

Adsorption Properties of Nitrogen Monoxide on Silver Ion-Exchanged Zeolites

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The adsorption properties of nitrogen monoxide (NO) on various silver ion-exchanged zeolites were examined by adsorption–desorption measurements in a fixed bed flow apparatus. Both reversible (q_{rev}) and irreversible (q_{irr}) adsorption of NO is dependent on the aluminum content in the zeolites and the zeolite structure. The amounts of reversible and irreversible adsorption of NO per silver ion increased with decreasing aluminum content of the zeolites and were constant, independent of the ion exchange level for ZSM-5 zeolites, but increased with the ion exchange level for mordenite zeolites (MOR). It was also found that the adsorption properties are dependent on the temperature and pressure of adsorption: q_{irr} and q_{rev} of Ag-MOR increased with decreasing adsorption temperature and increasing adsorption pressure. Furthermore, the influence of preadsorbed gases on the Ag-MOR zeolite was investigated, and an enhancement of q_{rev} was observed when NO₂ was preadsorbed. The NO species adsorbed on the Ag-MOR zeolite were characterized by infrared (IR). Most of the reversibly adsorbed NO species are NO^{δ+} and some N₂O adsorbed on Ag⁺, and the irreversibly adsorbed NO species are some N₂O, NO^{δ+}, and a small amount of NO^{δ-}, NO₂^{δ+}.

1. Introduction

The removal of nitrogen oxides (NO_x) which cause acid rain and air pollution is an important global environmental problem which needs to be solved soon. The three-way automotive catalysts, based on the use of Pd–Pt–Rh, have been highly successful in controlling exhaust emissions from gasoline engines.¹ SCR (selective catalytic reduction of NO_x with ammonia) is also a commercially available technology to remove NO_x from stationary streams.² In recent years, numerous efforts have been devoted to the abatement of NO_x by catalytic decomposition and selective reduction with hydrocarbons.^{3,4} However, these methods are not suitable for the removal of low concentration NO_x due to the efficiency and the running cost. Selective adsorption is one of the most suitable techniques for removal and/or enrichment of low-concentration adsorbates.⁵ In particular, pressure swing adsorption (PSA) has been widely applied to various industry processes such as the production of oxygen from air⁶ and purification of hydrogen.⁷ Hence, PSA is a promising technique to remove or enrich low-concentration NO_x diluted in air. A high reversible

adsorption ability of NO is required for the adsorbents of PSA. Although active carbon,^{8,9} silica,¹⁰ zeolite,^{11–13} α-FeOOH dispersed activated carbon fiber,¹⁴ and chelate resin¹⁵ have been reported as adsorbents of NO, little work on the reversible adsorption has been carried out so far. Recently, the present authors have found that metal ion-exchanged zeolites have a high reversible adsorbability of NO.^{16,17} In our previous work,¹⁸ we have investigated the adsorption properties of NO on various silver ion-exchanged zeolites and found that the amounts of reversible and irreversible adsorption were dependent on the zeolite structure; among the samples tested, Ag-MFI, Ag-MOR, and Ag-FER showed a high capacity for reversible adsorption of NO at 273 K, indicating that these samples are the strong candidates for PSA.

In this study, the effects of aluminum content, silver ion-exchanged level, adsorption temperature, adsorption

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pressure, and preadsorbed gases on adsorption properties were discussed in detail. In addition, the adsorbed species of NO on Ag-MOR were also investigated by means of infrared spectroscopy (IR).

2. Experimental Section

2.1. Adsorbent Preparation. The parent zeolites ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 23.3$), mordenite (15.0, 18.9), ferrierite (12.3), offretite/erionite (7.7), Y-type (5.6), L-type (6.0), X-type (2.6), and A-type (2.0) were used and are denoted as MFI, MOR, FER, OFF/ERI, FAU, LTL, FAU, and LTA, respectively.

Silver ion-exchanged zeolites were prepared as described previously.¹⁶ The level of exchange of silver ions was determined by atomic absorption spectrometry after the sample was dissolved in hydrofluoric acid solution. Hereafter, the sample is abbreviated as Ag-MFI(23.3)-100 [silver ion-zeolite type ($\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio)-degree of exchange].

2.2. Adsorption-Desorption Measurement. The adsorption-desorption measurements were carried out in a fixed bed adsorption apparatus as described previously.¹⁶ The adsorbent (0.5–1.0 g) was placed in a stainless steel column and was heated at 773 K for 5 h under a helium stream ($50 \text{ cm}^3 \cdot \text{min}^{-1}$) just before the adsorption run as a usual pretreatment. In the adsorption experiment, 0.1–2% of NO in He was introduced at a rate of $100 \text{ cm}^3 \cdot \text{min}^{-1}$ into the column. Subsequently, pure He ($100 \text{ cm}^3 \cdot \text{min}^{-1}$) was introduced into the column in a counter current flow to desorb the reversibly adsorbed NO from the adsorbent. The adsorption or desorption time was ca. 45–120 min; the time of each operation was varied with the amount of adsorbed NO to obtain complete adsorption/desorption. The temperature of adsorbent was controlled in the range of 195–273 K by using an ice box and a cooling system. The effluent concentration and composition were continuously monitored by an online connected thermal conductivity detector (TCD) and a quadrupole mass spectrometer (QPMS; ANELVA, AQA-100), respectively. Mass spectra were recorded for N_2 (28), NO (30), O_2 (32), N_2O (44), and NO_2 (46). The breakthrough and elution curves obtained were used to estimate the amounts of reversible and irreversible adsorption of NO (denoted as q_{rev} and q_{irr} , respectively).

2.3. IR Measurement. IR spectra were recorded by using a Nicolet Impact 410 spectrometer. A quartz IR cell with CaF_2 windows was used. A self-supporting wafer ($3\text{--}4 \text{ mg} \cdot \text{cm}^{-2}$) of the adsorbent was obtained by pressing the powder at $200 \text{ kg} \cdot \text{cm}^{-2}$ for 30 min. The resulting wafer was heated from room temperature to 773 K, kept at 773 K for 2 h, and cooled to room temperature under a dynamic vacuum. IR measurements were performed at room temperature and the spectra of the adsorbed species were obtained by subtracting the spectrum of the wafer.

3. Results and Discussion

3.1. Effect of Aluminum Content and Zeolite Structure on Adsorption Properties. Figure 1 shows the relationship between the amounts of reversible and irreversible adsorption of NO per silver ion exchanged (denoted as q_{rev}^* and q_{irr}^* , respectively) and the aluminum content of the zeolite. Both q_{rev}^* and q_{irr}^* decreased with the increase of the aluminum content in the zeolites. These results indicate that the adsorption ability of NO was mainly controlled by the aluminum content. It should be noted, however, that the results of some samples obviously deviate from the fitted curve, suggesting the possibility that the zeolite structure might be one factor controlling the adsorbability. Generally, the chemical and physical properties of zeolites

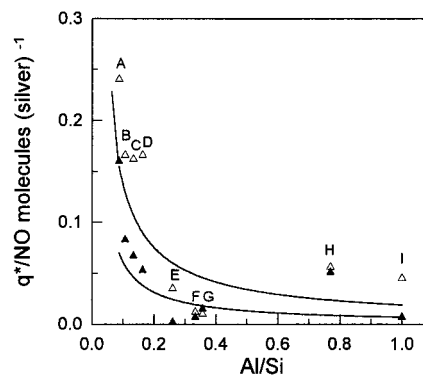


Figure 1. Relationship between the amounts of NO adsorption and the Al contents in silver ion-exchanged zeolites. Δ , q_{rev}^* ; \blacktriangle , q_{irr}^* ; A, MFI(23.3); B, MOR(18.9); C, MOR(10.5), D, FER(12.3); E, OFF/ERI(7.7); F, LTL(6.0); G, FAU(5.6); H, FAU(2.6); I, LTA(2.0); adsorption time, 60 min; desorption time, 120 min; concentration of NO, 0.19%; adsorption temperature, 273 K.

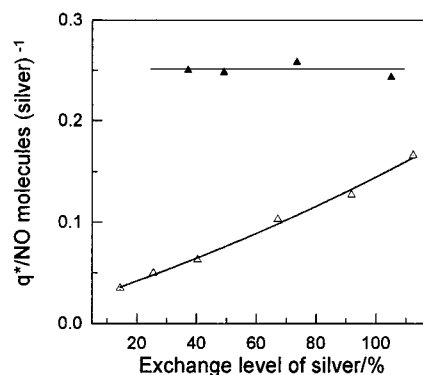


Figure 2. Dependencies of q_{rev}^* upon the exchange level of silver ion. \blacktriangle , Ag-MFI(23.3); Δ , Ag-MOR(15.0); adsorption time, 60 min; desorption time, 120 min; concentration of NO, 0.19%; adsorption temperature, 273 K.

depend on the zeolite structure and/or the Si/Al ratio.¹⁹ Recently, XPS study has also revealed that the binding energies of each constituent element of the zeolites were fairly correlated with the Al content.²⁰ Consequently, the relationship in Figure 1 probably reflects the electronic state of the zeolite.

3.2. Effect of Silver Ion-Exchange Level. The adsorbability of silver ion-exchanged zeolites was dependent on the exchange level. q_{rev}^* and q_{irr}^* of Ag-MFI(23.3) and Ag-MOR(15.0) increased with the exchange level. Figure 2 shows the dependencies of q_{rev}^* upon the exchange level of silver ion at 273 K. q_{rev}^* of Ag-MFI(23.3) was constant against the exchange level of silver ion; however, q_{rev}^* of Ag-MOR(15.0) increased monotonically with the exchange level of silver ion. It follows that the effectiveness of each silver ion introduced into MFI zeolite for NO adsorption is independent of its exchange level or that the ratio of the effective to ineffective silver ion for NO adsorption is constant, reflecting that exchange sites in MFI are uniform, while the silver ions exchanged into MOR zeolite have selectivity for NO adsorption or exchange sites in MOR have selectivity for silver ion exchange.

3.3. Effect of Adsorption Temperature and Pressure. Figure 3 shows the values of q_{rev} and q_{irr} of Ag-

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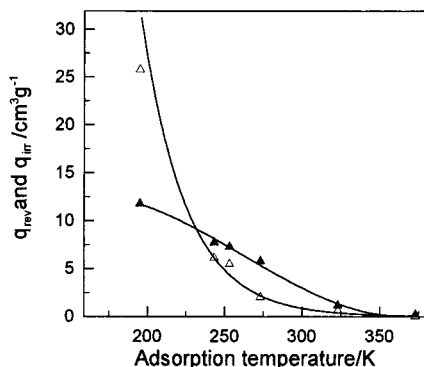


Figure 3. Temperature dependence of q_{rev} and q_{irr} on Ag-MOR(15.0)-112. \blacktriangle , q_{irr} ; \triangle , q_{rev} ; adsorption time, 60 min; desorption time, 120 min; concentration of NO, 0.19%.

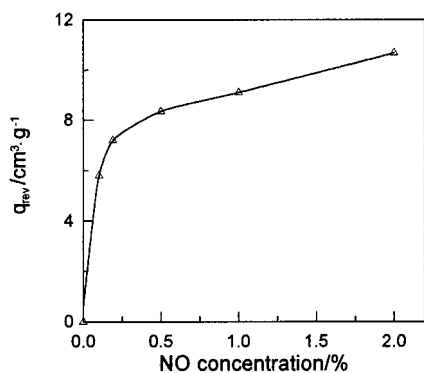


Figure 4. Pressure dependence of q_{rev} on Ag-MOR(15.0)-112. \triangle , q_{rev} ; adsorption time, 60 min; desorption time, 120 min; adsorption temperature, 273 K.

MOR(15.0)-112 as a function of the adsorption temperature. Both q_{rev} and q_{irr} increased significantly with the decrease of adsorption temperature. At 195 K q_{rev} and q_{irr} were 11.49 and 25.78 $\text{cm}^3 \cdot \text{g}^{-1}$, respectively. The apparent density of NO (the sum of q_{rev} and q_{irr}) adsorbed in the micropore of Ag-MOR(15.0)-112 zeolite (0.227 $\text{cm}^3 \cdot \text{g}^{-1}$) at 195 K is 0.22 $\text{g} \cdot \text{cm}^{-3}$ and corresponds to 17.3% of the density value (1.269 $\text{g} \cdot \text{cm}^{-3}$) of the bulk liquid at 123 K.²¹ This result suggests that Ag-MOR is an effective adsorbent for PSA in a lower temperature range of 195–273 K.

Figure 4 shows the adsorption isotherms of q_{rev} on Ag-MOR(15.0)-112 zeolite at 273 K. q_{rev} increased monotonically with an increase of the concentration of NO. The isotherm of q_{rev} can be expressed by the Langmuir isotherm, eq 1

$$q_{\text{rev}} = q_m p K / (1 + p K) \quad (1)$$

where q_{rev} is the adsorbed amount at p , q_m is saturated amount of adsorption, and K is the Langmuir adsorption equilibrium constant. q_m and K are 11.19 $\text{cm}^3 \cdot \text{g}^{-1}$ and 708.64 atm^{-1} , respectively.

3.4. Influence of Preadsorbed Gases. From the practical point of view, it is important to clarify the influence of coexisted gases, such as nitrogen dioxide, oxygen, carbon dioxide, carbon monoxide, sulfur dioxide, and water vapor (NO_2 , O_2 , CO_2 , CO , SO_2 , and H_2O). The influence on the adsorbability was investigated by

Table 1. Effect of Preadsorbed Gases on the Adsorption Properties of Ag-MOR(15.0)-112 Zeolite^a

preadsorbed gas ^b	amount of adsorption of NO ($\text{cm}^3 \cdot \text{g}^{-1}$)	
	reversible	irreversible
NO_2 (0.47%)/He	6.75	3.09
O_2 (99.5%)	5.48	1.69
CO_2 (20%)/He	4.88	1.25
SO_2 (0.22%)/He	0.30	0.69
CO (0.19%)/He	0.25	0.20
H_2O (3%)/He	0.31	0.60
none	5.76	2.18

^a Adsorption time, 60 min; desorption time, 120 min; concentration of NO, 0.19%; adsorption temperature, 273 K; adsorbent weight, 0.5 g; flow rate, 100 $\text{cm}^3 \cdot \text{min}^{-1}$. ^b The adsorbent was at 273 K for 5 h under a helium stream (50 $\text{cm}^3 \cdot \text{min}^{-1}$) before the preadsorption treatment. After the preadsorption the sample was purged with helium at room temperature.

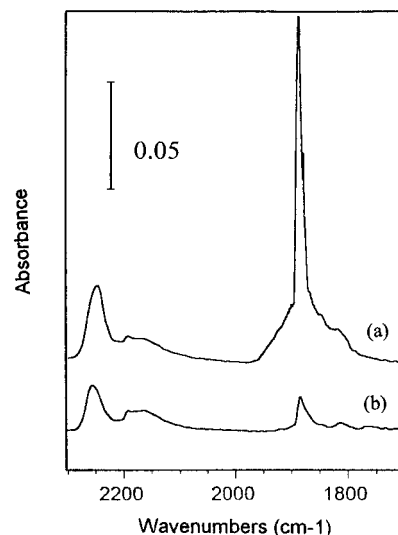


Figure 5. IR spectra after adsorption of NO on Ag-MOR(15.0)-112: (a) exposure to 20 Torr of NO for 30 min and (b) evacuation at room temperature for 2 min.

preadsorption of those gases on Ag-MOR(15.0)-112. Preadsorption was carried out at 273 K after the usual pretreatment. Subsequently, the adsorption column was purged with pure He (50 $\text{cm}^3 \cdot \text{min}^{-1}$) for 5 h to remove reversibly adsorbed species. After the preadsorption procedure, adsorption-desorption measurement of NO was carried out. The results are summarized in Table 1. An enhancement of q_{rev} and q_{irr} was observed by preadsorption of NO_2 . A similar phenomenon has been observed by Naruse et al.¹² This result suggests that preadsorbed NO_2 can work as new adsorption sites for the reversible adsorption of NO, probably due to the formation of N_2O_3 , which is in equilibrium with NO and NO_2 , and the formation of N_2O_3 has indeed been observed on zeolites.^{22,23} When O_2 or CO_2 was preadsorbed, both q_{rev} and q_{irr} were decreased, but the decrements were relatively small. After preadsorption of SO_2 , CO , or H_2O , both q_{rev} and q_{irr} were greatly decreased, indicating that the adsorbent was poisoned for NO adsorption.

3.5. IR Study of the Adsorbed Species of NO on Ag-MOR(15.0)-112. The reversibly and irreversibly

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adsorbed NO on Ag-MOR(15.0)-112 zeolite was characterized by IR measurements. Figure 5a illustrates the IR spectrum of 20 Torr of NO adsorbed on the sample in the region of 2300–1700 cm^{-1} . After 30 min of exposure, strong bands are observed at 1884 and 2255 cm^{-1} , together with weaker features at 2191, 2162, and 1812 cm^{-1} . On the basis of the previous IR study on metal ion-exchanged zeolites,^{23–25} the strong band at 1884 cm^{-1} can be assigned to $\text{NO}^{\delta+}$ species, 2255 cm^{-1} is due to adsorbed N_2O , 2191 and 2162 cm^{-1} are attributable to $\text{NO}_2^{\delta+}$, maybe associated with Ag^+ and Bronsted acid sites, and 1812 cm^{-1} is assigned to $\text{NO}^{\delta-}$. Upon evacuation of NO at room temperature for 2 min (Figure 5b), the band of $\text{NO}^{\delta+}$ decreased greatly, that of N_2O decreased somewhat, and the band of $\text{NO}_2^{\delta+}$ and $\text{NO}^{\delta-}$ was almost unchanged. These results lead to the conclusion that the major reversibly adsorbed species are $\text{NO}^{\delta+}$ and some N_2O , and the irreversibly adsorbates are mainly some $\text{NO}^{\delta+}$, N_2O , as well as a small amount of $\text{NO}_2^{\delta+}$, $\text{NO}^{\delta-}$ species.

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4. Conclusions

(1) Both reversible and irreversible adsorption of NO is dependent on the aluminum content in zeolites and the zeolite structure and increased with the increase of silver ion exchanged level.

(2) Both q_{rev} and q_{irr} increased significantly with the decrease of adsorption temperature. The isotherm of q_{rev} corresponds to the Langmuir isotherm equation.

(3) On Ag-MOR zeolite, preadsorption of SO_2 , CO, or H_2O poisoned the adsorbent for NO adsorption; when O_2 or CO_2 was preadsorbed, both q_{rev} and q_{irr} were decreased slightly, and an enhancement of q_{rev} was observed when NO_2 was preadsorbed.

(4) For Ag-MOR, the reversibly adsorbed species are attributed to $\text{NO}^{\delta+}$ and some N_2O , and the irreversibly adsorbed NO species are some N_2O , $\text{NO}^{\delta+}$, as well as a small amount of $\text{NO}^{\delta-}$, $\text{NO}_2^{\delta+}$.

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