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Disproportionation reaction of Nitrogen Monoxide on CaHY-type Zeolite

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The disproportionation reaction of NO was investigated on CaHY-type zeolite. The relation between pretreatment temperature and activity was determined by the pulse reaction technique, and the dependence of the initial formation rate of N_2O on NO pressure was investigated with a gas circulation system. The rate of initial formation of N_2O is third order in NO pressure in the lower pressure region (*ca.* 30 Torr, 1 Torr≈133.322 Pa) and 2.2th order in NO pressure in the higher pressure region (*ca.* 200 Torr). TPD spectra are composed mainly of three peaks: The first peak is assigned to the unreactive adsorbed NO, the second to the NO produced by the decomposition of N_2O_3 and left on the zeolite surface, and the third to the N_2O remaining. On the basis of the reaction mechanism proposed by Chao and Lunsford, the rate equation for the initial formation of N_2O has been derived as $\alpha=\bar{k}_2K_1P^3/(1+K_1P^2)$, where P, K_1, and $\bar{k}_2$ are the pressure of NO, an equilibrium constant, and a rate constant, respectively. This equation is in good agreement with experimental results obtained with the gas circulation system.

In a study on sorption and reactivity of NO, Addison and Barrer[1)] found that the disproportionation reaction of NO, $4NO=N_2O+N_2O_3$, occurs on chabazite, faujasite, and A-type zeolites at 0 °C or lower temperatures; the resulting N_2O can be removed quantitatively, whereas the N_2O_3 stays occluded in the zeolites. Later, Alekseyev *et al.*[2)] studied infrared spectra of NO adsorbed on A- and X-type zeolites. Chao and Lunsford[3)] also studied those on NaY- and CaY-type zeolites and proposed a mechanism for the disproportionation reaction.

Recently, the disproportionation reaction on MgHY-type zeolites with different degrees of ion exchange was studied by use of a pulsed microreactor, and it was revealed that active sites for this reaction are Mg^{2+} located on Site II.[4)] This reaction on alkaline earth metal oxides[5,6)] has further been investigated, with a result that the activity order is MgO>CaO>SrO>BaO. Pulse technique studies[7—9)] of this reaction on Y-type zeolites with various metal ions exchanged disclosed that alkaline earth Y-type zeolites possess higher activities, whereas the zinc family, alkali metals, and LaY-type zeolites possess lower activities, as detailed by the activity sequence: CaY>CdY>MgY>ZnY>LaY>BeY>NaY>LiY>KY$\gg$SrY>BaY, AgY, HgY, FeY, AlY=0.

Understanding the reactivity of NO, on the other hand, is of great value for studies on the transformation and elimination of atmospheric pollutants.[10—18)] The disproportionation reaction, therefore, is important not only from a fundamental viewpoint but also from a practical aspect.

The present study has been carried out to collect kinetic information on the disproportionation reaction of NO. Measurements for activity and TPD chromatogram were made on CaHY-type zeolites.

Experimental

Materials and Reagents. A synthetic Y-type zeolite (Union Carbide Co.) in the sodium form (SK-40) was ion-exchanged 16 times at 90 °C with 10 wt% solution of ammonium nitrate. A $CaNH_4Y$-type zeolite was prepared *via* ion-exchange of the resultant NH_4Y-type zeolite with a solution of calcium nitrate at 90 °C. The resultant $CaNH_4Y$-type zeolite was washed 3 times with 0.05 mol dm^{-3} calcium nitrate solution and dried overnight at 110 °C. The composition of the $CaNH_4Y$-type zeolite prepared in this way corresponds to $Ca_{24}(NH_4)_8Na(AlO_2)_{57}(SiO_2)_{135}\cdot nH_2O$ per unit cell. A chemical analysis of samples was done by flame spectrophotometry (Na^+) and atomic absorption spectrophotometry (Ca^{2+} and Al^{3+}); the sample was pressed at about 10 ton/cm^2 and ground into pieces of 32 to 60 mesh and of 1 to 2 mm.

Powder X-ray diffraction patterns and values of specific surface area measured with a BET apparatus confirmed that no structual damages were caused during the sample preparation. Prior to various measurements, a CaHY-type zeolite was prepared by a treatment for ammonia removal of the $CaNH_4Y$-type zeolite. Details of the treatment will be described in the following section. The helium used (for the pulsed microreactor and TPD experiment) was passed through a Yanagimoto RT003 purifier. NO was obtained from a commercial cylinder (Takachiho Chemical Industry, Ltd.) and purified first by passage through a dry NaOH-packed column (for the pulse method and TPD experiment) and then by a repetition of distillations at −196 °C (for the closed gas circulation system).

Apparatus and Procedure. 1. *Pulsed Microreactor*: After a treatment at 150 °C for 3 h in a stream of dry CO_2-free air, the temperature of a sample of *ca.* 10 mg was increased up to the desired temperature (this temperature will be called the pretreatment temperature) at a constant rate of 0.5 °C/min, where the sample was kept for 4 h before being annealed in a stream of He for 2 h. After the temperature of the sample was lowered down to the reaction temperature, 2.26 cm^3 of NO was injected onto the zeolite in a stream (10.0 cm^3/min) of He.

2. *Temperature-programmed Desorption*: TPD studies were carried out as follows: After a run of the pulsed reaction described above was finished, the temperature of reaction vessel was raised at a constant rate of 7.14 °C/min in a stream of He (10 cm^3/min). The effluent gas was periodically analyzed with a gas chromatograph, equipped with a Porapak T and Molecular Sieve 13X column at 50 °C and using He as carrier gas, for contents of NO, N_2O, O_2, and N_2.

3. *Closed Gas Circulation System*: A closed gas circulation system (*ca.* 705 cm^3) equipped with a pyrex reaction vessel was used to study the kinetics of the disproportionation reaction of NO. A zeolite (*ca.* 2 cm^3) was treated at 500 °C in acoordance with the procedure described above under the heading in

"Pulsed Microreactor" and was evacuated (10^{-6} Torr) at a constant temperature (500 °C) for 2 h. After a series of these treatments, the temperature of vessel was adjusted to the reaction temperature and NO gas was introduced into the reaction system. The amount of products was measured by gas chromatography.

Results

Activity and Pretreatment Temperature. The activity was measured at 15 °C with a pulsed microreactor. Since the activity decreased markedly with increasing number of pulses, it is expressed by the rate of N_2O formation in the first pulse, which is taken to indicate the activity for the disproportionation reaction of NO. The gas analysis showed that the only gaseous product is N_2O, in agreement with the result of Addison and Barrer.[1]

Figure 1 shows the relation between activity and pretreatment temperature in the range 400—900 °C. The activity increases with an increase in pretreatment temperature, reaches a broad maximum at 700 °C, and decreases gradually with a further increase in pretreatment temperature. A powder X-ray diffraction examination of zeolites activated at each pretreatment temperature revealed that this gradual decrease in activity is caused by a collapse of the crystalline structure of zeolite pretreated at 800 or 900 °C.

TPD Profile. Addison and Barrer[7] insisted that the N_2O_3 produced by the disproportionation reaction of NO would be stabilized in the zeolite. On the other hand, Chao and Lunsford[2] suggested that the adsorbed N_2O_3 will decompose to give NO and NO_2 when the excess NO gas is removed by evacuation from the reaction mixture. In the procedure described above for temperature-programmed desorption, therefore, the NO_2 gas desorbed by raising temperature was removed by a dry NaOH-packed column in order to avoid complexity. TPD profiles were measured after the first pulse reaction. The change in TPD profile with pretreatment temperature was disclosed. Figure 2 shows the TPD profile of zeolites treated at 700 °C, the numerical values indicating the desorption temperature.

The TPD profile is composed of five signals α, β, γ, δ, and ε arranged in parallel with the increasing temperature scale, of which signals δ and ε are negligibly small. One can consider that peaks α, β, and γ offer information about adsorbed species staying on the zeolite surface after the disproportionation reaction of NO. According to an analysis of desorbed gases, peak α consists of NO, *ca.* 90% of peak β is composed of NO with the residual portion as N_2O, and *ca.* 90% of peak γ is N_2O with the rest as NO.

TPD profiles of zeolites treated at various pretreatment temperatures are also composed of five signals and the area of each peak (α, β, γ) varied independently of the others. In spite of the low resolution of TPD peaks (α, β, γ), the area of each peak (α, β, γ) was determined by drawing a supplementary line in order to separate the three peaks. Figure 3 shows the relation between the area of each peak (α, β, γ) and the pretreatment temperature. The plot breadth in Fig. 3 indicates the experimental error range in connection with the arbitrariness of the method to draw the supplementary lines. The area of peak α decreases gradually with an increase in pretreatment temperature, and those of peaks β and γ increase with increasing pretreatment temperature, reach a broad maximum at *ca.* 700 °C, and decrease with a further increase in pretreatment temperature. The variation in peak areas of β and γ showed a tendency similar to the variation in the activity illustrated in Fig. 1, hence it follows that peaks β and γ reflect the activity. The desorption temperatures for peaks α, β, and γ were approximately constant in all experiments, indicating that the respective adsorp-

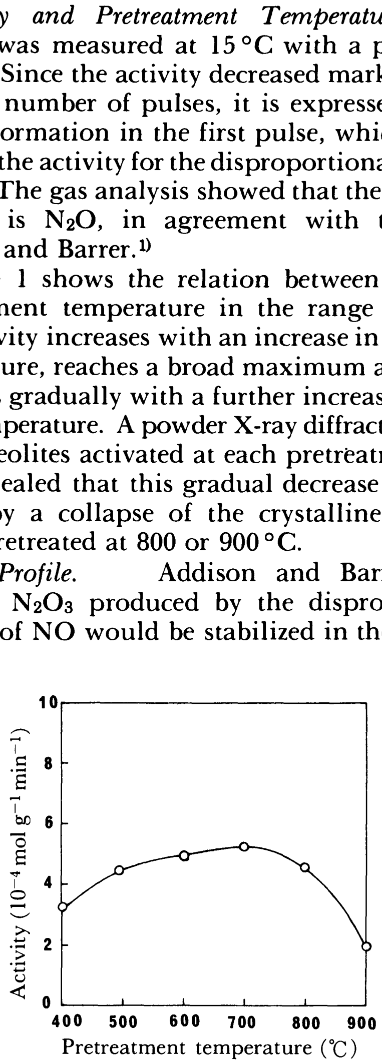


Fig. 1. Activity plotted against pretreatment temperature.

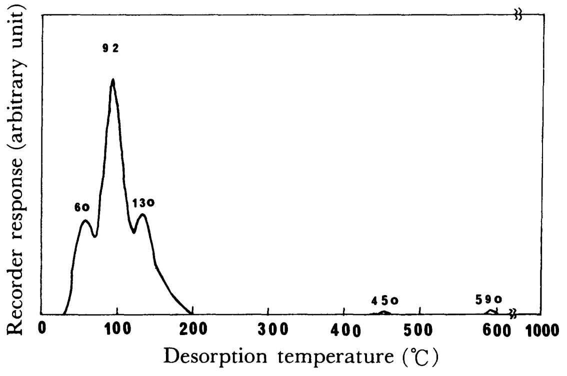


Fig. 2. TPD spectrum of CaHY zeolite heat treated at 700 °C.

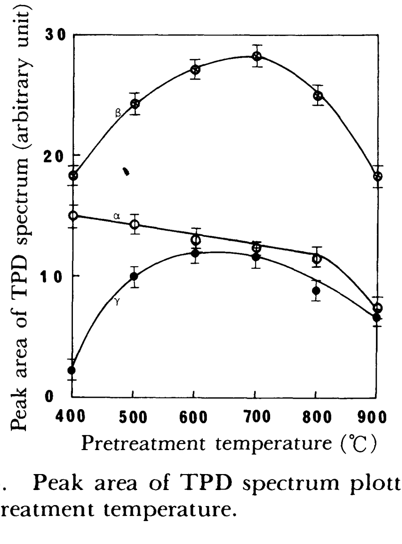


Fig. 3. Peak area of TPD spectrum plotted against pretreatment temperature.

tion states are almost independent of pretreatment temperature.

Reaction Kinetics. The desorption peak of N_2O was recognized in the TPD experiment after a pulse reaction, indicating that readsorption of N_2O formed by the disproportionation of NO will occur. However, we assume for convenience in this paper that irreversible adsorption of N_2O should occur only in the initial stage of reaction, so that the formation rate of N_2O may be expressed as the rate of Reaction 2, specified in the following section, for a comparatively prolonged stage of reaction pass time.

The Elovich equation in wide use is one of the most convenient ways of describing chemisorption kinetics, especially when the chemisorption is slow. The Elovich equation is written in its differential form as $dQ/dt=\alpha \exp(-\beta Q)$ where Q (mol g^{-1}) is the amount of N_2O produced at a reaction pass time t (min) and α and β are constants for each system at a fixed temperature. In its integrated form, the equation can be written as $Q=(1/\beta)\ln(t+t_o)-(1/\beta)\ln t_o$, $t_o=1/\alpha\beta$ (constant) where α (mol g^{-1} min^{-1}) is the initial formation rate of N_2O, *i.e.*, the formation rate of N_2O taken when the reaction pass time t approaches zero.

The dependence of the initial formation rate of N_2O on NO pressure was studied on zeolites pretreated at 500 °C by using a closed gas circulation system at reaction temperature 0 °C. Figure 4 shows the relation between the amount of N_2O produced and the reaction pass time t obtained when the pressure P_o of introduced NO is equal to 110 Torr. The curve in Fig. 4 shows an initial rapid upturn, in good correspondence to the Elovich equation. The best-fit value of t_o as obtained by using the integrated formula of Elovich equation is given in Fig. 5 as 9.87 min, which in turn evaluates α as 1.58×10^{-6} mol g^{-1} min^{-1}. In accordance with this procedure, the relation between the introduced-NO pressure P_o and the initial formation rate α was determined. Figure 6 shows the relation between log P_o and log α. The reaction order of the initial formation rate of N_2O was determined from the slope of the curve in Fig. 6; α is proportional to the third order of P_o in the lower pressure region (*ca.* 30 Torr). In an intermediate pressure region, the slope of the curve in Fig. 6 gradually decreases with an increase in NO pressure and α obeys the 2.2th order of P_o in the higher pressure region (*ca.* 200 Torr). Therefore, it is concluded that the initial formation rate of N_2O is third order with respect to NO pressure, and that the reaction order gradually decreases with an increase in NO pressure.

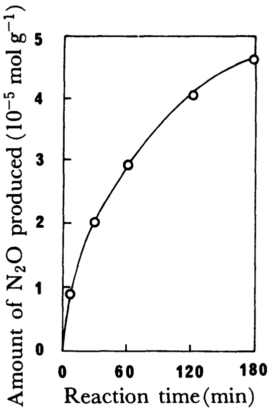


Fig. 4. Amount of N_2O produced plotted against reaction time.
$P_0=110.2$ Torr: Reaction temp. 0 °C

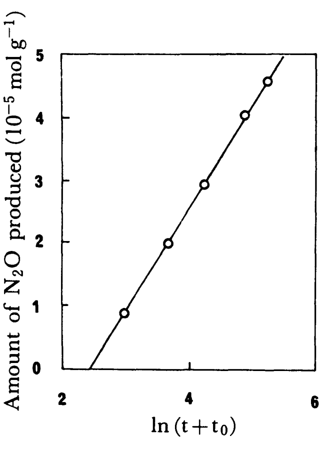


Fig. 5. Relationship between Q and $\ln(t+t_0)$.
$Q=1/\beta \ln(t+t_0)-1/\beta \ln t_0$, $t_0=1/\alpha\beta$, $t_0=9.87$ min

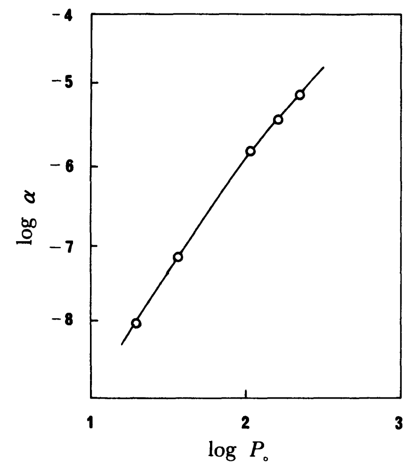
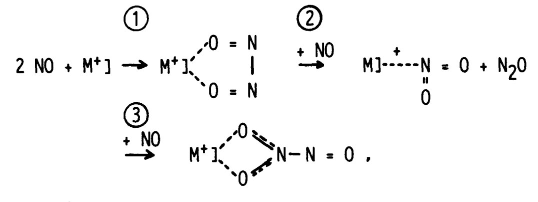


Fig. 6. Relationship between log α and log P_o.

Discussion

Rate Equation for Initial Formation of N_2O. The mechanism proposed by Chao and Lunsford for the disproportionation reaction of NO,[3] is



(from Chao and Lunsford's model[3])

where M^+ refers to Na^+ and Ca^{2+} for NaY- and CaY-type zeolites, respectively. For derivation of the initial formation rate of N_2O, we assume that the backward reaction of step ② is negligible. On this assumption, *i.e.*, the rate determining step is step ②, we have the following effective reaction sequence for the initial formation of N_2O:

$$[\quad] + 2NO \overset{K_1}{=} [N_2O_2], \qquad (1)$$

$$[N_2O_2] + NO \xrightarrow{\vec{k}_2} [NO_2] + N_2O, \tag{2}$$

$$[N_2O_2] + [\quad\ ] = 1, \tag{3}$$

where [ ] denotes vacant adsorption sites, $[N_2O_2]$ denotes N_2O_2 adsorption sites, K_1 is the equilibrium constant for Eq. 1, and $\vec{k}_2$ is the rate constant for Eq. 2. By using Eqs. 1, 2, and 3, the initial formation rate α is formulated as

$$\alpha = \vec{k}_2[N_2O_2]\,P = \vec{k}_2K_1P^3/(1+K_1P^2), \tag{4}$$

where P is the pressure of NO. Therefore, the reaction order n is given by

$$n = \partial \ln \alpha/\partial \ln P = 3 - 2K_1P^2/(1+K_1P^2). \tag{5}$$

Equations 4 or 5 indicates that the initial formation rate of N_2O is expected to obey a third-order relation with respect to NO pressure at the lower pressure region if K_1P^2 is negligibly smaller than 1, and that the reaction order will decrease with an increase in NO pressure. On the other hand, a first-order relation is available if K_1P^2 is so large as to make 1 negligible. These characteristics may interpret the relation between log P_o and log α shown in Fig. 6.

Active Sites. Figure 1 shows that the activity increases with an increase in pretreatment temperature. In a study on the relation between the cation destribution and the residual water content in faujasites with metal cations exchanged, Dempsey and Olson[19] found that the occupancy of Sites I′ and II′[20] increase with an increase in the residual water content. Yamada *et al.*[21] studied chemisorptions of two kinds of gases having different adsorption properties, CO and NO, on NiHY-type zeolites, and concluded that the distribution of Ni^{2+} in the cation Site II increase with an increase in pretreatment temperature. From a study on the disproportionation reaction of NO on MgHY-type zeolites with different degrees of ion exchange, we derived[4] that the concentration of Mg^{2+} serving as active sites increases with an increase in pretreatment temperature. Thus, the effect of pretreatment temperature, shown in Fig. 1,may be considered to originate from an increase in Ca^{2+} distributed in Site II on Y-type zeolite.

In relation to activity and pretreatment temperature, we have described that the activity decreases markedly with increasing number of pulses. This drastic decrease in activity may be interpreted as follows: Most of the active sites or Ca^{2+} distributed in Site II are covered with N_2O_3 produced by the disproportionation reaction immediately after the NO in the first pulse has been introduced onto a CaHY-type zeolite, so that the resulting drastic decrease in the number of active sites will lead to the disappearance of catalytic activity. We[6] formerly reported that the apparent activation energy for the disproportionation of NO on CaY-type zeolite in the temperature range between −24 and 45 °C is −6.9 kcal/mol. Therefore, even if the disproportionation reaction of NO were carried out at 200 °C where NO, N_2O_3, and N_2O once adsorbed are desorbed, it would be most probable that nobody should be able to get a steady state activity of catalyst.

Reaction Mechanisms. On the basis of infrared spectra relating to NO adsorbed on CaY-type zeolite, Chao and Lunsford[3] deduced that the infrared peak assignable to N_2O disappears after the reaction mixture has been pumped out. In our study, however, peak γ of TPD profile has been assigned to N_2O. This discrepancy seems to be due to the fact that the TPD experiment was carried out in a He carrier gas flow with no pumping applied after the activity had been measured according to the pulse method. In addition, an experiment in which N_2O instead of NO was pulsed into the reactor has led to a conclusion that most of induced N_2O molecules remain adsorbed on a CaHY-type zeolite, without being allowed to desorb out into the gas phase. This experimental information is in support of the idea that the adsorptive power of N_2O is stronger than that of NO.

In accordance with the reaction mechanism proposed by Chao and Lunsford,[3] an N_2O_2 adsorbed at a cationic active site causes a rearrangement by reaction with a gas phase NO molecule to produce N_2O and NO_2, and the resulting NO_2 reacts rapidly with an NO molecule in the gas phase, leaving the spieces N_2O_3 on the zeolite surface. This reaction stage is step③ in Chao and Lunsford's model.

A comparison of Figs. 1 and 3 leads us to notice that peaks β and γ have a certain relation in activity. The results can be explained as follows: As is well known, N_2O_3 dissociates easily into NO and NO_2 and thus, the N_2O_3, formed by the disproportionation reaction and left on the surface, is caused to dissociate into NO and NO_2 when heated in the TPD experiment, the resulting NO corresponding to peak β in the TPD profile, whereas the resulting NO_2 is removed during passage through the dry NaOH-packed column before entering the detector.

Peak γ in the TPD profile is expected to be composed of a part of the N_2O formed by disproportionation and still remaining in the zeolite. The diameter of N_2O molecule is larger than that of NO molecule, hence it may follow that N_2O molecule is harder to desorb than NO molecule. This may be the reason for the observation that peak γ appears in a higher temperature region than peak β. On the other hand, peak α may be regarded as corresponding to the unreactive NO which is weakly adsorbed on the zeolite surface.

As seen from Fig. 3 for the pretreatment temperature range 600—700 °C, the areas of TPD peaks β and γ are *ca.* 1.5 and 4 times as large as those for the pretreatment temperature 400 °C. On the basis of these facts, the effect of pretreatment temperature on the area of TPD peak may be deduced as follows: As the pretreatment temperature is increased, *i.e.*, the number of water molecules in the zeolite structure is decreased, the amount of empty sites increases so that the N_2O produced by the disproportionation reaction of NO is made liable to adsorb on empty sites.

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20) The nomenclature adopted in this paper is based on that used by Breck (D. W. Breck, "Zeolite Molecular Sieves," John Wiley and Sons, New York (1974), p. 97). Site I is at the center of a hexagonal prism and Site I′ is in the sodalite cage and on the other side of the 6-membered ring of the hexagonal prism. Site II and II′ are associated with the 6-memberered ring of sodalite cage, which lead to super cages. Site II is displaced towards the center of the super cage, whereas Site II′ is displaced towards the inside of the sodalite cage.

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