Dependence of selective reduction of NO with C_3H_6 on acid properties of ion-exchanged zeolites

Atsushi Satsuma [1], Kenji Yamada, Tokuharu Mori, Miki Niwa [2],
Tadashi Hattori and Yuichi Murakami

Department of Applied Chemistry, School of Engineering, Nagoya University,
Furo-cho, Chikusa-ku, Nagoya 464-01, Japan

Received 14 September 1994; accepted 11 January 1995

The effect of amount and strength of acid sites on the activity and selectivity for the selective reduction of NO with C_3H_6 in the presence of excess oxygen over H-form and ion-exchanged zeolites has been investigated. The activity was found to be proportional to the acid amount determined by NH_3-temperature programmed desorption, but independent of the acid strength of the zeolites. The selectivity, i.e., the ratio of the reduction of NO with C_3H_6 to the oxidation of C_3H_6 by O_2, was independent of the amount and strength of acid sites.

Keywords: nitrogen monoxide; selective reduction; propene; oxidizing atmosphere; H-form zeolite; ion-exchanged zeolite; acid amount; acid strength

1. Introduction

Much attention has been paid to the removal of NOx from the exhaust, especially to the selective reduction of NO with hydrocarbons by using ion-exchanged zeolites, such as Cu-ZSM-5 [1,2], Ce/ZSM-5 [3,4], Ga/ZSM-5 [5,6], Co/ZSM-5 [7] and so on. Since the loaded cations can be regarded as the active species of the reduction of NO, there are many investigations focused on the role of loaded metal cations, especially redox properties [8–13], and on the reaction mechanism over those exchanged ions [14–19]. On the other hand, acid sites of parent zeolites are expected to play an important role for the reaction. Hamada and co-workers [20,21] reported the high activity of mixed oxides and solid superacid catalysts on the reduction of NO with hydrocarbons, and claimed that the amount of acid sites is the essential factor for the reaction. Li and Armor [22] pointed out that as well as in the oxide catalysts Brønsted acid sites in Ga-HZSM-5 are also essential for the

---

[1] To whom correspondence should be addressed.

[2] Present address: Department of Material Science, Faculty of Engineering, Tottori University, Tottori 680, Japan.

reaction. Yogo et al. [23] reported the selectivity of NO reduction with CH_4 depends on the amount of acid sites of H-form zeolites. However, the knowledge of the role of acid sites is still limited, i.e., the amount and strength of acid sites have not been quantitatively correlated to the activity and selectivity.

The aim of this study is to reveal the quantitative correlation between the acid sites of H-form and ion-exchanged zeolites and the activity and selectivity for the reduction of NO with C_3H_6 in the presence of excess oxygen. In order to eliminate redox properties of the loaded cations, exchanged cations have been restricted to alkaline earth, Ga and La.

2. Experimental

The profile of the catalysts examined in the present study is summarized in table 1. H-mordenites, HM(10), HM(15) and HM(20), and HZSM-5(76) were supplied from the Committee on Reference Catalyst of Catalysis Society of Japan. Norton 100H was commercially supplied and HZSM(42) was prepared by a method described in the Mobil patent. Numbers in parentheses in the catalyst symbols represent the SiO_2/Al_2O_3 ratio. Ion-exchanged mordenites were prepared by ion-exchange of HM(15) at 353 K for 24 h using an aqueous solution of acetate or nitrate. The amount and strength of acid sites were determined from NH_3-TPD spectra by using a conventional apparatus [24]. After the evacuation at 773 K for 30

Table 1
List of catalysts

Catalyst	Parent zeolite	SiO_2/Al_2O_3 ratio	Ion exchange	
			degree of exchange (%)	source material
HM(60)	Norton100H	59.5	–	HCl[a]
HM(20)	JRC-Z-HM20[d]	19.9	–	–[b]
HM(15)	JRC-Z-HM15[d]	14.9	–	–[b]
HM(10)	JRC-Z-HM10[d]	9.9	–	–[b]
HZSM-5(76)	JRC-Z5-70H	76.4	–	–[b]
HZSM-5(42)	prepared[c]	41.8	–	–[c]
LaHM	JRC-Z-HM15[d]	14.9	41.8	$La(CH_3COO)_3$
GaHM	JRC-Z-HM15[d]	14.9	54.2	$Ga(NO_3)_3$
BaHM	JRC-Z-HM15[d]	14.9	44.5	$Ba(CH_3COO)_2$
SrHM	JRC-Z-HM15[d]	14.9	44.0	$Sr(CH_3COO)_2$
CaHM	JRC-Z-HM15[d]	14.9	45.8	$Ca(CH_3COO)_2$

[a] Dealuminated with aqueous solution of HCl.
[b] Protonated before supply.
[c] Prepared by a method described in the Mobil patent.
[d] Reference catalysts supplied from Catalysis Society of Japan.

min, the catalyst was exposed to 13 kPa of NH_3 at 373 K, followed by evacuation at 373 K for 5 h. Then, the measurement was made from 373 K with a heating rate of 10 K min^{-1} and with He as a carrier gas having a flow rate of 60 cm^3 min^{-1} until ammonia was desorbed completely [25].

The NO–C_3H_6–O_2 reaction was carried out in a conventional continuous-flow apparatus at atmospheric pressure. A mixture of 940 ppm NO, 288 ppm C_3H_6 and 6.6% O_2 diluted with He was fed to 0.5 g of catalyst at a rate of 42.2 cm^3 min^{-1}, corresponding to a space velocity equal to 3600 h^{-1}. Effluent gases were analyzed after reaching steady state by means of gas chromatography, and a good carbon balance was achieved without HZSM-5 and HM(60).

3. Results and discussion

Fig. 1 shows a typical result of the NO–C_3H_6–O_2 reaction as a function of the reaction temperature. Conversion of NO into N_2 increased with the reaction temperature, showed the maximum at 673 K, and then decreased with further increase in temperature. The conversion of C_3H_6 was complete above 673 K. Similar results have been observed on the other ion-exchanged zeolites [10, 26–28] and oxide catalysts [21]: N_2 yield decreased at high temperature. In these cases, since the conversion of hydrocarbon was complete at high temperature, the decrease in N_2 yield at high temperature can be attributed to the selective oxidation of hydrocarbon with O_2 in comparison with the reaction of hydrocarbon with NO.

As shown in the figure, a good carbon balance was achieved. Although similar results were obtained for most catalysts, the carbon balance was only around 60%

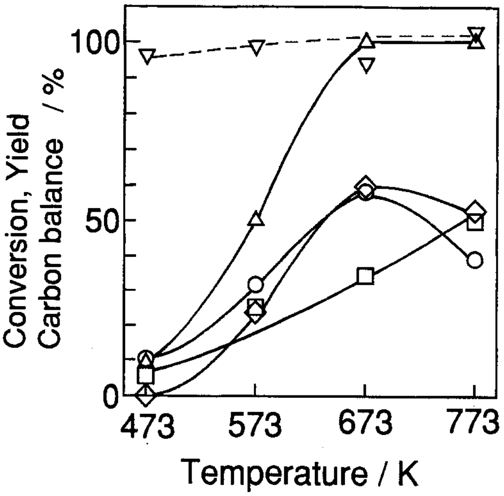

Fig. 1. Temperature dependence of catalytic activity on reduction of NO with C_3H_6 with excess oxygen over HM(15). N_2 yield (○), C_3H_6 conversion (△), CO_2 yield (□), CO yield (◇) and carbon balance (▽).

below 573 K over high silica zeolites, i.e., HZSM-5(76), HZSM-5(42) and HM(60). In separate experiments, formation of aromatic compounds, such as benzene, toluene, naphthalene, was observed below 673 K, indicating C_3H_6 was consumed over these high silica zeolites through other reactions such as aromatization and oligomerization. Another remark on the catalytic run is the change in color of the catalyst sample during the reaction. All the samples of HM were darkened after the catalytic run, indicating the deposition of carbonaceous materials. While, in the case of HZSM-5 and ion-exchanged HM, noticeable color change was not observed.

Fig. 2 compares the activities of various zeolites for the reduction of NO. Ion-exchanged zeolites showed higher activity than H-form mordenites, and siliceous zeolites showed only poor activity. The activity at 573 K was in the following order; CaHM > SrHM = BaHM > LaHM = GaHM > HZSM(42) = HM(10) = HM(20) = HM(15) > HZSM(76) > HM(60). The decrease in the activity of ion-exchanged mordenites and H-form mordenites above 673 K can be attributed to the consumption of C_3H_6, as shown in fig. 1. It should be noted that Ga-exchanged zeolite was the most active catalyst at higher temperature (673 K), although C_3H_6 was completely consumed, similarly to the results reported by Yogo et al. [5,6] and Armor et al. [22].

Fig. 3 shows the NH_3-TPD profiles on HM(15) and CaHM before and after the $NO–C_3H_6–O_2$ reaction. Solid lines in the figure represent the profiles before the $NO–C_3H_6–O_2$ reaction. In the case of HM(15), two peak maxima were observed at 470 and 780 K. When the time of evacuation after the adsorption of NH_3 was varied from 1 to 5 h, only the peak at 470 K was remarkably decreased, but that at high temperature remained unchanged. Niwa et al. also reported that the amount

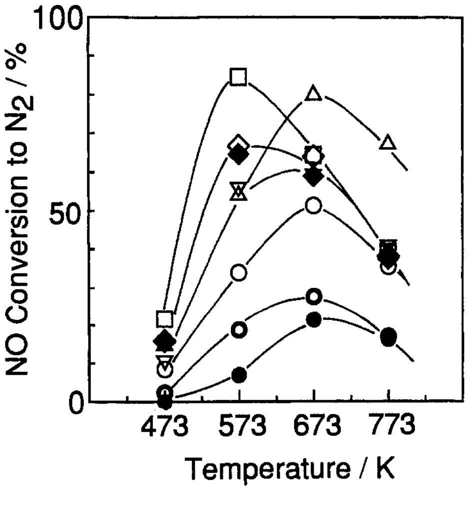

Fig. 2. Comparison of activity of $NO–C_3H_6–O_2$ reaction over H-form and ion-exchanged zeolites. HM(10) (○), HM(60) (●), HZSM(76) (○), CaHM (□), SrHM (◇), BaHM (◆), GaHM (△), LaHM (▽).

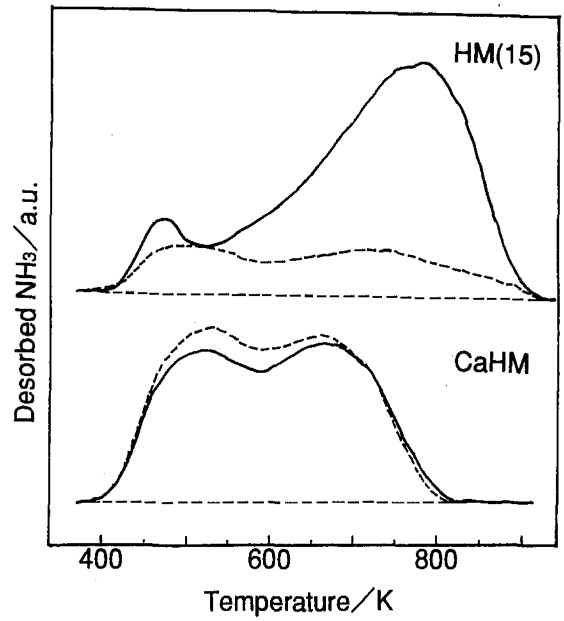

Fig. 3. NH_3-TPD profiles of HM(15) and CaHM before (——) and after (- - -) the $NO–C_3H_6–O_2$ reaction.

of the peak at lower temperature varies with the contact time *W*/*F* [27]. Thus, the peak around 470 K should arise from weakly adsorbed NH_3, and the peak at higher temperature can be regarded as NH_3 strongly chemisorbed on strong acid sites of zeolites. In order to reduce the low temperature peak in TPD profiles, the adsorbed NH_3 was evacuated for 5 h at 373 K hereafter. In the case of CaHM, two peak maxima were observed at 530 and 675 K, even after the elimination of the low temperature peak by evacuation for 5 h. The peak at 530 K indicates the existence of acid sites having moderate strength, which may be generated by the effect of exchanged Ca-ion. According to the results of NH_3-TPD, summarized in table 2, zeolite samples used in the present study can be classified into three groups: (1) HM, LaHM and GaHM having only strong acid sites, (2) HZSM-5 also having only one kind of acid sites which are slightly weaker than those of group 1 zeolites, and (3) alkaline earth ion-exchanged mordenites having moderate and strong acid sites.

Dashed lines in fig. 3 show the NH_3-TPD profiles of HM(15) and CaHM after the $NO–C_3H_6–O_2$ reaction. The amount of desorbed NH_3 was significantly decreased in the case of HM(15). Similar results were observed on the other H-mordenites which changed their colors during the reaction due to coke deposition. In the case of CaHM which changed its color only slightly, however, the TPD-profile after the reaction agreed well with that of fresh catalysts, as shown in fig. 3.

Fig. 4 shows the dependence of the activity for NO reduction at 573 K on the acid amount determined by NH_3-TPD method. Except for H-form mordenites, the

Table 2
Results on NH_3-temperature programmed desorption

Catalyst	Desorbed ammonia (mmol g^{-1})				$T_{\max}$ [a] (K)		Al content (mmol g^{-1})
	temperature		high + moderate	after reaction	moderate	high	
	moderate	high					
HM(60)	none	0.33	0.33	0.10	none	670	0.51
HM(20)	none	0.98	0.98	0.38	none	730	1.34
HM(15)	none	1.43	1.43	0.63	none	780	1.73
HM(10)	none	1.28	1.28	0.63	none	710	2.43
HZSM-5(76)	none	0.29	0.29	–[b]	none	610	0.38
HZSM-5(42)	none	0.47	0.47	–[b]	none	625	0.63
LaHM(15)	none	0.67	0.67	–[b]	none	690	1.73
GaHM(15)	none	1.06	1.06	–[b]	none	725	1.73
BaHM(15)	0.39	0.60	0.99	–[b]	520	675	1.73
SrHM(15)	0.50	0.59	1.09	–[b]	550	685	1.73
CaHM(15)	0.55	0.65	1.20	1.20	530	675	1.73

[a] Temperature at peak maxima.

[b] Not measured because of only a little change in the color of samples after the reaction.

activity of NO reduction increased in proportion to the acid amount. In most cases, colors of the catalysts were changed only slightly after the reaction and TPD-profiles after the reaction were essentially similar to those before the reaction. On the other hand, H-form mordenites were highly darkened after the reaction and the acid amount was remarkably decreased, as shown in fig. 3 and table 2. These results indicate that lower activities of H-form mordenites are due to the blockage of acid sites by carbonaceous materials. Solid circles in the figure represent the relation between the activity and the acid amount of these catalysts after the reaction. As shown, the solid circles agree well with the solid line correlating the activity and the acid amount of the other zeolites, although zeolite samples have been classified into three groups according to their acid strength. Thus, it can be concluded that the activity for NO reduction with C_3H_6 simply depends on the amount of acid sites of zeolites in the working state.

For the discussion of the selectivity of NO reduction, a simple parameter, (conversion of NO)/(conversion of hydrocarbon), has been used by Yogo et al. [5,6] and Hall et al. [28]. Li and Armor used a parameter α which was defined as the fraction of the reductant (CH_4) that is used up to reduce NO to N_2 [22]. These parameters may be useful to know the efficiency of the hydrocarbons for the reduction of NO, irrespectively of the ratio of CO to CO_2 formed. The present reaction, however, can be regarded as competitive oxidation of hydrocarbon by NO and O_2. The

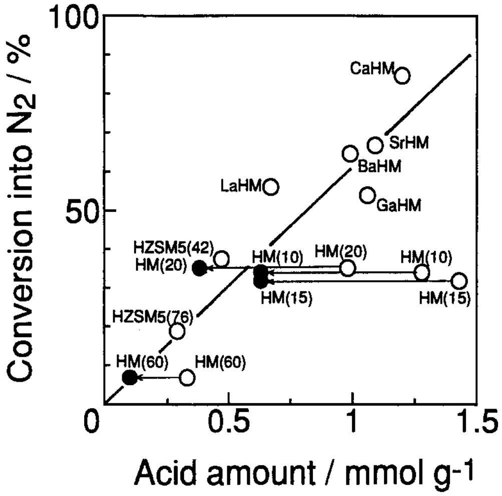

Fig. 4. Catalytic activity of the reduction of NO with C_3H_6 at 573 K as a function of acid amount of various zeolites measured by NH_3-TPD before (open symbols) and after (closed symbols) the reaction.

amount of consumed NO is equal to twice of N_2 formed and that of consumed oxygen atom to $2CO + 3CO_2$, as can be seen from the following stoichiometry:

$$C_3H_6 + 6O \rightarrow 3CO + 3H_2O \tag{1}$$

$$C_3H_6 + 9O \rightarrow 3CO_2 + 3H_2O \tag{2}$$

$$C_3H_6 + 6NO \rightarrow 3N_2 + 3CO + 3H_2O \tag{3}$$

$$C_3H_6 + 9NO \rightarrow \tfrac{9}{2}N_2 + 3CO_2 + 3H_2O \tag{4}$$

Thus, the ratio of $2N_2/(2CO + CO_2)$ represents the reactant selectivity of NO in C_3H_6 oxidation. In the case of 100% selective oxidation of C_3H_6 with NO, i.e., only reactions (3) and (4) occur, the ratio should be equal to unity. When O_2 is simultaneously used, the ratio should be decreased. Fig. 5 shows the rate of formation of $2N_2$ as a function of the rate of formation of $2CO + 3CO_2$. The dashed line stands for the relation: rate($2N_2$) = rate($2CO + 3CO_2$), representing 100% reactant selectivity of NO. All the plots are lower than the broken line, indicating that O_2 is also used for the oxidation of C_3H_6.

A linear correlation was observed between the formation of N_2 and carbon oxides with a few exceptions, suggesting the selectivity is independent of the acid amount and acid strength of zeolites. HZSM-5(76) and HM(60) showed rather low selectivity which may be related to the formation of aromatic compounds. On the other hand, GaHM and CaHM showed rather high selectivity of NO reduction. The solid line in fig. 5 corresponds to 30% reactant selectivity of NO, or, in other

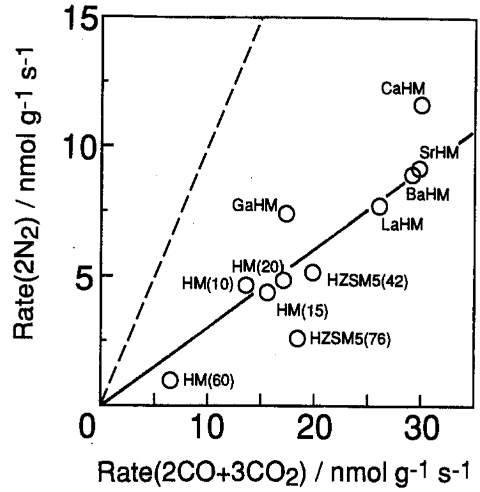

Fig. 5. Correlation between the rate of produced $2N_2$ and $2CO + 3CO_2$ at 573 K. Dashed line represents the 100% selective reduction of NO with C_3H_6.

words, the molar ratio of NO/O_2 consumed is close to unity. In the case of GaHM and CaHM, the selectivity was improved up to 40–45%, which partly agreed with previous papers reported by Yogo et al. [5,6] and Armor et al. [22] that Ga-ZSM-5 shows high selectivity for the reduction of NO with lower alkanes. Since there was no correlation between the promotion effect on selectivity and the acid properties, this promotion effect on the selectivity may be due to the function of exchanged cations.

4. Conclusion

The effect of the acid properties on the activity and selectivity of the reduction of NO with C_3H_6 can be summarized as follows:

(1) The activity depends on the acid amount of zeolites, but not on the acid strength.

(2) The acid properties of zeolites are not major factors determining the selectivity of the reduction of NO with C_3H_6.

References

[1] W. Held, A. Konig, T. Richter and L. Pupper, SAE Paper 900496 (1990).
[2] S. Sato, Y. Tu-u, H. Yahiro, N. Mizuno and M. Iwamoto, Appl. Catal. 70 (1991) L1.
[3] M. Misono and K. Kondo, Chem. Lett. (1991) 1001.
[4] C. Yokoyama and M. Misono, Chem. Lett. (1992) 1669.
[5] K. Yogo, S. Tanaka, M. Ihara and E. Kikuchi, Chem. Lett. (1992) 1025.

[6] K. Yogo, M. Ihara, I. Terasaki and E. Kikuchi, Appl. Catal. B 2 (1993) L1.

[7] Y. Li and J.N. Armor, Appl. Catal. B1 (1992) L31.

[8] J. Valyon and W.K. Hall, Catal. Lett. 19 (1993) 109.

[9] D.J. Liu and H.J. Robota, Catal. Lett. 21 (1993) 291.

[10] Y. Li and J.N. Armor, Appl. Catal. B 2 (1993) 239.

[11] E.S. Shpiro, W. Grunert, R.W. Joyner and G.N. Baeva, Catal. Lett. 24 (1994) 159.

[12] G. Spoto, A. Zecchina, C. Bordiga, G. Ricchiardi, G. Martra, G. Leofanti and G. Petrini, Appl. Catal. B 3 (1994) 151.

[13] J.O. Petunchi and W.K. Hall, Appl. Catal. B 3 (1994) 239.

[14] M. Sasaki, H. Hamada, Y. Kintaichi and T. Ito, Catal. Lett. 15 (1992) 297.

[15] J.O. Petunchi, G. Sill and W.K. Hall, Appl. Catal. B 2 (1993) 303.

[16] J.L. d'Itri and W.M.H. Sachtler, Appl. Catal. B 2 (1993) L7.

[17] J.O. Petunchi and W.K. Hall, Appl. Catal. B 2 (1993) L17.

[18] R. Burch and P.J. Millington, Appl. Catal. B 2 (1993) 101.

[19] G.P. Ansell, A.F. Diwell, S.E. Golunski, J.W. Hayes, R.R. Rajaram, T.J. Truex and A.P. Walker, Appl. Catal. B 2 (1993) 81.

[20] Y. Kintaichi, H. Hamada, M. Tabata, M. Sasaki and T. Ito, Catal. Lett. 6 (1990) 239.

[21] H. Hamada, Y. Kintaichi, M. Tabata, M. Sasaki and T. Ito, Chem. Lett. (1991) 2179.

[22] Y. Li and J.N. Armor, J. Catal. 145 (1994) 1.

[23] K. Yogo, M. Umeno, H. Watanabe and E. Kikuchi, Catal. Lett. 19 (1993) 131.

[24] R.J. Cvetanovic and Y. Amenomiya, Adv. Catal. 17 (1967) 103.

[25] M. Sawa, M. Niwa and Y. Murakami, Zeolites 10 (1990) 307.

[26] Y. Teraoka, H. Ogawa, H. Furukawa and S. Kagawa, Catal. Lett. 12 (1992) 361.

[27] R. Gopalakrishnan, P.R. Stafford, J.E. Davidson, W.C. Hecker and C.H. Bartholomew, Appl. Catal. B 2 (1993) 165.

[28] F. Witzel, G.A. Sill and W.K. Hall, Stud. Surf. Sci. Catal. 84 (1994) 1531.

[29] M. Niwa, M. Iwamoto and K. Segawa, Bull. Chem. Soc. Jpn. 59 (1986) 3735.