion with coexisting excess oxygen.

It has been shown in our previous work that Ga and In containing H-ZSM-5 catalysts are active and selective for the reduction of NO with hydrocarbons, particularly even with methane as a reductant (9). Methane can react selectively on these catalysts with NO_2 formed by the oxidation of NO on zeolitic acid sites (19, 21). The role of Ga and In on H-ZSM-5 is mainly to accelerate the reaction [2]:

$$NO + 1/2O_2 \rightarrow NO_2 \quad \text{[zeolite acid sites]} \qquad [1]$$

$$NO_2 + CH_4 + NO_x \rightarrow N_2 + CO_x + 2H_2O \quad \text{[Ga or In sites]}. \qquad [2]$$

It would be beneficial if methane can be used as the selective reductant for NO_x reduction, since this hydrocarbon can be found in most combustion exhausts, particularly in the exhaust from the natural gas cogeneration system in which methane is an exclusive hydrocarbon. Selective reduction of NO_x with methane has been studied using H-ZSM-5 containing Co (7), Mn (7), Pd (10), and H-ZSM-5 itself (11) as well as Ga (6, 18) and In/H-ZSM-5 (9).

Ga containing zeolites have ever been studied as the catalyst for aromatization of light paraffins (12–17). In these studies, several types of Ga species, for instance Ga^{3+}(12), Ga^+(13), and $Ga_2O_3 + H^+$ (synergism) (14–16), have been proposed as the active sites for this reaction. Little has been studied on the active species of Ga for the NO reduction with hydrocarbons. It has been reported by Yakerson *et al.* for the aromatization (17) and more recently by Li and Armor for the NO reduction (18) that Ga loaded on H-ZSM-5 was mainly found as a Ga_2O_3 phase and located on the surface of the zeolite, not in the pores of the zeolite. We have reported (9) that Ga cation sites in H-ZSM-5 seems to be responsible for the reaction between NO_2 and

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CH_4 even though only a small portion of Ga may exist in the exchanged form on the zeolite.

In-loaded H-ZSM-5 behaved similarly to Ga-containing H-ZSM-5 for the NO_x reduction with CH_4. The aim of the present work is to study the nature of active sites formed by Ga or In and also to promote the cation exchange of Ga and In to H-ZSM-5 for showing that such sites are active for the reduction of NO_2.

METHODS

Catalyst Preparation

H-ZSM-5 was prepared by the ion exchange of Na-ZSM-5 having a SiO_2/Al_2O_3 molar ratio of 23.3 supplied by Tosoh Corporation using an aqueous solution of NH_4NO_3. Ga- and In-containing H-ZSM-5 catalysts were prepared either by the ion exchange method (abbreviated as Ga/H-ZSM-5, In/H-ZSM-5) or by the physical mixing method (abbreviated as Ga_2O_3/H-ZSM-5, In_2O_3/H-ZSM-5). The ion-exchange method was conventional: stirring the ammonium form ZSM-5 in an aqueous solution of $Ga(NO_3)_3$ or $In(NO_3)_3$ at 368 K for 24 h, followed by filtration and washing with decationized water. The physically mixed catalysts were prepared by gently grinding Ga_2O_3 or In_2O_3 with H-ZSM-5 in an agate mortar. As a reference, the physical mixture of Ga_2O_3 or In_2O_3 with the Na-ZSM-5 was used, being abbreviated as Ga_2O_3/Na-ZSM-5 or In_2O_3/Na-ZSM-5. The catalysts were normally pretreated prior to reaction calcined at 813 K for 30 min in a dry O_2 stream. The catalyst prepared by the ion-exchange method, however, was calcined for 3 h at the same temperature in a dry air stream to remove NH_3 and NO_x remaining on the samples. The chemical composition of these catalysts was determined by use of inductively coupled plasma (ICP) atomic emission spectroscopy. The content of Ga or In in H-ZSM-5 was shown in Table 1.

TABLE 1

Chemical Composition of the Ga or In Containing Catalysts

	Ga (wt%)	In (wt%)
Ga/H-ZSM-5(ion exchanged)	2.4	—
Ga_2O_3/H-ZSM-5(physically mixture)	2.4	—
Ga_2O_3/Na-ZSM-5(physically mixture)	2.4	—
In/H-ZSM-5(ion exchanged)	—	3.7
In_2O_3/H-ZSM-5(physically mixture)	—	4.2
In_2O_3/Na-ZSM-5(physically mixture)	—	3.9

Catalytic Activity Test

The catalytic activity was measured using a microcatalytic reactor in a steady-state plug flow mode, by feeding the mixture of 1000 ppm NO (or NO_2), 1000 ppm CH_4, 10% O_2 in He balance at a rate of 100 cm^3 min^{-1} to 0.1–0.5 g catalyst, corresponding to $GHSV = 7200-36{,}000\ h^{-1}$. The reactor was made of a quartz tube with a 10 mm diameter and reaction did not completely occur in the absence of catalyst at the temperature tested. Catalysts were pelletized and crushed into 32–60 mesh size to reduce the pressure drop in the catalyst bed. Effluent gases were analyzed by means of gas chromatography and chemiluminescence NO_x analysis. A gas chromatograph with a TCD detector was used with a molecular sieve 5A column (3 mm i.d.) and a Porapak QS column to separate O_2, N_2, CH_4, and CO in the former, and CO_2, N_2O, and H_2O in the latter. N_2O was not detected in the reaction conditions employed. The catalytic activity was evaluated by the level of NO conversion to N_2. The steady-state conversion was obtained by the level of NO_x conversion to N_2 at 2–3 h on stream. The same levels of NO_x conversion were reproduced in raising and descending modes of reaction temperature. The ratio in conversion of NO_x to CH_4 was a measure of selectivity, which was calculated according to the following equation:

$$\text{Selectivity (\%)} = \frac{0.5 \times [\mathrm{NO}]_0 \times C_{\mathrm{NO}}}{[\mathrm{CH_4}]_0 \times C_{\mathrm{CH_4}}} \times 100.$$

Infrared Spectroscopy Measurement

Fourier–transform infrared spectra were recorded with a Valor-III (JASCO) FT-IR spectrometer with a quartz cell using CaF windows. Catalyst samples were pressed under 400 kg/cm^2 into a self-supporting disk of 20 mm diameter. Before recording a spectrum, the sample was heated up to a definite temperature at 10 K/min and treated in a He stream for 30 min, evacuated for 30 min, and then cooled to ambient temperature. The spectra were collected in the frequency range of the acidic OH group vibrations (3000–4200 cm^{-1}) with a resolution of 2 cm^{-1}.

RESULTS

Figures 1a and 1b show the activities of Ga and In/H-ZSM-5 catalysts for NO reduction in the NO–CH_4–O_2 reaction, respectively. Both catalysts showed high activities in the relatively wide range of reaction temperature. In/H-ZSM-5 had a maximum NO conversion at 673 K, while Ga/H-ZSM-5 had maximum NO conversion at 773 K. It is also obvious that Ga and In/H-ZSM-5 gave different selectivities for CH_4 usage, which were 89% at 773 K for the former and 85% at 673 K or 52% at 773 K for the latter. The ratio in CO_2/CO formed was also different between these two catalysts: CO was predominantly formed on Ga/H-ZSM-5 and CO_2 on In/H-ZSM-5 even at lower temperatures.

Figure 2 shows the catalytic activities of Ga_2O_3, Ga_2O_3/H-ZSM-5, Ga_2O_3/Na-ZSM-5, and Ga/H-ZSM-5 for NO_2 reduction with CH_4. As shown previously (11), H-ZSM-5 is active for this reaction. Unsupported Ga_2O_3 and Ga_2O_3/Na-

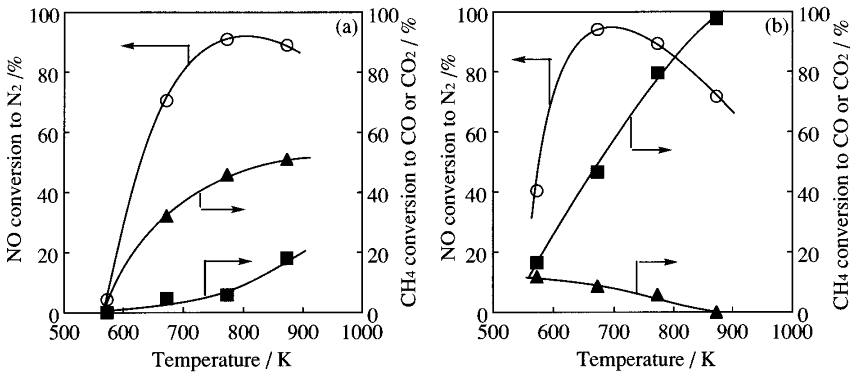

FIG. 1. NO and CH_4 conversion on Ga/H-ZSM-5 (a) and In/H-ZSM-5 (b) as a function of reaction temperature. ○, NO conversion to N_2; ▲, CH_4 conversion to CO; ■, CH_4 conversion to CO_2. Catalyst weight, 0.5 g.

ZSM-5 were almost inactive, while Ga_2O_3/H-ZSM-5 exhibited a catalytic activity which was smaller than that of Ga/H-ZSM-5 and comparable to that of H-ZSM-5. These results seem to show that there is little important interaction between Ga_2O_3 and H-ZSM-5 and that Ga_2O_3 is intrinsically inactive for this reaction.

On the other hand, In_2O_3/H-ZSM-5 showed a higher activity than Ga_2O_3/H-ZSM-5, as shown in Fig. 3. It is interesting to note that In_2O_3/H-ZSM-5 showed high NO_2 conversion close to In/H-ZSM-5. The catalytic activities of In_2O_3 and In_2O_3/Na-ZSM-5 for this reaction were extremely small, and CH_4 was oxidized to CO or CO_2, resulting in lower selectivity for NO_2 reduction compared with In-containing H-ZSM-5 catalysts. It is obvious from these results that there is a remarkable interaction between In_2O_3 and protonic acid sites on H-ZSM-5 and also that this interaction creates the active site for the selective reduction of NO_2 with CH_4.

Infrared spectra in the region of OH groups on H-ZSM-5, In/H-ZSM-5, and In_2O_3/H-ZSM-5 are shown in Fig. 4. A sharp absorption peak at 3610 cm^{-1} attributed to the acidic OH group was observed on H-ZSM-5, while the same absorption band was noticeably weaker on In/H-ZSM-5 and In_2O_3/H-ZSM-5 treated at 823 K. The peak around 3748 cm^{-1} could be attributed to the terminal SiOH, which did not change on heat treatment. It is obvious that In_2O_3/H-ZSM-5 gave a sharper absorption peak than In/H-ZSM-5. Heat treatment of In_2O_3/H-ZSM-5 at a higher temperature was accompanied by a further decrease in the intensity of the OH group, while that on In/H-ZSM-5 hardly changed on heat treatment.

Figure 5 shows the catalytic activities of In/H-ZSM-5, In_2O_3/H-ZSM-5, and H-ZSM-5 for the NO_2 reduction with CH_4 at 673 K as a function of heat treatment temperature. The catalytic activity of In/H-ZSM-5 was almost unchanged by the heat treatment in this temperature range, while that of In_2O_3/H-ZSM-5 increased with increasing temperature. On the other hand, the selectivity of In_2O_3/H-ZSM-5 was hardly varied by the heat treatment and it was similar to that of In/H-ZSM-5. The selectivities of In_2O_3/H-

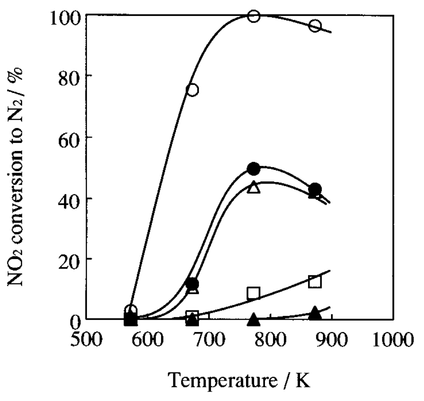

FIG. 2. NO_2 conversion to N_2 as a function of reaction temperature on Ga-containing catalysts: ○, Ga/H-ZSM-5; △, Ga_2O_3/H-ZSM-5; ▲, Ga_2O_3/Na-ZSM-5; □, Ga_2O_3, treated at 813 K. Also shown is the activity of H-ZSM-5 (●). Catalyst weight, 0.5 g.

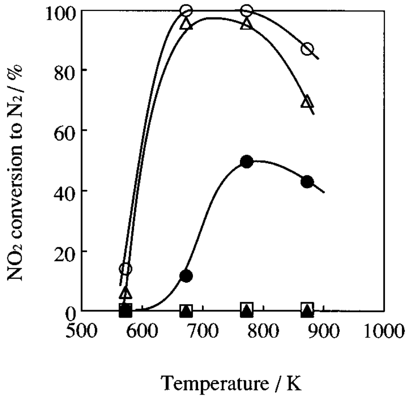

FIG. 3. NO_2 conversion to N_2 as a function of reaction temperature on In-containing catalysts: ○, In/H-ZSM-5; △, In_2O_3/H-ZSM-5; ▲, In_2O_3/Na-ZSM-5; □, In_2O_3, treated at 813 K. Also shown is the activity of H-ZSM-5 (●). Catalyst weight, 0.5 g.

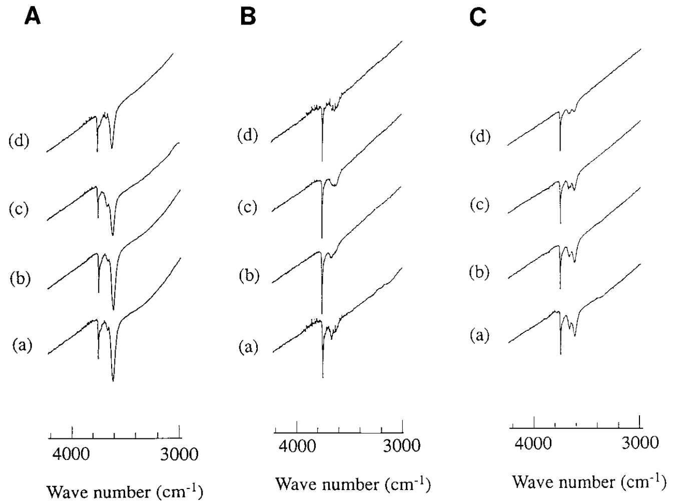

FIG. 4. IR spectra of OH groups on H-ZSM-5 (A), In/H-ZSM-5 (B), and In_2O_3/H-ZSM-5 (C). Heat treatment at (a) 823 K, (b) 873 K, (c) 923 K, (d) 973 K.

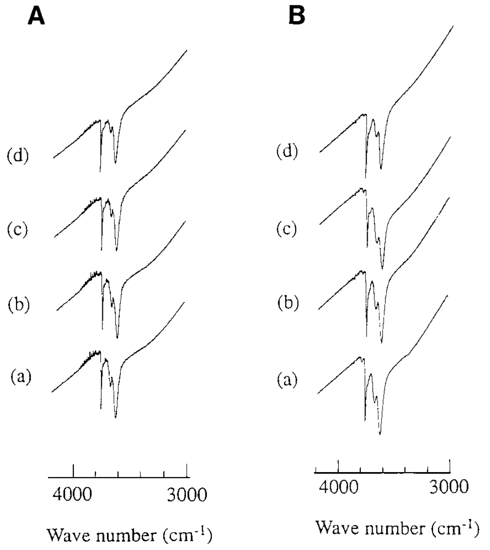

FIG. 6. IR spectra of OH groups on Ga/H-ZSM-5 (A) and Ga_2O_3/H-ZSM-5 (B). Heat treatment at (a) 823 K, (b) 873 K, (c) 923 K, (d) 973 K.

ZSM-5 and In/H-ZSM-5 were 87 and 83%, respectively, and they were considerably higher than those of H-ZSM-5 which were 41 and 51%, when treated at 823 and 923 K, respectively.

Infrared spectra in the region of OH groups on Ga/H-ZSM-5 and Ga_2O_3/H-ZSM-5 are shown in Fig. 6. The change in the intensity of acidic OH band on Ga/H-ZSM-5 with heat treatment was small compared with In/H-ZSM-5. Also, Ga_2O_3/H-ZSM-5 showed a similar intensity of OH band as H-ZSM-5, and the decrease by heat treatment temperature was observed a little more than that on H-ZSM-5, most of which may be attributed to the dehydration from the zeolite support. Both of these samples containing Ga species gave a small change in the intensity of acidic OH band on heat treatment, compared with the case of the samples containing In species. These results show that Ga species would hardly be ion exchanged into ZSM-5.

The effect of heat treatment on the catalytic activities of Ga-containing catalysts is shown in Fig. 7. The Ga_2O_3/-H-ZSM-5 catalyst also became more active with increasing heat treatment temperature, although the promotive effect was not remarkable compared with the case of In_2O_3/-H-ZSM-5. With increasing heat treatment temperature from 823 to 973 K, the selectivity of Ga_2O_3/H-ZSM-5 increased from 49 to 59%, which was still smaller than that of Ga/H-ZSM-5, that is 81%.

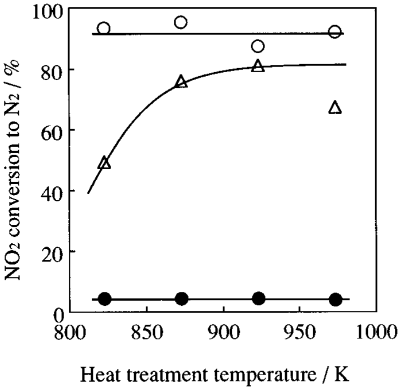

FIG. 5. Effect of heat treatment on the catalytic activities of In/H-ZSM-5 (○), In_2O_3/H-ZSM-5 (△), and H-ZSM-5 (●) for NO_2 reduction with CH_4. Catalyst weight, 0.1 g. Reaction temperature, 673 K. These catalysts were treated at individual temperatures in N_2 flow for 1 h.

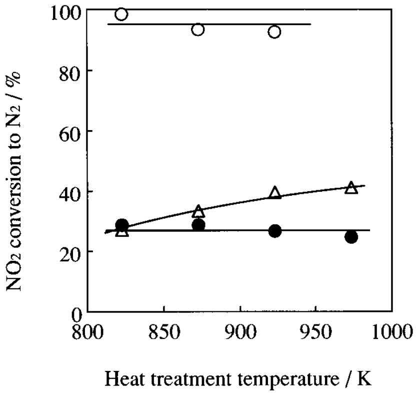

FIG. 7. Effect of heat treatment on the catalytic activities of Ga/H-ZSM-5 (○), Ga_2O_3/H-ZSM-5 (△), and H-ZSM-5 (●) for NO_2 reduction with CH_4. Catalyst weight, 0.1 g. Reaction temperature, 773 K. These catalysts were treated at individual temperatures in N_2 flow for 1h.

DISCUSSION

It was previously reported in our work (9) that Ga and In/H-ZSM-5 had high catalytic activities and selectivities for NO reduction with CH_4, and that two molecules of NO were stoichiometrically reduced by the consumption of one molecule of CH_4, as shown in reactions [1] and [2]. On the catalysts like Co (7) or Pd/H-ZSM-5 (10), CH_4 is oxidized not only by NO_2 but also by molecular oxygen at high temperatures, resulting in less selectivity for CH_4 consumption. On the other hand, only NO_2 can activate CH_4 on Ga and In/H-ZSM-5, so that the reduction of NO and NO_2 by CH_4 occurs selectively on these catalysts.

The difference in the catalytic properties between In/H-ZSM-5 and Ga/H-ZSM-5 was found in the selectivity for CO_2 and CO produced with N_2. In_2O_3/H-ZSM-5 behaved similarly to In/H-ZSM-5 as to this selectivity. It was found that the catalytic activity for NO reduction with CH_4 rapidly increased on the ion-exchange of In to H-ZSM-5, while the ratio in CO_2/CO in the product gradually increased with increasing amount of added In. These results show that the catalytic site for CO oxidation coexists with the active sites for NO reduction. As In_2O_3 is well-known to catalyze the oxidation of CO to CO_2, it is reasonable to consider that In/H-ZSM-5 contains a certain amount of In_2O_3 which catalyzes oxidation of CO to CO_2.

Ga_2O_3/H-ZSM-5, when treated at 823 K, gave a catalytic activity and selectivity for NO_2 reduction comparable to H-ZSM-5. The selectivity of this catalyst increased with increasing temperature of heat treatment. This means that more selective active sites were generated by the interaction between Ga_2O_3 and H-ZSM-5. According to Li and Armor, Ga-containing H-ZSM-5, even when prepared by the ion-exchange method, contains Ga_2O_3 precipitated on the outer surface of zeolite grains as the main species of Ga. It was found in this work, however, that Ga_2O_3 was inactive for the reaction of NO_2 with methane, as shown in Fig. 2. Therefore, it seems that Ga/H-ZSM-5 has a different type of sites active for NO_2 reduction, in addition to Ga_2O_3.

Similarly, In_2O_3 was inactive for the reduction of NO_2 with methane. In the case of In_2O_3/H-ZSM-5, however, the catalytic activity and selectivity were close to those of In/H-ZSM-5. A similar selectivity between these catalysts indicates a common active site for NO_2 reduction on these catalysts. In_2O_3 seems to interact with H-ZSM-5 more readily than Ga_2O_3. To understand the active site generated by the interaction between Ga_2O_3 or In_2O_3 with H-ZSM-5, it must be recalled that either Ga_2O_3 or In_2O_3 mixed with Na-ZSM-5 was catalytically inactive for this reaction. The formation of these sites requires the existence of zeolitic H^+ and Ga_2O_3 or In_2O_3.

The interaction between acidic OH groups and In_2O_3 was confirmed by IR measurements, as shown in Fig. 4. The OH band of In/H-ZSM-5 treated at 823 K was remarkably small, while In_2O_3/H-ZSM-5 treated at the same temperature showed the absorption band weaker than H-ZSM-5 and stronger than In/H-ZSM-5. Faster decrease in concentration of acidic OH groups on In_2O_3/H-ZSM-5 was observed than those on H-ZSM-5 when treated at higher temperatures. These results are indicative of the solid-state ion exchange reaction taking place between In_2O_3 and H-ZSM-5 to form $[InO]^+$ cation sites on H-ZSM-5, for instance as follows:

$$In_2O_3 + 2H^+ - Z^- \rightarrow 2[InO]^+ - Z^- + H_2O. \qquad [3]$$

This kind of interaction likely occurs with the incorporation of metal oxide into zeolite pores at high temperatures. Similar solid–solid interactions between various metal oxides and protonic zeolite have been reported for many systems. As for NO reduction, Wichterlová *et al.* (20) have reported that CuO interacts with NH_4–Y zeolite to form copper ions and/or Cu–O species incorporated into the zeolitic cationic sites via the exchange with the zeolite bridging OH groups, as shown by infrared spectroscopic data of decreasing OH band. The interaction resulted in a dramatic increase of the catalytic activity for $NO–NH_3–O_2$ reaction. In our work, the increase in the number of $[InO]^+$ site results in the enhancement of the catalytic activity and selectivity for NO_2 reduction, while the protonic sites of H-ZSM-5 give a low selectivity.

The increase in the number of $[GaO]^+$ or $[InO]^+$ site leads to the decrease in that of protonic acid site of the zeolite, as shown in Fig. 8. The OH band of In_2O_3/H-ZSM-5 treated at 823 K was much smaller as compared with that of H-ZSM-5. On the other hand, the OH band of In/H-ZSM-5 was smaller than that of In_2O_3/H-ZSM-5. This indicates that $[InO]^+$ sites were easily formed on H-ZSM-5 by ion exchange and solid-state ion exchange and that a large amount of $[InO]^+$ site was formed by ion exchange compared with

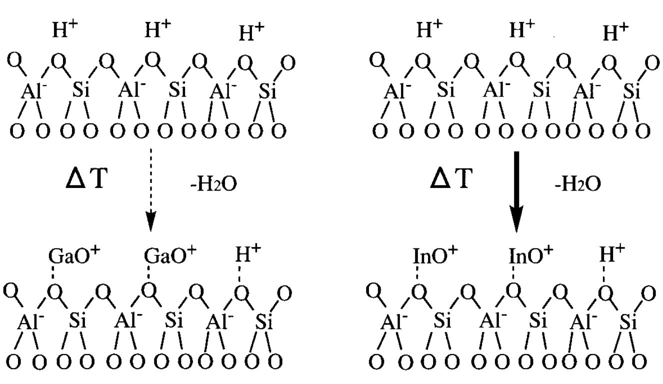

FIG. 8. Solid–solid exchange reaction between Ga_2O_3 (a) or In_2O_3 (b) and protonic acid site of zeolite.

solid ion exchange. However, the catalytic activities for NO_2 reduction on In/H-ZSM-5 and In_2O_3/H-ZSM-5 were similar (In_2O_3/H-ZSM-5 showed relatively low catalytic activity), while the selectivities of these catalysts for NO_2 reduction were equally high. These results lead us to conclude that the selective reduction of NO_2 with CH_4 takes place on a certain amount of $[InO]^+$ site.

We have already reported the information about the catalytic activity for NO oxidation on Ga and In ion-exchanged H-ZSM-5 as follows (9): The catalytic activity for NO oxidation on H/Na-ZSM-5 increased with increasing proton exchange level. Na-ZSM-5 was inactive for this reaction. The catalytic activity for NO oxidation decreased and the level of NO_2 conversion in the NO_2–CH_4 reaction increased with increasing Ga content. As In/H-ZSM-5 showed a similar performance to Ga/H-ZSM-5, therefore, we have concluded that NO reduction with CH_4 on Ga and In loaded H-ZSM-5 catalysts proceeds in the same reaction pathways (1) and (2). The reactions taking place on Ga or In/H-ZSM-5 can be summarized as follows:

$$NO + 1/2O_2 \rightarrow NO_2 \qquad \text{[on zeolite acid sites]} \qquad [1]$$

$$NO_2 + CH_4 + NO_x \rightarrow N_2 + CO_x + 2H_2O \quad (x = 1 \text{ or } 2)$$
$$\text{[on GaO}^+ \text{ or InO}^+ \text{ sites]} \qquad [2]$$

$$CO + O_2(\text{or } NO_2) \rightarrow CO_2$$
$$\text{[on Ga}_2\text{O}_3 \text{ or In}_2\text{O}_3 \text{ sites].} \qquad [4]$$

It seems that a certain amount of Ga or In is ion-exchanged as $[GaO]^+$ or $[InO]^+$ for instance, and this species is effective for NO_2 reduction with CH_4 and that some of Ga or In species exist as oxides (Ga_2O_3, In_2O_3) and especially In_2O_3 showed high catalytic activity for CO oxidation, and then different ratio of CO_2/CO during the reduction was observed between Ga and In/H-ZSM-5.

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