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Intrapore catalysis in reduction of nitric oxide with methane

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Abstract

Catalytic activities of In/H-ZSM-5 and Ir/In/H-ZSM-5 for selective reduction of NO with methane were investigated with in situ measurements of NO_x adspecies by FT-IR method under reaction conditions. The reaction proceeded in the following two stages: NO was oxidized to NO_2 on Ir and NO_2 was reduced to N_2 by CH_4 on InO^+. Studies on chemisorption of NO_x indicated that NO_2 chemisorbed on InO^+ sites is important for this reaction. Two intense NO_2 adspecies were observed at 1610 and 1575 cm^{-1} under the reaction conditions: one of these species at 1610 cm^{-1} is reactive with CH_4. These adspecies are assigned to nitro or nitrite species. Nitrates adsorbed on InO^+ (1450 cm^{-1}) and zeolite acid sites (1635 cm^{-1}) cannot consume CH_4. Chemisorption of NO_2 on InO^+ sites were shown by IR measurements to be a slow step on In/H-ZSM-5, while Ir accelerated the chemisorption of NO_2 on InO^+ not only on the outer surface but also in the pores of ZSM-5. It is concluded that bifunctional catalysis in identical zeolite pores, named "intrapore catalysis", brings forth high catalytic activity and selectivity.

Keywords: NO reduction; Methane; NO_x chemisorption; Intrapore catalysis

1. Introduction

Nitrogen oxides (NO_x) in the exhaust from automobiles and industries are one of the major threats to environmental quality. Such concerns about our environment have stimulated much extensive research on catalysts for SCR (selective catalytic reduction) of NO_x utilizing hydrocarbons as reductants. Cu-ZSM-5 and many other catalysts have been reported to show activity for SCR by various hydrocarbons, including methane [1–8]. The utilization of CH_4 has many advantages over other hydrocarbons, since this hydrocarbon can be found in most combustion exhausts, particularly in exhaust from the natural gas cogeneration system.

We have previously reported that indium ion-exchanged into H-ZSM-5 showed high catalytic activity for the CH_4-SCR [5]. Reduction of NO with CH_4 on the catalyst seems to proceed in two stages; firstly NO is oxidized to NO_2 and then NO_2 reacts with CH_4 into N_2. It has also been indicated [9] that NO oxidation on the acidic site of zeolite is strongly retarded by water vapor. On the other hand, InO^+ site, which is ion-exchanged in the zeolites [10], moderately catalyzed NO_2–CH_4 reaction even in the wet conditions. Addition of precious metals, particularly Ir which can catalyze NO oxidation in the wet condition, enhanced the catalytic activity of In/H-ZSM-5 for NO reduction [9,11]. It has been previously deduced [12,13] that the role of Ir is not only to enhance NO oxidation activity,

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but also NO_2 chemisorption. When Ir was added on In/H-ZSM-5, the amount of NO_2 adsorbed on InO^+ sites increased even though NO was admitted onto the catalyst with O_2 under the reaction conditions. The amounts of NO_2 chemisorbed on In/H-ZSM-5 and Ir/In/H-ZSM-5 are well correlated to the catalytic activities of these catalysts for NO and NO_2 reduction with CH_4. Therefore, adsorbed NO_2 on InO^+ sites is an important adspecies for NO reduction with methane. This work on the effect of Ir on the catalytic activity, investigated in terms of kinetics and NO_x chemisorption under the same experimental conditions, allowed us to deduce that these consecutive reactions take place bifunctionally on Ir and InO^+ in zeolite pores. We propose for such bifunctional reactions in a zeolite pore as "intrapore catalysis" [13]. The rate of overall reaction is enhanced by coexistence of consecutively working sites in identical pores of zeolite. However, it has not been clear whether the adsorbed NO_2 on InO^+ sites is involved in the reaction mechanism for NO reduction with CH_4. In this study, the reactivity of the NO_2 adspecies with CH_4 and the effect of intrapore catalysis on Ir/In/H-ZSM-5 will be investigated with a pressure swing adsorption method and in situ infrared spectroscopy from the viewpoint of NO_x chemisorption under the reaction conditions.

2. Experimental

In (4 wt%)/H-ZSM-5 and Ir (1 wt%)/H-ZSM-5 catalysts were prepared by the ion exchange of NH_4-ZSM-5 derived from Na-ZSM-5 (a molar SiO_2/Al_2O_3 ratio=23.8) supplied by Tosoh with aqueous solutions of $In(NO_3)_3$ (Mitsuwa Pure Chemicals) at 368 K for 8 h and $[IrCl(NH_3)_5]Cl_2$ (N.E. Chemcat) at room temperature for 24 h, respectively. 1 wt% Ir was loaded onto In/H-ZSM-5 by impregnating the In/NH_4-ZSM-5 with an aqueous solution of $[IrCl(NH_3)_5]Cl_2$. These catalysts were calcined at 813 K for 3 h prior to the reaction.

Reactions were carried out in a fixed bed reactor, connected to a diffuse-reflectance IR cell using a KBr window by passing a reactant gas mixture of 1000 ppm NO_x (NO or NO_2), 0 or 1000 ppm CH_4, and 10% O_2 in He at a rate of 100 cm^3 (STP) min^{-1} over 0.1 g of catalysts (GHSV=36 000 h^{-1}). The experimental apparatus used in this study is shown in Fig. 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. Reaction products were analyzed by means of on-line gas chromatography and chemiluminescence NO_x

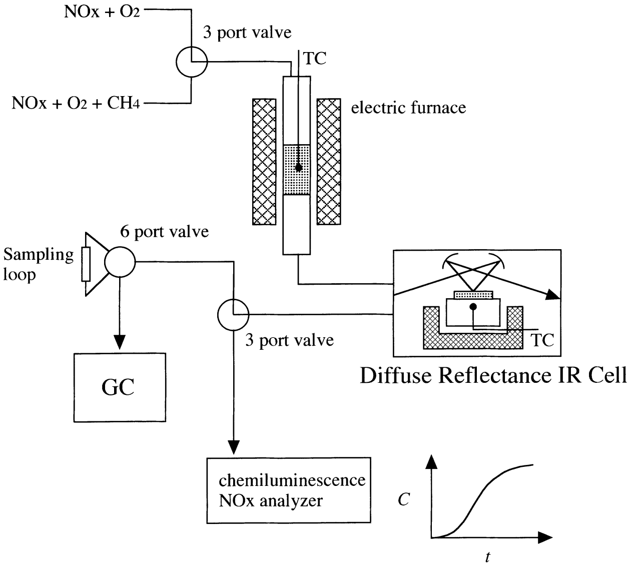

Fig. 1. Schematic diagram of experimental apparatus for simultaneous measurements of the activity and the adspecies on the catalyst.

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 conversion of NO_x into 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.

Infrared spectra were recorded with a Valor-III (JASCO) single-beam FT-IR spectrometer. 30 mg of a catalyst sample was set in a sample cup holder, and before recording a spectrum, the sample was heated up to 813 K at 10 K min^{-1}, calcined in a O_2 stream for 30 min, and then cooled to each reaction temperature. A spectrum was measured as a background before analysis of adspecies from NO_x–O_2 with or without CH_4 on the sample at each temperature. The spectra were collected with a resolution of 4 cm^{-1}.

Chemisorption of NO_x was measured by a pressure swing adsorption method reported in the literature [11–13] under the same conditions as those for reaction, using the same gas mixture as that for reaction excluding CH_4. The concentration of NO_x passing through the catalyst bed was detected using a NO_x analyzer (NOA-305 A, Shimadzu). The amount of adsorbed NO_x was calculated from a breakthrough curve. The curve through a catalyst was measured till the slope of the curve was below 5 mmol s^{-1}. The reactor used in this measurement was made of a quartz tube with 8 mm diameter and 25 cm long filled with glass beads to reduce dead volume, and NO_x adsorption did not completely occur in the absence of catalyst at the temperature tested. A time lag was not so significant that the amount of chemisorbed NO_x can be calculated within the experimental error.

3. Results

Fig. 2 shows the catalytic activities of H-ZSM-5, In/H-ZSM-5, Ir/H-ZSM-5, and Ir/In/H-ZSM-5 for NO reduction with CH_4. It has been reported that In/H-ZSM-5 shows high catalytic activity and selectivity for NO reduction with CH_4 at 673 K [5], as does H-ZSM-5 itself above 773 K [14]. In the temperature range used for this study, these activities were low, while the activity for NO_2 reduction on In/H-ZSM-5 was very high. These results mean that at a lower temperature H-ZSM-5 and In/H-ZSM-5 had low catalytic activity for NO oxidation, which is indispensable for the usage of CH_4 as a reductant on Ga, In, Co, and Pd loaded H-ZSM-5 catalysts [6–9]. Ir/In/H-ZSM-5 showed high catalytic activity for NO oxidation and NO reduction in the whole temperature range. Ir/H-ZSM-5, on the other hand, hardly catalyzed NO reduction but had high NO oxidation activity. This catalyst also exhibited catalytic activity for CH_4 com-

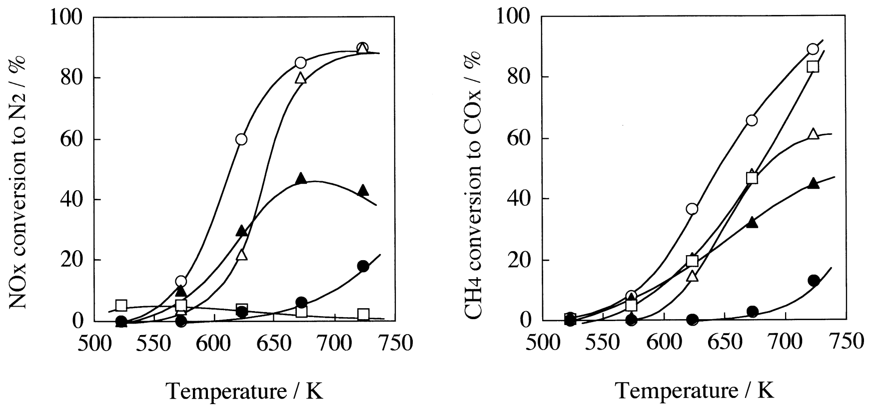

Fig. 2. Reduction of NO with CH_4 on H-ZSM-5 (●), In/H-ZSM-5 (▲), Ir/H-ZSM-5 (□), and Ir/In/H-ZSM-5 (○) catalysts, and of NO_2 with CH_4 on In/H-ZSM-5 (△). NO (or NO_2), 1000 ppm; CH_4, 1000 ppm; O_2, 10%; total flow rate, 100 cm^3 min^{-1}; catalyst weight, 0.1 g.

bustion with O_2 at a higher temperature. Therefore, the role of Ir on Ir/In/H-ZSM-5 is the acceleration of NO oxidation, not of NO reduction itself. CH_4 is selectively consumed for catalysts containing both Ir and InO^+ on H-ZSM-5. These results indicate that selective oxidation activity of NO is necessary for NO reduction with CH_4.

Infrared spectra of NO_x adsorbed on In/H-ZSM-5 and Ir/In/H-ZSM-5, which were measured in a static mode are shown in Fig. 3. These spectra were collected after adsorption of NO (or NO_2)+O_2 at room temperature, followed by evacuation at 623 K. For H-ZSM-5 and Ir/H-ZSM-5 no NO_2 adspecies were observed under this measurement condition. On In/H-ZSM-5 NO_x adspecies were seen when NO+O_2 was adsorbed at room temperature, but they were easily desorbed by evacuation at a high temperature of 623 K. In the case that NO_2+O_2 was adsorbed and the sample was evacuated, two bands were observed at 1619 and 1575 cm^{-1}. From the results of H-ZSM-5 and Ir/H-ZSM-5 it is observed that these catalysts had no peaks around the wavenumbers of 1619 and 1575 cm^{-1}, and these two species were attributed to chemisorbed NO_2 species on ion-exchanged InO^+ sites. Note that the same but more intense spectrum was obtained on Ir/In/H-ZSM-5 when NO+O_2 was admitted, and no other bands were observed. Addition of Ir to In/H-ZSM-5 had no effect on the wavenumber of the irreversibly chemisorbed NO_2 on InO^+. Thus, new NO_2 chemisorption sites are not created by interaction of Ir and In, such as an Ir–In alloy.

Fig. 4 shows the IR spectra during chemisorption of NO (spectra (a) and (d)) or NO_2 (spectra (b) and (c)) in the presence of O_2 at 623 K. It is apparent that almost no intense peaks were observed on H-ZSM-5 (spec-

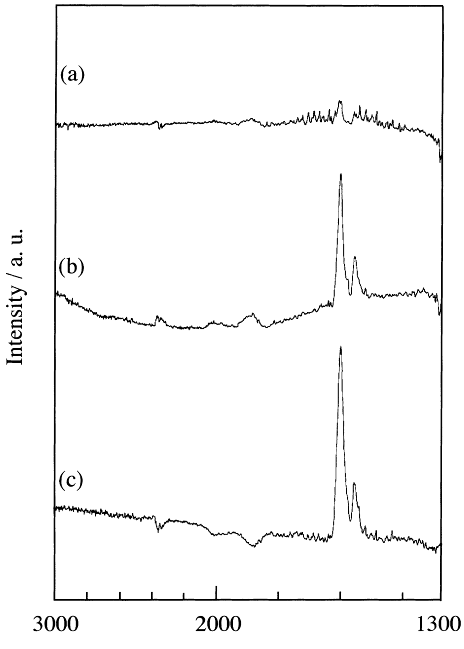

Fig. 3. Infrared spectra of (a) NO on In/H-ZSM-5, (b) NO_2 on In/H-ZSM-5, and (c) NO on Ir/In/H-ZSM-5. For all spectra, 1000 ppm NO_x with 10% O_2/balance He was admitted on to the catalyst at 100 cm^3 min^{-1} at room temperature for 30 min, followed by evacuation at 623 K for 10 min.

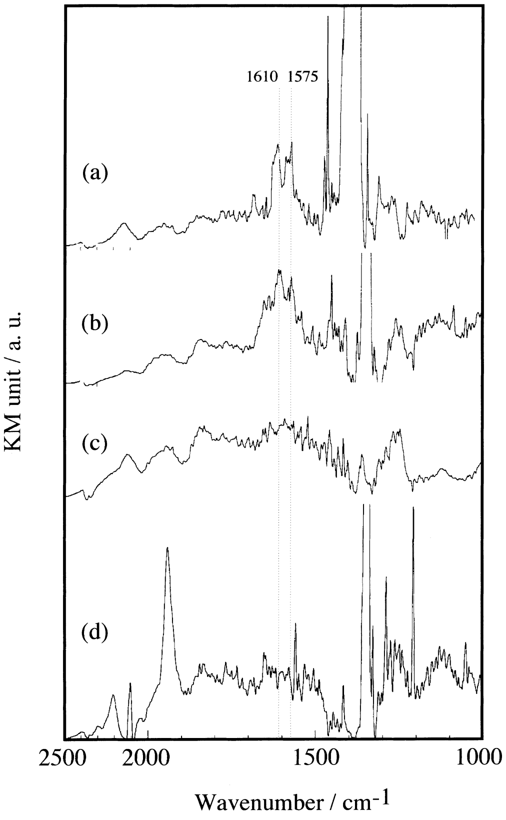

Fig. 4. Infrared spectra of (a) NO on Ir/In/H-ZSM-5, (b) NO_2 on In/H-ZSM-5, (c) NO_2 on H-ZSM-5, and (d) NO on Ir/H-ZSM-5. For all spectra, 1000 ppm NO_x with 10% O_2/balance He was admitted on to the catalyst at 100 cm^3 min^{-1} at 623 K.

trum (c)). In/H-ZSM-5 (spectrum (b)) and Ir/In/H-ZSM-5 (spectrum (a)) gave the same adspecies at around 1610 and around 1575 cm^{-1}, which were slightly shifted to lower wavenumbers than those observed in static measurements (Fig. 3). Under reaction conditions probably the same NO_2 adspecies on InO^+ sites were observed as were seen in Fig. 3. Additional peaks were obtained at 1635 and 1450 cm^{-1} on In/H-ZSM-5 and Ir/In/H-ZSM-5, and a sharp one at 1950 cm^{-1} on Ir/H-ZSM-5.

Fig. 5 shows the IR spectra during reduction of NO (spectra (a) and (d)) or NO_2 (spectra (b) and (c)) with CH_4 in the presence of O_2 at 623 K, which were taken after the measurements of Fig. 4, followed by mixing CH_4 in the reactant feed. When CH_4 was added to the reactant, a certain amount of N_2 was formed (see in Fig. 2). It can be observed that the peak at around 1610 cm^{-1} almost disappeared on Ir/In/H-ZSM-5, while that on In/H-ZSM-5 slightly decreased in intensity, compared with those in Fig. 4. Intensities of the peaks at 1635, 1559, and 1450 cm^{-1} were unchanged by addition of CH_4. On In/H-ZSM-5 and Ir/In/H-ZSM-5, no additional peaks to those in Fig. 4 were observed in this experimental condition. The NO_2 adspecies at 1610 cm^{-1} were recovered in intensity after CH_4 was excluded from the reactant feed. From these results, it can be deduced that chemisorption of NO_2, in particular NO_2 chemisorbed on InO^+, is important for NO reduction with CH_4, and that the adspecies at 1610 cm^{-1} is closely related to the important reaction intermediates to form N_2.

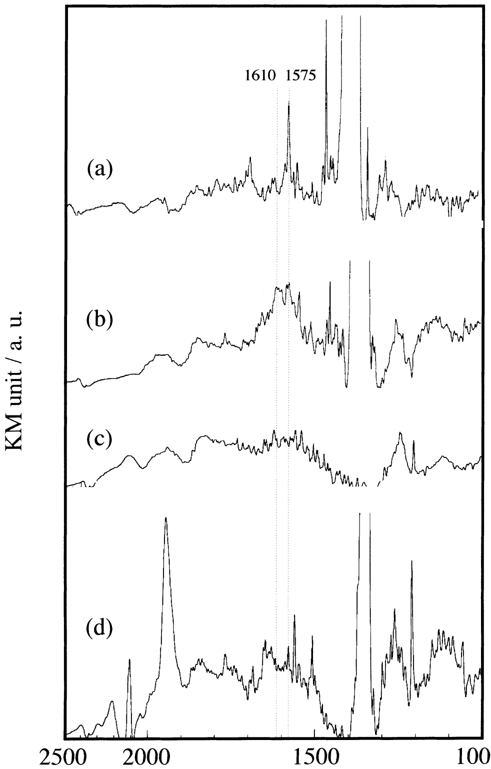

Fig. 5. Infrared spectra of (a) NO on Ir/In/H-ZSM-5, (b) NO_2 on In/H-ZSM-5, (c) NO_2 on H-ZSM-5, and (d) NO on Ir/H-ZSM-5. For all spectra, 1000 ppm NO_x with 1000 ppm CH_4 and 10% O_2/balance He was admitted on to the catalyst at 100 cm^3 min^{-1} at 623 K.

Fig. 6 shows the breakthrough curves measured downstream of the reactor and the time courses of NO_2 adspecies at 1610 cm^{-1} on In/H-ZSM-5 and Ir/In/H-ZSM-5. It has been previously reported in these PSA studies [13] that the effluent gas from In/H-ZSM-5 was mainly NO_2 and that from Ir/In/H-ZSM-5 was a mixture of NO and NO_2 in the same measurements. This result indicated that In/H-ZSM-5 had no catalytic activity for NO_2 decomposition to NO: almost all chemisorption sites of InO^+ were exposed by NO_2, and that Ir/In/H-ZSM-5 had high activity for NO oxidation to NO_2: all InO^+ sites were exposed by NO and NO_2. NO_x in the outlet from In/H-ZSM-5 was detected much earlier than that from Ir/In/H-ZSM-5. This means that NO_2 was adsorbed more on Ir/In/H-ZSM-5 than on In/H-ZSM-5, even though $NO+O_2$ gas was admitted onto Ir/In/H-ZSM-5. However, it took more time on In/H-ZSM-5 to reach the adsorptive equilibrium than on Ir/In/H-ZSM-5. It seems that diffusion of NO_2 in the zeolite structure is more difficult than that of NO, therefore NO_2 diffuses slowly through In/H-ZSM-5. Formation of NO_2 adspecies and the increase in intensity had dependence on time after admittance of NO_2 onto In/H-ZSM-5. It is worthy to note that the peak at 1610 cm^{-1} on Ir/In/H-ZSM-5 was more intense at the initial stage than that on In/H-ZSM-5, and that the intensity of this adspecies hardly changed for 1 h from admittance of $NO+O_2$. These results mean that NO_2 adspecies forms much more rapidly on Ir/In/H-ZSM-5 even though $NO+O_2$ is admitted, rather than on In/H-ZSM-5 on which NO_2 is admitted.

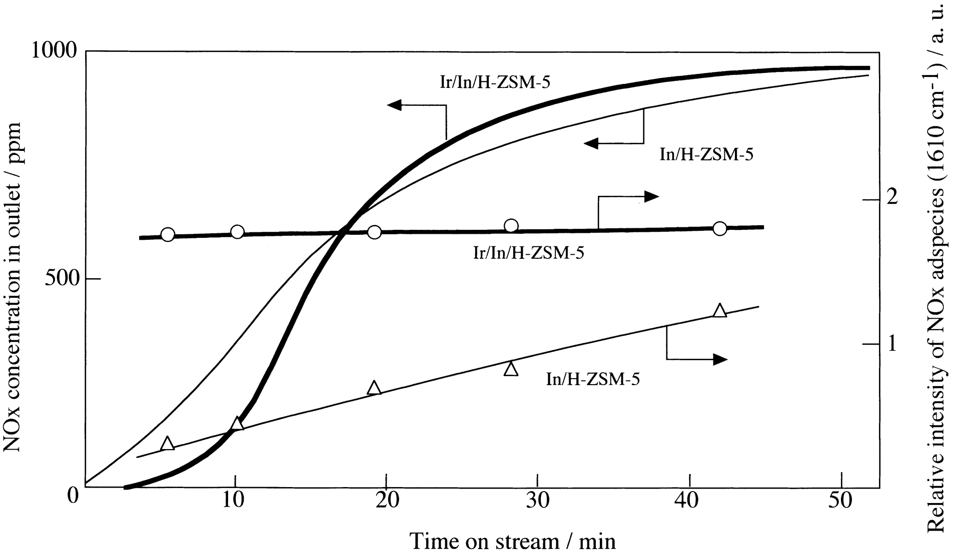

Fig. 6. Breakthrough curves of NO_x through In/H-ZSM-5 (feeding NO_2) and Ir/In/H-ZSM-5 (feeding NO), and the changes in intensity of NO_x adspecies (1610 cm^{-1}). 1000 ppm NO_x with 10% O_2/balance He was admitted on to the 0.1 g of catalyst at 100 cm^3 min^{-1} at 623 K.

4. Discussion

Table 1 shows the peak assignment of NO_x adspecies on In/H-ZSM-5 based catalysts. The observations of IR spectra suggest that two kinds of NO_2 species chemisorbed on InO^+ sites exist under the reaction conditions of NO_x+O_2 chemisorption. Furthermore, it is interesting to note that the reactivities of these two NO_2 adspecies with CH_4 seem to be different: the one observed at around 1575 cm^{-1} hardly react when CH_4 was involved in the reactant stream on In/H-ZSM-5, while the other at 1610 cm^{-1} slightly decreased. On Ir/In/H-ZSM-5, these two species almost disappeared with CH_4 addition. One peak remained at 1559 cm^{-1} on Ir/In/H-ZSM-5 is attributed to NO_2 adspecies on Ir sites. The peaks at 1635, 1570, and 1521 cm^{-1}, were formed when NO+O_2 or NO_2 was admitted onto every catalyst. Therefore, these species are assigned to NO_2 adspecies bonding directly to the support of ZSM-5 zeolite. There are two possibilities to determine the assignment of two NO_2 adspecies on InO^+ sites: one is that they are attributed to

Table 1
Peak assignments of NO_2 adspecies under reaction conditions on In/H-ZSM-5 based catalysts

	Wave number (cm^{-1})						
	1635	1610	1575	1570	1559	1521	1450
Ir/In/H-ZSM-5[a]	VS	S	S	VS	S	VS	S
In/H-ZSM-5[a]	VS	VS	VS	VS	None	VS	S
H-ZSM-5[a]	VS	None	None	VS	None	VS	None
Ir/H-ZSM-5[a]	m	None	None	m	S	m	None
In(NO_3)$_3$/H-ZSM-5[b]	VS	None	None	None	None	None	S
Assigment	NO_3^- on H^+	NO_2(ONO) on InO^+	NO_2 on InO^+	NO_2 on H^+	NO_2 on Ir	NO_2 on H^+	NO_3^-on InO^+

[a] From the results of Fig. 4.

[b] This sample was prepared by impregnation of H-ZSM-5 with In(NO_3)$_3$ solution, and the spectrum was measured at room temperature after evacuation at 363 K.

NO_2, such as nitro or nitrite species, and the other is that they are nitrate. Indium nitrate impregnated onto H-ZSM-5 gave two peaks: a broad one at 1635 and a sharp one at 1450 cm^{-1}. The former was observed on every catalyst, while the latter was on In/H-ZSM-5 and Ir/In/H-ZSM-5 under the reaction conditions. It seems that the latter is the nitrate on In cation, and the former is the one on acidic sites of ZSM-5 zeolite. It has been deduced in our previous work [12] that NO_2 chemisorbed on the catalysts is needed for the activation of CH_4, and that the concentration of NO_2 adspecies in the pores of zeolite is important for CH_4-SCR. Bulky nitrate species have difficulty to form in the zeolite pore structure, therefore a certain amount of indium nitrate might be formed on the outer surface of zeolite grains of In/H-ZSM-5 and Ir/In/H-ZSM-5. Since these nitrate species hardly consume CH_4, and they may be independent of the important reaction intermediate. From these results, the NO_2 adspecies involved in the reaction mechanism of NO reduction are proposed to be nitro or nitrite species. According to the literature [15], the peaks at 1650–1600 cm^{-1} are assigned to a nitrite species, and those at 1590–1530 cm^{-1} to a nitro species. NO_2 adspecies on InO^+ sites at 1610 cm^{-1} may be a nitrite species. Sachtler and co-workers [8] have claimed that the only nitrite species on Co-ZSM-5 can activate CH_4, while nitrate species formed on Cu-ZSM-5 cannot. However, $-NO_2$ and –ONO chemisorbed on InO^+ sites cannot be distinguished from each other. Further information is needed to assign the two NO_2 bands to specific sorbed intermediates, such as those in the consideration from some computational studies [16] that, in the case of GaO^+ in ZSM-5, N atom in NO_2 molecule is bound to an extraframework oxygen atom, which is the one in GaO^+, and O atom in NO_2 molecule is attached to Ga cation.

The role of Ir in Ir/In/H-ZSM-5 is not only to accelerate the rate of NO oxidation. It was previously mentioned that the amount of NO_2 chemisorbed on InO^+ sites was increased by addition of Ir to In/H-ZSM-5. From the results of PSA studies, it has been shown that NO diffuses easily into zeolite pore structure, while NO_2 diffuses more slowly. Ir also catalyzed NO_2 decomposition to NO: therefore, most of NO_x in the zeolite porous structure of Ir/In/H-ZSM-5 is NO and NO_2 is concentrated only around the InO^+ sites. Formation rate of NO_2 adspecies on InO^+ sites was found in this study to be more rapid on Ir/In/H-ZSM-5 than on In/H-ZSM-5, even though NO was admitted onto the former with O_2. Studies of Ir dispersion with H_2 chemisorption at room temperature [13] and TEM observation led us to deduce that Ir is located not only on outer surface of the zeolite, but inside the pore structures of zeolite. The siting of InO^+ was not affected by Ir: indium can be easily ion-exchanged and highly dispersed into the zeolite H^+ sites, as has been shown in our previous work [10]. This means that highly dispersed Ir inside the zeolite pores highly catalyzes the oxidation of NO, which diffuses fast into the zeolite structure, followed by the chemisorption of NO_2 on InO^+ sites even in the zeolite pores. Desorbed NO_2 could be easily decomposed by Ir; therefore Ir and InO^+ might locate closely, that is, in the identical pore.

The NO_2 adspecies on InO^+ sites showed reactivity with CH_4: NO_2 adspecies might play an important role to form an important reaction intermediate subsequently. Other investigations have claimed that the adspecies as R–NO_2 (R is an organic compound) [17], –CN [18,19], or –NCO [20,21] are important intermediates for HC-SCR. These species may form during NO_x reduction in this study. NO_2 adspecies needs one more molecule of NO_x to form N_2. During NO–CH_4–O_2 reaction on Ir/In/H-ZSM-5, easily diffusible CH_4 and NO are likely to attack NO_2 adspecies or the intermediate, so that NO_2 adspecies almost disappeared and a large amount of N_2 was formed (see in Fig. 2). On the other hand, during NO_2–CH_4–O_2 reaction on In/H-ZSM-5 there is no NO available. In the case that the rate-determining step exists in the reaction between NO_2 and the intermediate to form N_2, the intermediate is detectable on In/H-ZSM-5. However, no additional peaks were observed under the NO_x reduction conditions used in this study, even in the region around 2500–3000 cm^{-1}, where the absorption band attributed to C–H bond can be observed. It can be deduced from the results of this study that the rate-determining step is a cleavage of C–H bond of gaseous CH_4 with chemisorbed NO_2 on InO^+ sites on In/H-ZSM-5, as has been shown by Cant and co-workers [6] on Co-ZSM-5.

As a result of this study, IR observations strongly support our deduction of bifunctional catalysis, named ‘‘intrapore catalysis’’. It is possible to design a better catalyst by supporting two separate catalytic components more intimately. Microporous zeolites may be more appropriate than macroporous oxide supports in this sense.

5. Conclusions

The roles of Ir in Ir/In/H-ZSM-5, investigated with in situ IR measurements under the reaction conditions, are not only to accelerate the rate of NO oxidation, which is an indispensable step for CH_4-SCR. Two intense peaks, attributed to NO_2 adspecies on InO^+ ion-exchanged sites, are observed even under the reaction conditions of NO_x chemisorption and NO_x reduction. NO_2 adspecies at $1610\,cm^{-1}$ is reactive with CH_4: it almost disappeared on Ir/In/H-ZSM-5 when CH_4 is involved in the reactant feed, while a slight decrease in intensity was observed on In/H-ZSM-5. Nitrate species on InO^+ or on zeolite acid sites hardly consumes CH_4. The reactive NO_2 species are formed more rapidly on Ir/In/H-ZSM-5 than on In/H-ZSM-5. Ir in Ir/In/H-ZSM-5 allows NO to form the NO_2 adspecies rapidly on InO^+ sites even in the zeolite pore structures.

Acknowledgements

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