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Adsorption-desorption Properties of Nitrogen Monoxide on Metal Ion-exchanged Zeolites[1)]

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Among the samples tested, the amounts of reversible and irreversible adsorption of NO were the largest on copper ion-exchanged ZSM-5 zeolite and cobalt ion-exchanged ZSM-5 zeolite, respectively. In the former case, the amounts of reversible and irreversible adsorption of NO were dependent on the aluminum content of zeolite and linearly increased with increasing the exchange level.

The removal of nitrogen oxides (NO_x) which cause acid rain and air pollution is an important problem to be solved. The catalytic decomposition and reduction have been proposed for removing NO_x;[2)] however, these methods are not suitable for the removal of low concentration of NO_x. It is well known that adsorption is one of the most suitable technique for removal of thin adsorbates. In particular, pressure swing adsorption (PSA) has been widely applied to the production of oxygen from air[3)] and purification of hydrogen,[4)] and would be effective to concentrate NO_x diluted in air. For PSA, the adsorbent must possess a high capacity to adsorb NO reversibly for the ready regeneration. Though active carbon,[5,6)] silica,[7)] zeolite,[8-10)] α-FeO(OH)-dispersed activated carbon fiber,[11)] and chelate resin[12)] have been reported as adsorbents of NO so far, little is known of the amount of reversible adsorption of NO, which is important for PSA. Here we wish to report that copper ion-exchanged ZSM-5 zeolite shows the largest amount of reversible adsorption of NO among the various cation-exchanged zeolites and is one of the strong candidates of adsorbents for NO removal by PSA. The concentration of NO was set at 1000 - 2000 ppm in this study for the quick evaluation of the adsorption properties of adsorbents though the concentration is much lower under the practical conditions. The results reported here would be also useful to understand the catalytic activities of zeolites for decomposition/reduction of NO.[2,13)]

Parent zeolites, ZSM-5 (SiO_2/Al_2O_3=23.3), mordenite (10.5), ferrierite (12.3), offretite/erionite (7.7), Y- (5,6), L- (6.0),and X-type (2.6) were supplied by Tosoh Corporation and designed as MFI, MOR, FER, OFF/ERI, Y, LTL, and X, respectively. Metal ion-exchanged zeolites were prepared as described previously.[13)] The exchange level of cation was determined by atomic absorption spectroscopy after the zeolite sample obtained was dissolved in HF solution. Hereafter the sample was abbreviated as M-MFI-100 (cation-zeolite structure-degree of exchange).

The adsorption and desorption runs were carried out in a fixed bed adsorption apparatus. The adsorbent of 0.5 - 1.0 g was placed in a stainless steel column and was heated at 773 K for 5 h

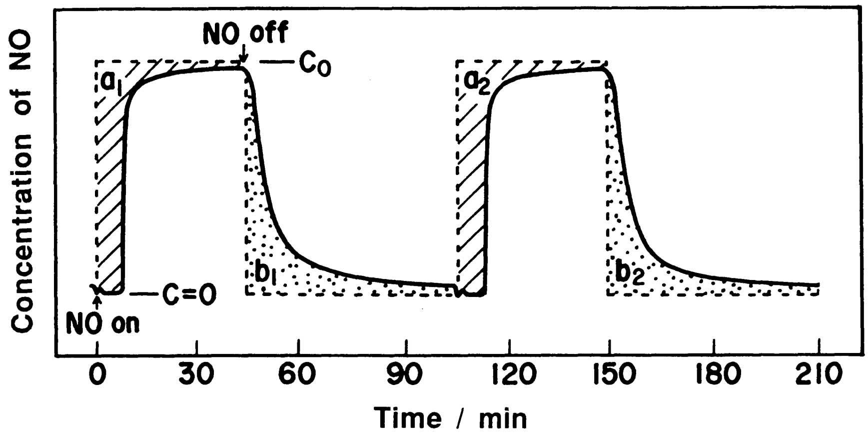

Fig. 1. Breakthrough and elution curves of NO over Cu-MFI-60. Adsorption time, 45 min; desorption time, 60 min; concentration of NO, 1910 ppm; flow rate, 100 $cm^3 \cdot min^{-1}$; adsorption temperature, 273 K; adsorbent weight, 1.0 g. Solid line, with adsorbent; broken line, without adsorbent; C_0, initial concentration of NO; a_1, a_2, b_1, b_2, see text.

under a helium stream (50 $cm^3 \cdot min^{-1}$) just before the adsorption run. In the adsorption run, 1000 - 2000 ppm of NO in He was fed at a rate of 100 $cm^3 \cdot min^{-1}$ into the column. After adsorption run, pure He (100 $cm^3 \cdot min^{-1}$) was introduced into the column in a counter current flow to desorb NO from the adsorbent. The temperature of the adsorbent was 273 K and the adsorption or desorption time was 45 - 120 min. The effluent concentration and composition were monitored by using thermal conductivity detector (TCD) and mass spectrometer, respectively.

When the adsorption and desorption runs were repeated, the breakthrough and elution curves were obtained as shown in Fig. 1. In this figure, the solid and the broken lines indicate the response of TCD with and without adsorbent, respectively. N_2 and N_2O were formed only in the first run, but the amounts were much smaller than the amount of NO adsorbed. Therefore, the amount of adsorption of NO was estimated from the hatched area (denoted as a_n where n is the number of adsorption-desorption cycle), while that of desorption of NO was calculated from the dotted area (b_n). a_n was decreased with increasing n, reached a constant value, while b_n was almost constant independent of n. Usually a_n became approximately equal to b_n at 5th or 6th adsorption-desorption cycle. Here, the amount of reversible adsorption of NO (denoted as q_{rev}) is defined by a_m at $a_m = b_m$. The amount of irreversible adsorption of NO (denoted as q_{irr}) is defined by $\sum_{n=1}^{m}(a_n - b_n)$.

The q_{rev} and q_{irr} measured on various cation-exchanged MFI zeolites are summarized in Table 1. The q_{rev} and q_{irr} per weight of adsorbent greatly changed with metal ion introduced into zeolite. The properties of respective adsorbents are as follows: The values of q_{irr} of transition metal ion-exchanged zeolites were larger than those of q_{rev} except for Zn-MFI-96 and Ag-MFI-90. On the contrary, q_{rev} of alkaline earth metal ion-exchanged zeolites was greater than q_{irr}. The q_{rev} and q_{irr}

were very small on alkaline metal ion-, rare earth metal ion-, and proton-exchanged zeolites. With MFI zeolites, the order of q_{rev} was transition metal ion ≈ alkaline earth metal ion > rare earth metal ion ≈ proton. Among the adsorbents listed in Table 1, Cu-MFI-157 and Co-MFI-90 showed the largest q_{rev} and q_{irr}, respectively. On the assumption that NO adsorbed has the same density as that in liquid phase, the total amounts of NO adsorbed ($q_{rev}+q_{irr}$) on Cu-MFI-157 and Co-MFI-90 correspond to 11 and 14% of the theoretical micropore volume (0.162 $cm^3 \cdot g^{-1}$), respectively. Hereafter copper ion-exchanged zeolites were investigated in more detail.

Table 1. NO Adsorption Properties of Various Cation-exchanged ZSM-5 Zeolites[a)]

Adsorbent	Content of cation / wt%	Amount of adsorption of NO / $cm^3 \cdot g^{-1}$	
		reversible	irreversible
Na-MFI-100[b)]	2.81	0.16(0.006)[c)]	0.00(0.000)[c)]
Ca-MFI-54	1.32	1.81(0.246)	1.56(0.212)
Sr-MFI-105	5.45	2.71(0.195)	0.20(0.014)
Ba-MFI-80	6.44	1.50(0.143)	1.44(0.137)
Mg-MFI		0.69	0.22
Cu-MFI-157	5.90	4.28(0.206)	14.90(0.716)
Ag-MFI-90	10.85	3.38(0.150)	0.54(0.024)
Co-MFI-90	3.06	1.52(0.131)	19.69(1.693)
Mn-MFI-127	4.20	1.19(0.069)	5.81(0.339)
Ni-MFI-68	2.41	1.03(0.112)	6.64(0.727)
Zn-MFI-96	3.79	1.01(0.078)	0.50(0.039)
Fe-MFI-62	2.12	0.52(0.061)	3.08(0.362)
Cr-MFI-41	0.87	0.38(0.101)	1.16(0.308)
Ce-MFI		0.34	0.34
La-MFI		0.25	0.24
H-MFI-100	0.13	0.12(0.004)	0.32(0.011)

a) Adsorption time, 45 min; desorption time, 60 min; concentration of NO, 997 ppm; adsorption temperature, 273 K; adsorbent weight, 0.5 g; flow rate, 100 $cm^3 \cdot min^{-1}$. b) Concentration of NO, 1910 ppm. c) Unit / NO-molecules·$(cation)^{-1}$.

The adsorbability of NO on copper ion-exchanged zeolites was dependent on the framework structure of zeolites. The order of q_{rev} was Cu-MFI-78 (2.24 $cm^3 \cdot g^{-1}$) > Cu-MOR-76 (2.11) > Cu-FER-66 (1.42) > Cu-LTL-34 (1.23) > Cu-Y-83 (0.86). Cu-MFI showed the highest capacity for reversible adsorption of NO. The correlation between the amount of adsorption of NO and aluminum content is depicted in Fig. 2. Both q_{rev} and q_{irr} per copper ion decreased with the increment of aluminum contents in the zeolites, indicating that the amounts of adsorption of NO per copper ion are controlled by the aluminum content.

Figure 3 shows the dependence of the amounts of adsorption of NO upon the exchange level of copper ion. q_{rev} and q_{irr} are proportional to the exchange level of copper ion. This means that q_{rev} and q_{irr} per copper ion exchanged are constant, showing that the effectiveness of each copper ion in MFI zeolite for NO adsorption is independent of its loading level or the ratio of the effective Cu ions for NO adsorption to ineffective ones is always constant. Further studies on adsorption mechanism are in progress.

In conclusion, the copper ion-exchanged MFI zeolite is expected to be a potential adsorbent for the removal of NO by PSA.

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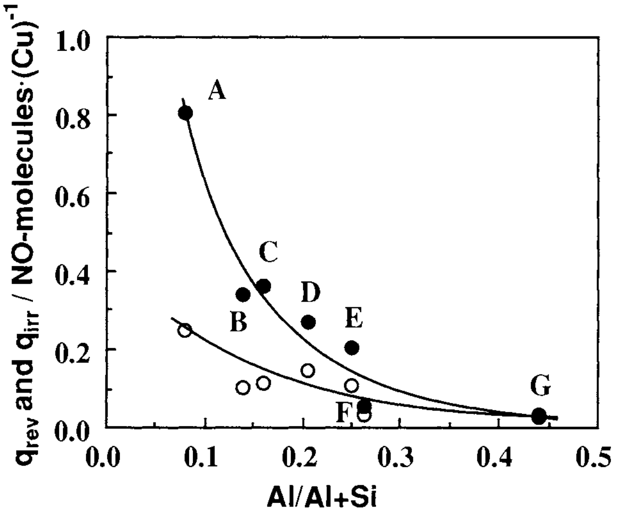

Fig. 2. Correlation between the amounts of NO adsorption and the Al contents in copper ion-exchanged zeolites.

Adsorption time, 45 min; desorption time, 60 min; concentration of NO, 1910 ppm; flow rate, 100 $cm^3 \cdot min^{-1}$; adsorption temperature, 273 K; adsorbent weight, 1.0 g; ●, q_{irr}; ○, q_{rev}.

A, MFI; B, FER; C, MOR; D, OFF/ERI; E, LTL; F, Y; G, X.

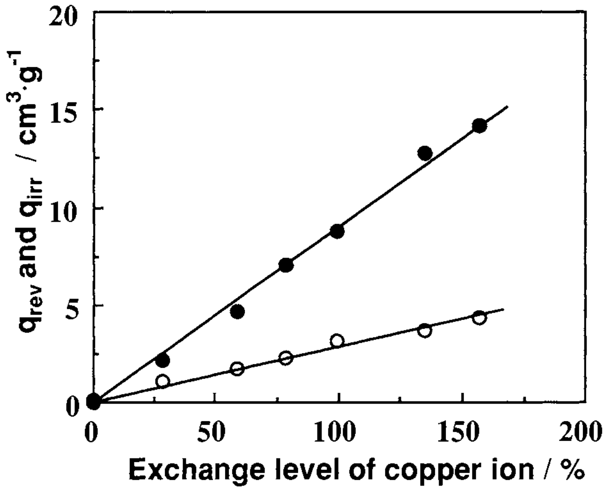

Fig. 3. Dependence of the amount of NO adsorption on the exchange level of copper ion of Cu-MFI zeolites.

Adsorption time, 60 min; desorption time, 120 min; concentration of NO, 1089 ppm; flow rate, 100 $cm^3 \cdot min^{-1}$; adsorption temperature, 273 K; adsorbent weight, 0.5 g; ●, q_{irr}; ○, q_{rev}.

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