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Reactions of Water and Dinitrogen Monoxide Adsorbed on Cation-Exchanged Zeolite with Excess Electrons Generated by Gamma-Radiation

Masayoshi Aoki, Takeshi Nakayama, Chiyoko Nakazato, and Takahiro Masuda*
Department of Chemistry, Faculty of Science, Tokyo Metropolitan University,
Minamiohsawa 1-1, Hachioji-shi, Tokyo 192-03

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Hydrogen formation from water and nitrogen formation from dinitrogen monoxide adsorbed on a zeolite during gamma-irradiation have been studied in order to clarify the role of the metal cation contained in the zeolite and the effect of the pore size; Molecular Sieve 4A, 5A, 13X, and cation-exchanged 13X were used for that purpose. The hydrogen yield from water was observed to increase with increasing amount of adsorbed water. The dependence of $G(H_2)$ on the amount of adsorbed water was affected by the exchange of metal cations and the pore size of the zeolite. For nitrogen formation from dinitrogen monoxide in cation-exchanged 13X, the saturation behavior of $G(N_2)$ could be roughly classified into two categories, namely one approaching ca. 3 and the other around 6. The results indicate that the metal cation participates in the reaction of an excess electron with an adsorbed water molecule, at least in the range of small amounts of water.

The radiolysis of a substance adsorbed on a solid surface often results in an enhancement of the product yield. This fact has generally been explained in terms of energy transfer from a solid (adsorbent) to an adsorbed substance (adsorbate). In a previous paper,[1)] we reported that water molecules adsorbed on an X-type zeolite (Molecular Sieve 13X) react with excess electrons, which are generated by gamma-radiation in the adsorbent, to produce molecular hydrogen. The *G*-value for the formation of hydrogen was observed to increase stepwise with increasing amount of adsorbed water. The range of the amount of adsorbed water where the first plateau appears was found to correspond approximately to the amount of sodium ions contained in 13X. To explain this result, the following mechanism was tentatively proposed:

$$e^- + Na^+ \longrightarrow Na, \tag{1}$$

$$Na + H_2O \longrightarrow H + NaOH, \tag{2}$$

and

$$H + H \longrightarrow H_2. \tag{3}$$

The argument is based on the fact that in the zeolite a water molecule exists in close proximity to Na^+ when it is physically adsorbed,[2)] and $(Na_4)^{3+}$–$(H_2O)_x$ is formed by trapping an excess electron.[3)] If this mechanism is relevant, hydrogen formation must be affected by an exchange of the metal cation in zeolite. The first purpose of this study was to verity the participation of the metal cation in hydrogen formation at small aounts of adsorbed water. Concomitantly, the mechanism is based on the assumption that the reaction takes place in a sodalite unit and a supercage as well as on the outer surface. The second purpose is to examine the effect of the pore size on hydrogen formation.

In a previous study,[1)] a kinetic analysis using some scavengers was applied for estimating the reaction mechanism. The reaction of a scavenger with an electron may also be affected by an exchange of the metal cation and depends on the pore size of the zeolite. Nitrogen formation from dinitrogen monoxide was, therefore, examined in several systems which were different from each other with respect to the metal cation or pore size.

The experimental results obtained in this study support the above mechanism, including the participation of metal cations. However, no decisive evidence could be obtained concerning the mechanism of nitrogen formation from dinitrogen monoxide in the zeolite during gamma-irradiation.

Experimental

Materials. Zeolite: Molecular Sieve 13X ($Na_{86}(AlO_2)_{86}(SiO_2)_{106}$, abbreviated to NaX hereafter), Molecular Sieve 4A ($Na_{12}(AlO_2)_{12}(SiO_2)_{12}$, abbreviated to 4A), and Molecular Sieve 5A ($Ca_6(SiO_2)_{12}(SiO_2)_{12}$, abbreviated to 5A) were purchased from Nippon Kuromatokogyo K. K. Dinitrogen monoxide, sulfur hexafluoride, and ammonia were obtained from Takachiho Kagakukogyo K. K. Carbon tetrachloride was of spectrograde from Merck. Ethyl bromide was purchased from B. D. H. Water was distilled three times after treatment with alkaline permanganate.

Preparation of Cation-Exchanged X-Type Zeolite. NaX powder obtained from Nishio Co., Ltd. was used as a starting material for the preparation of the cation exchanged X-type zeolite. NaX was immersed in an aqueous solution of ammonium, alkali, or alkaline earth metal chloride and stirred at 80 °C for 10 h. After filtration the procedure was repeated several times. Then, the cation-exchanged 13X was washed with distilled water and filtered. Washing and filtration were repeated until chloride could not be detected in the filtrate. The degree of cation-exchange was determined by atomic absorption spectrometry after hydrolysis with HCl. It was calculated on the basis of the ratio of content to Al. The obtained values are as follows: 86% for LiX, 92% for KX, 70% for MgX, 94% for SrX, 100% for BaX, 70% for CaX, and 73%

for NH_4X. The degree of crystallinity was checked by the X-ray powder method. The crystallinity is well kept for alkali metal exchanged 13X but was slightly lost for alkaline earth metal-exchanged 13X. NH_4-exchanged 13X was found to be amorphous after degassing at 600 °C. Cation-exchanged X-type zeolite is abbreviated as LiX, KX, etc. according to its cation. NH_4-exchanged 13X degassed at 600 °C is expressed as decationated X.

Procedures. Before experimental use, all zeolite samples were treated as follows. About 12 g of the zeolite was degassed in a quartz vessel at 400 to 600 °C for 24 h under a pressure below 10^{-2} Pa, since adsorbed water can be desorbed completely by degassing at a temperature above 350 to 400 °C,[4] and the structure of the zeolite is maintained below 770 °C.[5,6] The sample was divided into six ampoules attached to the vessel in 1 to 2 g each. The X-ray powder method showed no effect on the crystallinity after the treatment. The procedures for introducing adsorbates into the ampoules have been described elsewhere in detail.[7] The molecular hydrogen, nitrogen, and oxygen produced by gamma-irradiation were analyzed by gas chromatography according to the method employed in a previous study on silica gel.[8]

Gamma-irradiation was carried out at room temperature with a dose rate of 7.85×10^2 Gy h^{-1}. The total dose was 1.34×10^4 Gy.

Adsorption Isotherms. The adsorption isotherms were measured for CCl_4, N_2O, and SF_6 in order to obtain an effective amount of an adsorbate on the zeolite. For water, it was reported by Barrer and Bratt that 99.98% of the introduced water is adsorbed on NaX when 1.5×10^{-2} mol g^{-1} of water is introduced.[9] Therefore the effective amount of adsorbed water can be taken as being the introduced amount under the condition of this study. The adsorption isotherms for the above-mentioned three electron scavengers were measured in both the absence and presence of water. The obtained isotherms indicate that 99.7% of 8×10^{-4} mol g^{-1} CCl_4, 90% of 10^{-4} mol g^{-1} N_2O, and 90% of 10^{-4} mol g^{-1} SF_6 are adsorbed on NaX in the presence of 3.4×10^{-3} mol g^{-1} of water. In the absence of water, 100% of CCl_4, above 95% of N_2O, and 95% of SF_6 were adsorbed on NaX when the above-mentioned ammount was introduced, respectively. Since competition kinetics was applied for the data obtained in the region below 10^{-5} mol g^{-1} of the adsorbate, no correction was made for the adsorbed amounts of these adsorbates.

Results and Discussion

Figure 1 shows the dependence of $G(H_2)$ on the amount of adsorbed water for LiX, NaX, and KX. In this paper the amount of adsorbate is expressed by mol g^{-1}, which represents the mol of adsorbate per g of the zeolite. The most steep rising of the curve is observed for LiX among the three. For NaX and KX, the rise is almost the same, although a slight difference exists in the plateau value. Dzhigit and her co-workers reported that the heat of adsorption of water on some monovalent cations increases in the order Cs<K≈Na<Li.[10,11] Ward investigated the infrared spectra of the pyridine adsorbed on alkali and alkaline earth cations in the Y-type zeolite and indicated that the frequency of a band assigned to the adsorbate-cation interaction increases with decreasing radius of the cation or with increasing strength of the electrostatic field originating from the cation.[12] These facts indicate that an adsorbate interacts with the metal cation predominantly in the zeolite, and that the magnitude of the interaction is of the order of Cs<K≈Na<Li. The curves shown in Fig. 1 are consistent with these data, and support the assumption that the reaction of excess electrons with water takes place through the metal cations in the zeolite, at least in the region of small amounts of adsorbed water.

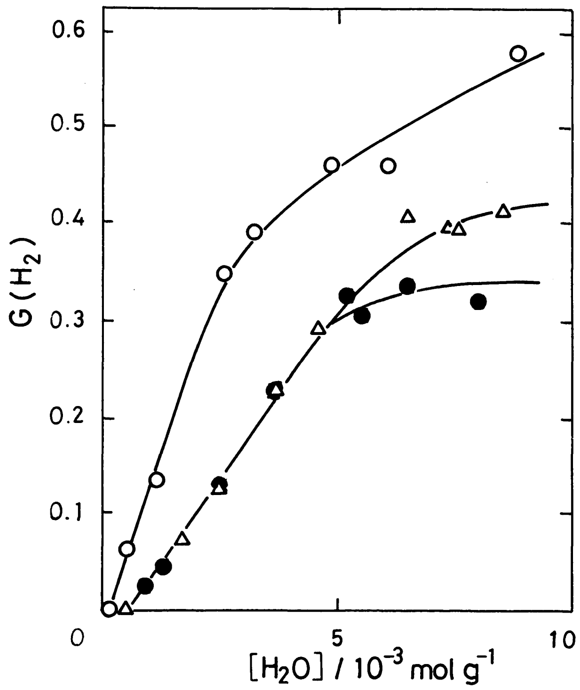

Fig. 1. Dependence of $G(H_2)$ on the amount of adsorbed water. ○: LiX, △: NaX, ●: KX.

The dependence of $G(H_2)$ on the amount of adsorbed water for 4A, 5A, and decationated X are shown in Fig. 2, together with that for NaX. The curve for 5A shows a double plateaux similar to that for NaX, while a simple saturation is seen in the curves for 4A and decationated X. In the case of 5A, the first saturation occurs in the range 1—3×10^{-3} mol g^{-1} of the adsorbed water, which is approximately half compared with the range of the first plateau for NaX. The content of Na^+ in NaX is 6.4×10^{-3} mol g^{-1} and that of Ca^{2+} in 5A is 3.6×10^{-3} mol g^{-1}. If a one-to-one correspondence is assumed, the first saturation for 5A can also be explained by the adsorption of water molecules on metal cations in this system. If excess electrons react with water molecules through the metal cations in the range of the first plateau, it is necessary to examine the reactivity of electrons in the range of the second plateau. A competition method has been applied for estimating the reactivity using some electron scavengers. At 1.2×10^{-2} mol g^{-1} of adsorbed water, N_2O, SF_6, or CCl_4 was added to the NaX–H_2O

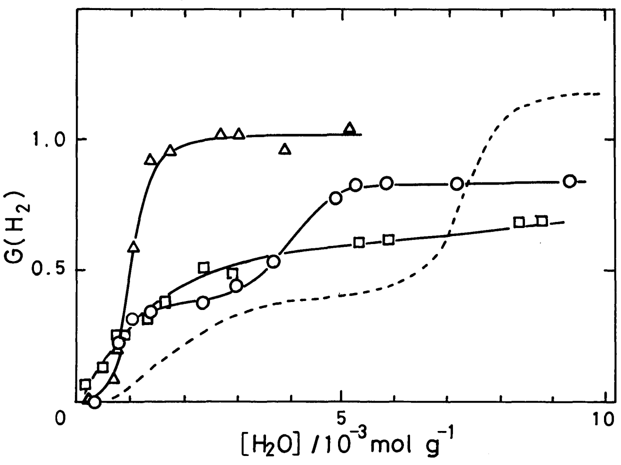

Fig. 2. Dependednce of $G(H_2)$ on the amount of adsorbed water. △: 4A(NaA), ○: 5A(CaA), broken line: NaX. □: decationated X.

system and $G(H_2)$ was measured. SF_6 was found to show no effect, but N_2O and CCl_4 caused a decrease in $G(H_2)$. Hydrogen formation from water adsorbed on zeolite is, as discussed in a previous paper,[1] explained as follows:

$$MS \rightsquigarrow MS^+ + e^-, \tag{4}$$

$$e^- + MS^+ \longrightarrow MS^*, \tag{5}$$

$$e^- + H_2O \longrightarrow H + OH^-, \tag{6}$$

$$e^- + S \longrightarrow \text{product}, \tag{7}$$

and

$$H + H \longrightarrow H_2. \tag{3}$$

Here, MS and S represent zeolite and a scavenger, such as N_2O, respectively. Reaction 6 is equivalent to a pair of reactions (1 and 2). From the above reactions, the following equation can be derived:

$$\frac{1}{G(H_2)} = \frac{2}{G_e}\left\{1 + \frac{k_5[MS^+] + k_7[S]}{k_6[H_2O]}\right\}. \tag{I}$$

By plotting $1/G(H_2)$ against (S), a straight line is obtained and the ratio of the rate constants (k_7/k_6) can be calculated from the slope for N_2O and CCl_4, respectively. Consequently, the ratio of the rate constant for the reaction of excess electrons with CCl_4 against that with N_2O, $k(CCl_4)/k(N_2O)$, is obtained. The ratio (2.9) is close to that for hydrated electron (3.6) rather than that obtained in the range of the first plateau (1.3). Therefore, molecular hydrogen is estimated to form through a reaction between "hydrated electrons" which are slightly different from hydrated electrons in liquid water,

$$\text{“}e_{aq}^-\text{”} + \text{“}e_{aq}^-\text{”} \longrightarrow H_2. \tag{8}$$

The simple saturation of $G(H_2)$ observed in 4A or decationated X system differs from the saturation behavior in the 5A or NaX system. The skeleton structure of 4A is the same with 5A, but differs from that of NaX. On the other hand, the metal cation is common between 4A and NaX. The supercage of 4A or 5A comprises eight sodalite units, but that of NaX is surrounded by twelve sodalite units. Therefore, the diameter of the supercage of NaX (ca. 1.3 nm) is slightly larger than that of 4A or 5A (ca. 1.14 nm). The content of the Na^+ ion in 4A (7.04×10^{-3} mol g^{-1}) is larger than that in NaX (6.41×10^{-3} mol g^{-1}). These data suggest that free space in the supercage of NaX allowed for the water molecule is larger than that of 4A. Probably in 4A, the water molecule is tightly adsorbed on Na^+ and exists alone, while in NaX, free space allows a loose adjacent existence of the water molecules, which may form a trap for excess electrons. It was revealed by the X-ray powder method that NH_4–X degassed at 600 °C is amorphous and hence, decationated X can be taken as silica gel. Hydrogen formation in the decationated X–H_2O system is also suppressed by electron scavengers. A kinetic analysis, however, could not be applied to the suppression curves of $G(H_2)$ by electron scavengers, since plots of $1/G(H_2)$ against [S] do not give a straight line. Therefore, the reactivity of the excess electrons generated in the decationated X–H_2O system cannot be estimated, although it is clear that an energy transfer from the adsorbent to water takes place through excess electrons.

In NaX–H_2O systems, excess electrons decay in two ways. One is reaction 1 and the other reaction 5. If reaction 1 is very fast and reaction 2 is rate-determinig, the competitive kinetics for $G(H_2)$ gives the following expression:

$$\frac{1}{G(H_2)} = \frac{2}{G_e}\left(1 + \frac{k_5[MS^+]}{k_2[H_2O_{ad}]}\right), \tag{II}$$

where $[H_2O_{ad}]$ represents the amount of adsorbed water and G_e is the initial G-value of electrons generated in the system. By plotting $1/G(H_2)$ against $1/[H_2O_{ad}]$, both G_e and $k_5[MS^+]/k_2$ are obtained from the intercept and slope of a straight line. For the 4A–H_2O system, G_e is 3.0 and $k_5[MS]/k_2$ is 0.47×10^{-3} mol g^{-1}, while 3.1 and 8.7×10^{-3} mol g^{-1} were obtained for the NaX–H_2O system, respectively.[1] The difference in $k_5[MS]/k_2$ between 4A and NaX cannot by explained at the present stage of the study. It is, however, conceivable that contact between Na^+ and water molecules is close and strong in 4A compared with NaX. In NaX, electron scavengers effectively suppress the formation of molecular hydrogen

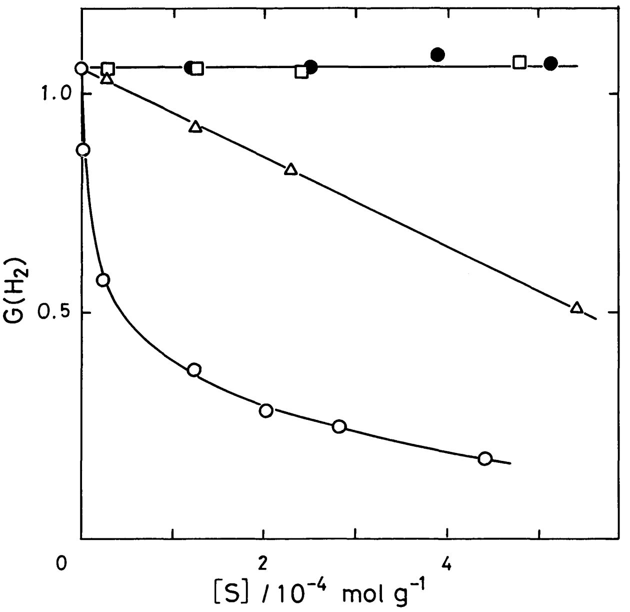

Fig. 3. Effect of some electron scavengers on hydrogen formation from water adsorbed on 4A. 2.7×10^{-3} mol g^{-1} of water adsorbed. ○: N_2O, △: SF_6, □: CCl_4, ●: C_2H_5Br.

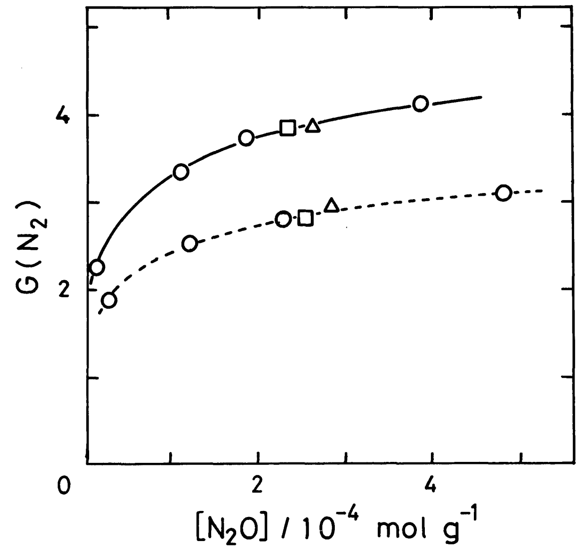

Fig. 4. Dependence of $G(N_2)$ on the amount of N_2O adsorbed on 4A and 5A. Solid line: 5A, broken line: 4A. △: SF_6, □: CCl_4.

from the water adsorbed on NaX. However, some scavengers are ineffective in 4A, as is shown in Fig. 3. Carbon tetrachloride and ethyl bromide have no effect and sulfur hexafluoride weakly inhibits the formation of molecular hydrogen. The molecular sizes of these electron scavengers (except for dinitrogen monoxide) are larger than the window size of 4A (0.42 nm in diameter); hence, the ineffective scavengers are probably adsorbed only on the outer surface of 4A. The outer surface is less than 1% of inner surface with respect to the area.[13] However, suppression is observed, if the reaction of scavengers with excess electrons is more than a hundred times faster than that of water with excess electrons. Since sulfur hexafluoride is highly reactive toward electrons in nonpolar liquids[14] and the excess electrons generated in zeolite were found to resemble excess electrons in nonpolar liquids with respect to reactivity toward some electron scavengers,[1,15] it may be due to the high reactivity toward electron that sulfur hexafluoride shows a weak suppression of the formation of hydrogen despite its molecular size. In the NaX system, the ratios of the rate constant for a reaction of excess electrons with scavengers to that with water molecules are estimated as 8.02×10^3, 1.04×10^4, and 1.71×10^4 for N_2O, CCl_4, and SF_6, respectively.[1] However, the difference in the reactivity toward excess electrons between CCl_4 and SF_6 in the 4A system suggests that excess electrons in the 4A system have a property close to that in 2,2-dimethylpropane, where the reactivity of SF_6 is several times larger than CCl_4.[14]

In the 4A–H_2O–N_2O system, the dependence of $G(H_2)$ on the amount of adsorbed N_2O can be analyzed on the basis of competition kinetics. However, plots of $1/G(H_2)$ against $[N_2O]/[H_2O]$ are not on straight lines. The plots deviate downward from straight lines with increasing amount of N_2O. This is suggests that only a part of the N_2O introduced into an ampoule is effective. Lowering of the suppression by N_2O in the 4A–H_2O–N_2O system would be due to competition of N_2O with H_2O toward the adsorption site on the inner surface of zeolite.

In the 4A–N_2O system, $G(N_2)$ approaches a saturated value of ca. 3, as can be seen in Fig. 4. This is very close to the values of G_e kinetically estimated from the formation of molecular hydrogen in 4A–H_2O and NaX-methanol systems,[15] or the formation of molecular nitrogen in the NaX–N_2O[16] system. The dependence of $G(N_2)$ on the amount of adsorbed N_2O can be explained by reaction 5 and 9:

$$e^- + N_2O \longrightarrow N_2 + O^-. \qquad (9)$$

Competition between these reactions gives the following expression:

$$\frac{1}{G(N_2)} = \frac{2}{G_e}\left(1 + \frac{k_5[MS^+]}{k_9[N_2O]}\right). \qquad \text{(III)}$$

Plots of $1/G(N_2)$ against $1/[N_2O]$ approximately form a straight line, as shown in Fig. 5. From the intercept and the slope, 3.3 and 3.7×10^{-5} mol g^{-1} are obtained as G_e and $k_5[MS^+]/k_9$, respectively. The dependence of $G(N_2)$ on the amount of adsorbed N_2O is shown in Fig. 6 for cation-exchanged 13X. They are roughly classified into two groups, namely those approaching ca. 3 and above 4. NaX, CaX, or SrX belongs to the first group and LiX,

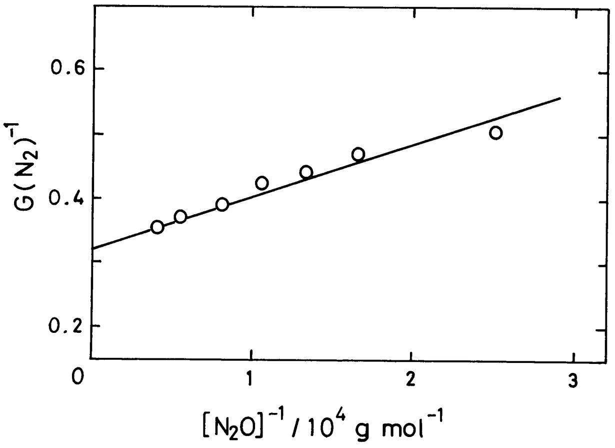

Fig. 5. $1/G(N_2)$ vs. $1/[N_2O]$. 4A–N_2O system.

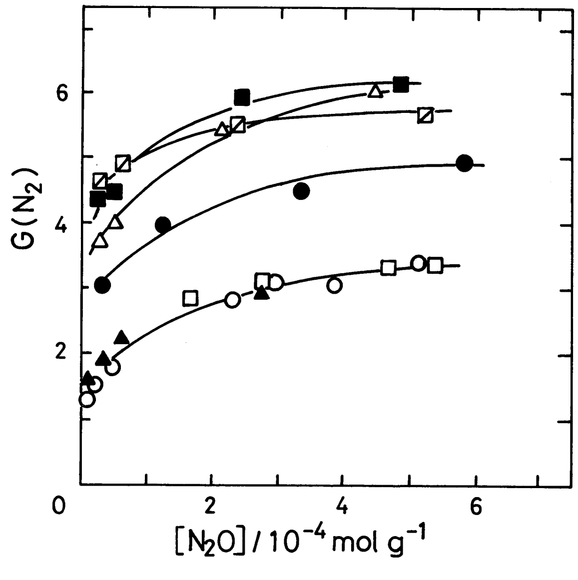

Fig. 6. Dependdence of $G(N_2)$ on the amountof N_2O adsorbed on various kinds of cation-exchanged X-type zeolites. ▨: LiX, □: NaX, ■: KX, ●: MgX, ▲: CaX, ○: SrX, △: BaX.

Table 1. G_e and the Values of $k_5[MS^+]/k_9$ for First Group of Cation-Exchanged Zeolites

Zeolite	G_e	$k_5[MS^+]/k_9$ mol g^{-1}
4A (NaA)	3.3	3.7×10^{-5}
5A (CaA)	4.3	2.6×10^{-5}
NaX	3.1	1.7×10^{-5}
SrX	2.9	1.5×10^{-5}
CaX	3.0	1.5×10^{-5}

Table 2. $G(N_2)$ and $G(O_2)$ for Second Group of Cation-Exchanged Zeolites

Zeolite	$G(N_2)$[a]	$G(O_2)$[a]
KX	6	2.5
LiX	6	1.2
MgX	5	0.1
BaX	6	0.6

a) Observed values at 5×10^{-4} mol g^{-1} of N_2O.

KX, BaX, MgX or 5A to the second. A kinetic treatment based on expression III gives G_e and $k_5[MS^+]/k_9$, similarly to the 4A–N_2O system. The values obtained for group 1 are summarized in Table 1 together with the values for 4A and 5A. The estimated G_e-values for group 1 are around 3, similar to the 4A system. However, the value of $k_5[MS^+]/k_9$ for 4A is apparently larger than those for members of group 1. The value for 5A lies between 4A and group 1. The factors causing the increase in $k_5[MS^+]/k_9$ are as follows: 1) an increase in $[MS^+]$, 2) increase in k_5, 3) a decrease in k_9, and 4) a decrease in the effective amount of N_2O. Since G_e is almost the same as in other systems, an increase in $[MS^+]$ is not a cause. If excess electrons generated in the 4A system resemble those in 2,2-dimethylpropane, even in the presense of H_2O, as already discussed above, their mobility in dry 4A may be larger than that in wet 4A. Therefore k_5 in 4A can be thought to be larger than that in X-type zeolite. In other words, the ratio of the rate constants (k_5/k_9) is large in dry 4A, compared with that in NaX. The decrease in the effective amount of N_2O may be neglected, because a liner relationship holds in plots of $1/G(N_2)$ vs. $1/[N_2O]$, as is shown in Fig. 5.

Saturated values of $G(N_2)$ for the second group are approximately double compared with the values for the first group, as is shown in Fig. 6. In the NaX–CH_3OH–N_2O system, a large $G(N_2)$, 10, was observed in the region of small amounts of methanol (2.5×10^{-3} mol g^{-1}) and the G-value was explained tentatively by a short chain reaction.[15] However, in the NaX–H_2O–N_2O system $G(N_2)$ was found to approach 4 in the presence of 4×10^{-3} mol g^{-1} of H_2O, although it is 2.8 in the NaX–N_2O system. A similar $G(N_2)$ is seen in the 5A–N_2O system. Saturated $G(N_2)$s for the second group are larger than these values. The values of $G(N_2)$ and $G(O_2)$ are summarized in Table 2. They suggest a one-to-two corresponsence toward excess electrons, although there is no stoichiometry between the formation of nitrogen and oxygen. The members of the second group have no common characteristics regarding the structure or properties of exchanged cations. In the radiolysis of hexane or cyclohexane, nitrogen formation from N_2O exceeding the consumed electrons was reported,[17,18] while a one-to-one correspondence holds in 2,2-dimethylpropane. This fact suggests a possible relation between the mechanism of nitrogen formation and the mobility of excess electrons. Unfortunately, this study is insufficient for discussing the possibility.

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