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Iron ion-exchanged zeolite: the most active catalyst at 473 K for selective reduction of nitrogen monoxide by ethene in oxidizing atmosphere

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Among various metal ion-exchanged zeolites, metal loading alumina, and oxides, iron ion-exchanged mordenite was the most active for the selective reduction of nitrogen monoxide to nitrogen by ethene in the presence of oxygen at the temperature as low as 473 K. The catalytic activities of iron ion-exchanged zeolites depended on the zeolite structure and the iron ion exchange level. The effects of the zeolite structure are in the order of MOR > FER > MFI > Y > LTL at 473 K. The activity of iron ion-exchanged mordenite increased with the increment in the exchange level and levelled off above about 60%.

Keywords: Nitrogen monoxide; selective reduction; iron; mordenite

1. Introduction

The removal of nitrogen oxides, especially nitrogen monoxide (NO), from the exhaust is a reaction of social interest. It is well known that the real exhaust gas except that from the usual gasoline engine contains a large quantity of oxygen and it competes with NO for adsorption sites or active sites for catalytic removal of NO. Therefore, no suitable catalysts of sustained high activity have been found for the removal of NO through decomposition or reduction by CO or hydrocarbon [1,2] in O_2. It has widely been accepted that ammonia is only reductant to yield N_2 selectively in the presence of O_2 [3]. Recently we [4,5] and Held et al. [4] independently reported that the selective catalytic reduction of NO by hydrocarbons is possible even in an oxidizing atmosphere. Afterwards, many catalysts have been revealed to be active for this reaction; for example, copper ion- [4–6], proton- [7], cobalt ion- [8], or cerium ion- [9] exchanged zeolites, Fe-silicate [10], alumina [11,12], and silica-alumina [13]. Among these catalysts, copper ion-exchanged ZSM-5 zeolite is the most active at the temperature as low as 573 K [4]. However, the temperature of 573 K is higher than those of exhaust gases from diesel and lean-burn gasoline engines in a state of idling.

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The catalysts which can operate at lower temperature have been desired from the practical point of view.

In the effort to clarify the factors controlling the selective reduction of NO and develop a new catalyst active at low temperature, we examined the catalytic activities of various oxide catalysts for the selective reduction of NO by ethene in an oxidizing atmosphere. Here we wish to report the correlation among reduction activity, decomposition activity, and acidity of oxides, and iron ion-exchanged mordenite as the most active catalyst at 473 K.

2. Experimental

Parent zeolite, ZSM-5 ($SiO_2/Al_2O_3 = 23.3$, abbreviated as MFI), ferrierite (12.3, FER), mordenite (18.9, MOR), and L- (6.0, LTL) and Y-type (5.6, Y) were supplied by Tosoh Corporation. Approximately 20 g of each zeolite was washed in 2 dm^3 of dilute $NaNO_3$ solution and then ion-exchanged in 1 dm^3 of the transition metal nitrate or acetate solution with 10–12 $mmoldm^{-3}$ overnight. After filtration, the resulting cake was washed and dried for 12 h at 383 K. Proton-exchanged zeolite was prepared as described previously [14]. The amount of transition metal ions in the zeolite was determined by atomic absorption spectroscopy. The degree of ion exchange level was calculated by (oxidation number of cation) · (number of cation)/(number of Al ion in the zeolite), where the number of aluminium ion was measured by the Si-MAS NMR method. The oxidation number of iron ion was temporarily defined as +2 though it should be exactly determined. Hereafter the sample was abbreviated as Cu-MFI-100 (cation-zeolite structure-degree of exchange). Al_2O_3 (JRC-ALO4), SiO_2-Al_2O_3, TiO_2, and SiO_2-TiO_2 were obtained from the Catalysis Society of Japan, Catalysts & Chemicals Ind. Co., Idemitsu Co., and Fuji Davison Co., respectively. $La_{0.8}Sr_{0.2}CoO_3$, $La_{1.5}Sr_{0.5}CuO_4$, and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ were prepared according to refs. [15], [16], and [17], respectively. Ferrosilicate was prepared in Kikuchi's group [10] and supplied to us.

The catalytic reduction of NO was carried out with a fixed bed flow reactor. The reactant gas contained 1000–2000 ppm of NO, 250–1000 ppm of C_2H_4 or C_3H_6, and 1–2% of O_2. The total flow rate was 100–150 $cm^3\ min^{-1}$ and the catalyst weight was 0.5–1.0 g. The catalytic activity for NO removal was evaluated by the conversion into N_2.

3. Results and discussion

CATALYTIC ACTIVITIES OF VARIOUS OXIDES

The catalytic activities for the selective reduction of NO on various catalysts are summarized in table 1 as a function of reaction temperature. Various

Table 1
Catalytic activity for selective reduction of NO

Catalyst	Reductant		Conversion into N_2 /% [a]					Ref.
	Gas	Conc./ ppm	743 K	523 K	573 K	673 K	773 K	
H-MOR-100 [b]	C_2H_4	250	–	5	13	27	23	This work
H-MOR-100 [c]	C_2H_8	330	–	–	58	65	48	[18]
Fe-MOR-97 [b]	C_2H_4	250	18	20	18	7	3	This work
H-MFI-100 [b]	C_2H_4	250	7	20	33	39	33	[8]
H-MFI-100 [c]	C_2H_8	330	–	–	60	62	43	[18]
Na-MFI-100 [b]	C_2H_4	250	7	0	0	0	0	This work
Ca-MFI-25 [b]	C_2H_4	250	–	–	2	5	10	This work
Cr-MFI-22 [b]	C_2H_4	250	–	0	3	1	2	This work
Mn-MFI-127 [b]	C_2H_4	250	–	16	27	23	17	This work
Fe-MFI-94 [b]	C_2H_4	250	12	9	6	3	3	This work
Co-MFI-90 [b]	C_2H_4	250	–	6	36	40	25	[8]
Ni-MFI-99 [b]	C_2H_4	250	–	11	30	38	21	This work
Cu-MFI-102 [b]	C_2H_4	250	9	41	32	16	–	[8]
Zn-MFI-96 [b]	C_2H_4	250	–	–	6	11	25	[8]
Ag-MFI-90 [b]	C_2H_4	250	–	–	13	21	47	[8]
Ce-MFI-16 [d]	C_2H_4	250	8	12	25	30	8	[9]
Fe-Silicate [e]	C_3H_6	1000	0	–	53	20	12	[10]
Fe-Silicate [b]	C_2H_4	250	6	8	7	2	–	This work
Al_2O_3 [b]	C_2H_4	250	0	–	5	6	22	[12]
Al_2O_3 [c]	C_3H_8	330	–	–	2	13	38	[19]
K/Al_2O_3 [b,f]	C_2H_4	250	0	–	0	0	7	[12]
Ca/Al_2O_3 [b,f]	C_2H_4	250	0	–	0	0	7	[12]
V/Al_2O_3 [b,f]	C_2H_4	250	3	–	5	8	17	[12]
Cr/Al_2O_3 [b,f]	C_2H_4	250	3	–	11	14	10	[12]
Mn/Al_2O_3 [b,f]	C_2H_4	250	2	–	2	7	22	[12]
Fe/Al_2O_3 [b,f]	C_2H_4	250	5	–	14	21	19	[12]
Co/Al_2O_3 [b,f]	C_2H_4	250	0	–	4	13	28	[12]
Co/Al_2O_3 [c,f]	C_3H_8	330	–	–	4	49	29	[19]
Ni/Al_2O_3 [b,f]	C_2H_4	250	0	–	4	6	24	[12]
Cu/Al_2O_3 [b,f]	C_2H_4	250	0	–	6	21	26	[12]
Zn/Al_2O_3 [b,f]	C_2H_4	250	0	–	4	6	21	[12]
Ag/Al_2O_3 [b,f]	C_2H_4	250	0	–	2	4	10	[12]
SiO_2 [g]	C_2H_4	500	0	–	0	0	0	This work
Cu/SiO_2 [b,f]	C_2H_4	250	0	–	0	0	2	This work
SiO_2-Al_2O_3 [b]	C_2H_4	250	2	–	3	6	6	[13]
Co/SiO_2-Al_2O_3 [b,f]	C_2H_4	250	–	–	2	5	3	This work
Cu/SiO_2-Al_2O_3 [b,f]	C_2H_4	250	5	5	6	15	16	[13]
TiO_2 [g]	C_2H_4	500	0	–	0	9	9	This work
SiO_2-TiO_2 [g]	C_2H_4	500	0	–	0	0	8	This work
Cu/TiO_2 [b,f]	C_2H_4	250	0	–	3	0	0	This work
SO_4^{2-}/TiO_2 [c]	C_3H_8	330	–	–	217	47	28	[18]
V_2O_5 [h]	C_3H_6	1000	0	–	0	0	0	This work
Cr_2O_3 [h]	C_3H_6	1000	–	–	2	0	0	This work
MnO_2 [h]	C_3H_6	1000	0	0	0	0	0	This work

Table 1 (continued)

Catalyst	Reductant		Conversion into N_2 /% [a]					Ref.
	Gas	Conc./ ppm	473 K	523 K	573 K	673 K	773 K	
Fe_2O_3 [h]	C_3H_6	1000	–	–	2	0	0	This work
CoO [h]	C_3H_6	1000	0	–	0	0	0	This work
NiO [h]	C_3H_6	1000	–	–	0	0	0	This work
ZrO_2 [c]	C_3H_8	330	–	–	–	23	20	[19]
SO_4^{2-}/ZrO_2 [c]	C_3H_8	330	–	–	11	22	33	[19]
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ [b]	C_2H_4	250	0	–	0	9	8	This work
$La_{0.8}Sr_{0.2}CoO_3$ [i]	C_3H_6	1000	0	–	0	0	0	This work
$La_{1.5}Sr_{0.5}CuO_4$ [i]	C_3H_6	1000	0	–	1	2	3	This work

[a] The symbol "–" indicates no data available.

[b] NO, 1000 ppm; C_2H_4, 250 ppm; O_2, 2%; and W/F, 0.2 g·s·cm^{-3},

[c] NO, 1000 ppm; C_3H_8, 330 ppm; O_2, 10%; and W/F, 1.0 g·s·cm^{-3}.

[d] NO, 1000 ppm; C_3H_6, 166 ppm; O_2, 2%; and W/F, 0.2 g·s·cm^{-3}.

[e] NO, 1000 ppm; C_3H_6, 1000 ppm; O_2, 10%; and W/F, 0.33 g·s·cm^{-3}.

[f] The amount of metal loaded is omitted.

[g] NO, 1000 ppm; C_2H_4, 500 ppm; O_2, 2%; and W/F, 0.6 g·s·cm^{-3}.

[h] NO, 1000 ppm; C_3H_6, 1000 ppm; O_2, 2%; and W/F, 0.6 g·s·cm^{-3},

[i] NO, 2000 ppm; C_3H_6, 1000 ppm; O_2, 1%; and W/F, 1.5 g·s·cm^{-3}.

cation-exchanged zeolites, Fe-silicate, and Al_2O_3-based catalysts were active for the reduction of NO by ethene or propene in O_2, while the active temperature regions and maximum conversions were dependent on the catalysts. It should be noted that iron ion-exchanged mordenite is also active.

On the other hand, perovskite-type oxides such as $La_{0.8}Sr_{0.2}CoO_3$ and $La_{1.5}Sr_{0.5}CuO_4$ active for the direct decomposition of NO [15,16] showed little activity for the selective reduction of NO. This concludes that the activity for selective reduction of NO is not correlated with the activity for the direct decomposition. This is further supported by the observations that the dependence of the reduction activity of the Cu-MFI zeolites on the exchange level of copper ion [8] is quite different from that of the decomposition activity [20].

The role of the acidity in the selective reduction of NO was examined. Hamada et al. [9] reported that the acidity of the catalysts is one of the important factors controlling the catalytic activity for the selective reduction. The activities of Al_2O_3, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, SiO_2-Al_2O_3, TiO_2, SO_4^{2-}/support, and SiO_2-TiO_2, and proton-exchanged zeolites having various acidities [21] were shown in table 1. The conversions into N_2 on these catalysts are less than 10% under the present condition except for Al_2O_3 and SO_4^{2-}/support. It is well known that Al_2O_3 has mainly the Lewis acid sites while the SO_4^{2-}/support catalysts have the Brønsted acidity. These results suggest that the catalytic activity of oxides for this reaction is not a simple function of the acidic property.

Based on the results of table 1, one can recognize that the supporting of Cu, Co, or Fe metals or ions on various supports such as zeolites and Al_2O_3 resulted in the generation and/or enhancement of the catalytic activity for the selective reduction of NO. By contrast, noble metals or non-transition elements do not show such effects. This possibly suggests that the selective reduction includes a redox cycle of the active site(s) and the metal ion, reducible and reoxidizable, more easily is more active for the reaction.

IRON ION-EXCHANGED ZEOLITES

It is not noted that Fe-MOR zeolite catalyst is the most active for the selective reduction of NO by ethene in the presence of oxygen at the temperature as low as 473 K among the catalysts listed in table 1 and reported so far [4–13]. It has been reported that iron ion-exchanged zeolites catalyze the reduction of NO by CO, and that Fe-mordenite shows very high catalytic activity for this reaction [22]. However, these experiments are carried out in the absence of oxygen in the reaction streams and the presence of oxygen usually decreases the catalytic activity [1]. Therefore, the present finding that the Fe-MOR zeolite catalyst is the most active for the selective reduction of NO by ethene in an oxidizing atmosphere is novel and of interest.

The activity of iron ion-exchanged zeolites depended on the concentration of C_2H_4, the framework structures of zeolites, and iron ion exchange level. When the concentration of C_2H_4 was increased to 1000 ppm from 250 ppm on Fe-MOR-71, the conversion to N_2 increased from 18% to 25% at 473 K and from 21% to 34% at 523 K. A similar increment in the conversion with the increase in the concentration of C_2H_4 was reported for Cu-MFI zeolite catalysts [5]. Fig. 1 shows the temperature dependence of the catalytic activity of various iron ion exchanged zeolites. The temperatures of the maximum activity were dependent on the zeolite structure. The order of the temperature of the maximum activity was Fe-MFI-94 (473 K) < Fe-MOR-97 (523 K) < Fe-Y-89 (548 K) ≈ Fe-LTL-53 (548 K) < Fe-FER-49 (573 K). Fe-MOR zeolite catalyst showed the highest activity in a NO (1000 ppm) + C_2H_4 (250 ppm) + O_2 (2%) system at 473 K. The order of activity at 473 K was as follows: Fe-MOR-97 ≈ Fe-MOR-58 > Fe-FER-49 ≈ Fe-MFI-94 > Fe-Y-89 > Fe-LTL-53. It should be noted that the MFI structure is not the best one for supporting iron ion, which is different from the combination of copper ion and the MFI structure [5]. It follows that suitable pairing or matching of metal ion with zeolite structure should be arranged to achieve better catalytic activity.

The dependency of the activities of Fe-MOR zeolite catalysts at 473 K on the exchange level of iron ion is shown in fig. 2. The activity increased with the increment in the exchange level and levelled off above about 60%. The temperature of the maximum activity changed little with the amount of iron ion loaded. The dependence of the activity on the exchange level of iron ion is different

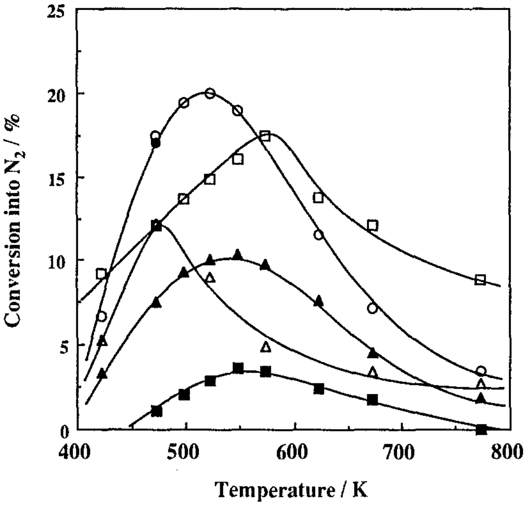

Fig. 1. Temperature dependence of the catalytic activities of iron ion-exchanged zeolites. ○, Fe-MOR-97; ●, Fe-MOR-58; □, Fe-FER-49; △, Fe-MFI-94; ▲, Fe-Y-89; and ■, Fe-LTL-53. Catalyst weight, 0.5 g. NO (1000 ppm); C_2H_4 (250 ppm); and O_2 (2%). Total flow rate, 150 $cm^3 \cdot min^{-1}$.

from that of the catalytic activity of copper ion-exchanged MFI zeolite on the exchange level [8]. The difference may be closely related to the reaction mechanisms; further studies are in progress.

Investigating the conversion into N_2 above 100000 h^{-1} of the space velocity (GHSV) is necessary from the practical viewpoint. The correlation between the

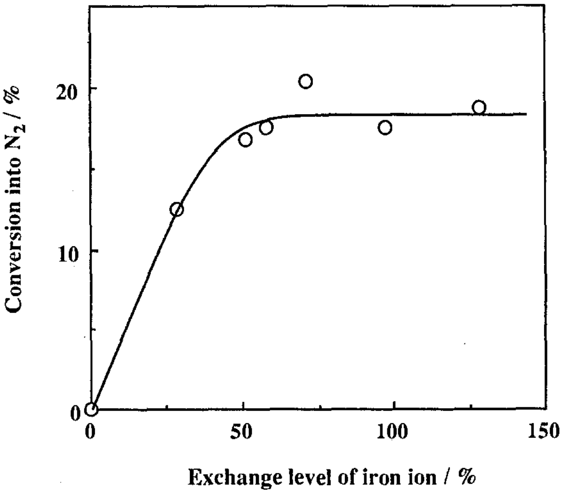

Fig. 2. Dependence of the catalytic activity of iron ion-exchanged mordenite on the exchange level of iron ion. Catalyst weight, 0.5 g. NO (1000 ppm); C_2H_4 (250 ppm); and O_2 (2%). Total flow rate, 150 $cm^3 \cdot min^{-1}$. Temperature, 473 K.

catalytic activity of Fe-MOR-71 and space velocity was measured in a NO (1000 ppm) + C_2H_4 (1000 ppm) + O_2 (2%) system at 473 K. The conversions into N_2 decreased with the increment in GHSV; the conversions were 25, 9, and 3% at 9000, 36000, and 144000 h^{-1}, respectively. On the other hand, the conversions into N_2 on Cu-MFI-105 at 473 K and GHSV of 36000 and 144000 h^{-1} were 1 and 0%, respectively. Therefore, the catalytic activity of Fe-MOR-71 is greater than that of Cu-MFI-105 at 473 K. In conclusion, Fe-MOR has been clarified to be the best catalyst at present for the removal of NO from exhaust in an oxidizing atmosphere at the temperature as low as 473 K.

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