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Radiolysis of Methanol Adsorbed on Zeolite

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Radiolysis of methanol adsorbed on synthesized zeolite was investigated by means of product analysis. Molecular hydrogen, formaldehyde, and ethylene glycol are produced as major products. The *G*-value for the formation of H_2 increases with increasing amount of methanol adsorbed on zeolite and approaches ca. 2.1 at about 10^{-2} mol of methanol per g of zeolite, where the coverage of methanol is approximately unity and *G*-values of ca. 1.0 are observed for formaldehyde and ethylene glycol. Addition of an electron scavenger causes decrease in $G(H_2)$. However, the hydrogen formation is not completely suppressed by N_2O, SF_6, or CCl_4. Kinetics in solution is useful for the interpretation of results and allows the estimation of the *G*-value for the generation of electron in zeolite and of its relative reactivity toward methanol and some electron scavengers.

Radiolysis of compounds adsorbed on the surface of solid has been extensively investigated because of much interest in the mechanism of energy transfer from adsorbent to adsorbate and in reaction specificity possibly observed in the adsorbed state.[1–6] In an irradiated solid such as silica gel or zeolite, formation of electron and positive hole has been confirmed by experiments using electron or hole scavenger.[7–12] Recently, we found that a part of electrons generated in an irradiated zeolite (Molecular Sieve 13X; abbreviated to MS) are very similar to quasi-free electrons produced in irradiated liquid 2,2-dimethylpropane with respect to reactivity toward some electron scavengers.[13,14] The result suggests that rate constants for reactions of electrons produced in irradiated MS with a substrate adsorbed on the solid may be estimated by competition kinetics using electron scavengers. The synthetic zeolite, MS, is characterized by the possession of many cages and channels. Especially, the supercavity of MS is known to allow passage of molecules below 1 nm in effective diameter. A variety of compounds, therefore, can be used as substrates or scavengers to clarify the detailed profile of radiolysis in heterogeneous systems.

This paper deals with a kinetic study on reactions of methanol adsorbed on MS with electrons or positive holes generated in irradiated MS. Yields of radiolytic products, molecular hydrogen, formaldehyde, and ethylene glycol, were discussed in terms of a mechanism which resembles one operative in solution.

Experimental

Zeolite (MS) was obtained from Nippon Kuromatokogyo K. K. The specific surface area is 1030 $m^2 g^{-1}$. Dinitrogen monoxide and sulfur hexafluoride were purchased from Takachiho Kagakukogyo K. K. Methanol (Uvasol) and carbon tetrachloride were obtained from Merck.

Samples were evacuated at 600 °C for 24 h prior to introduction of adsorbate(s). The experimental procedures were described in detail elsewhere.[13,14] Irradiation was carried out by ^{60}Co with a total dose of 1.34×10^4 Gy at room temperature. The amounts of molecular hydrogen and nitrogen were determined by gas chromatography according to the method employed in previous works.[11–14] Formaldehyde was determined colorimetrically by using chromotropic acid. Ethylene glycol was oxidized with periodic acid to formaldehyde after being extracted from the irradiated sample with methanol and subjected to the colorimetry.

Results

As shown in Fig. 1, the *G*-value for the formation of molecular hydrogen increases with increasing amount of methanol adsorbed on MS, but the increase rate is gradually reduced in the range of adsorbed amount above 5×10^{-3} mol of methanol per g of MS (the adsorbed amount on MS will be expressed in mol g^{-1} hereafter). $G(H_2)$ was observed to be ca. 2.1 at 1×10^{-2} mol g^{-1} where the coverage of methanol is unity approximately. On the other hand, the formation of H_2 was hardly observed in the region below 1×10^{-3} mol g^{-1}. This suggests that a limited amount of H_2 or H atom produced by irradiation is chemisorbed on MS or otherwise that some active sites of MS may consume a limited amount of methanol without irradiation, since chemisorption of ethanol was reported to proceed on high-surface silica (Cabosil) by Abrams and Allen.[3]

In the presence of an electron scavenger such as N_2O, $G(H_2)$ decreases with increasing amount of the scavenger. Figures 2 and 3 show the dependence of $G(H_2)$ on amounts of N_2O and CCl_4, respectively. The adsorbed amount of methanol is 9×10^{-3} mol g^{-1}. In

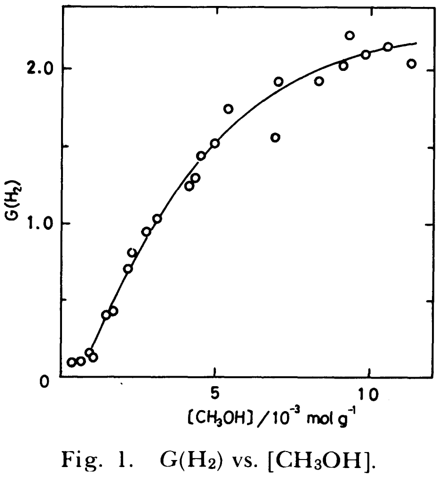

Fig. 1. $G(H_2)$ vs. $[CH_3OH]$.

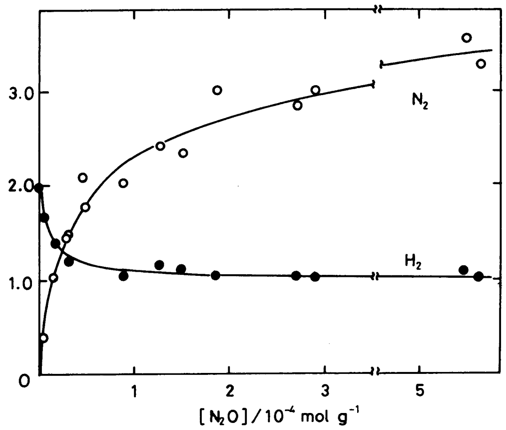

Fig. 2. $G(H_2)$ and $G(N_2)$ vs. $[N_2O]$. $[CH_3OH]=9\times10^{-3}$ mol g^{-1}.

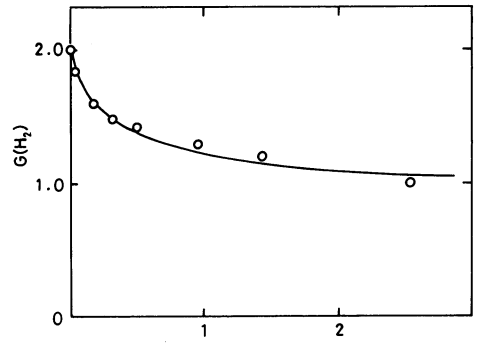

Fig. 3. $G(H_2)$ vs. $[CCl_4]$. $[CH_3OH]=9\times10^{-3}$ mol g^{-1}.

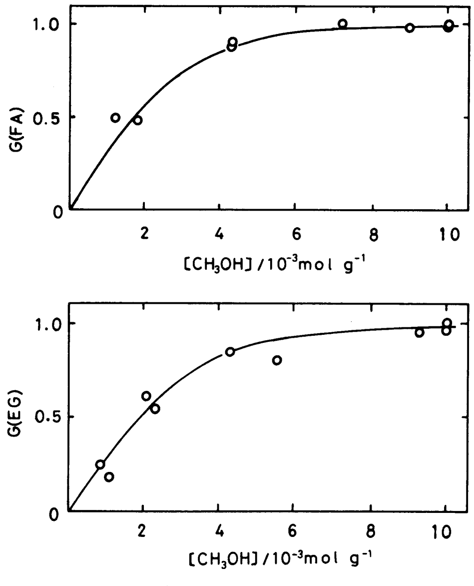

Fig. 4. G(FA) and G(EG) vs. $[CH_3OH]$.

both cases, $G(H_2)$ approaches to 1 and appears to be fixed over the region above 1×10^{-4} mol g^{-1} for N_2O and 2×10^{-4} mol g^{-1} for CCl_4. In the MS-CH_3OH-N_2O system, N_2 is produced from N_2O as expected. $G(N_2)$ increases also with increasing amount of N_2O and a small increase continues even in the region where $G(H_2)$ appears to be constant. At 5.5×10^{-4} mol g^{-1} N_2O, $G(N_2)$ amounts to 3.4. On the contrary, in the MS—N_2O system $G(N_2)$ is constant, 2.8, at amounts above 1×10^{-4} mol g^{-1} N_2O, as already reported.[14] With SF_6, the behavior of $G(H_2)$ is similar to that in the case of CCl_4, but not suitable for quantitative treatment because of a deviation of experimental points.

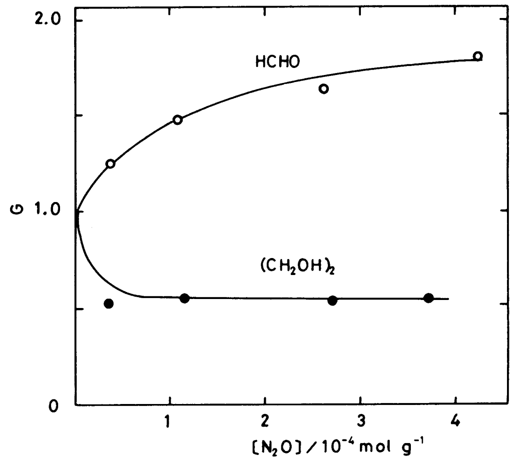

Fig. 5. G(FA) and G(EG) vs. $[N_2O]$. $[CH_3OH]=9\times10^{-3}$ mol g^{-1}.

As in liquid methanol, a considerable amount of formaldehyde or ethylene glycol has been detected and their G-values increase with increasing amount of methanol similarly to the case of $G(H_2)$ (Fig. 4). At 9×10^{-3} mol g^{-1}, the G-values for formaldehyde, G(FA), and ethylene glycol, G(EG), are ca. 1.0, as seen in Fig. 4. In the presence of N_2O, G(EG) is reduced to 0.57 and G(FA) increases with increasing amount of N_2O as seen in Fig. 5. At 4.2×10^{-4} mol g^{-1} of N_2O, G(FA) was observed to be 1.87.

Discussion

In this study, G-values are calculated on the basis of the total energy absorbed by adsorbent and adsorbate, because the energy absorbed by adsorbate cannot be neglected for such a large amount of methanol as 1×10^{-2} mol g^{-1}. In the range of adsorbed amount of methanol below 1×10^{-2} mol g^{-1}, the coverage is kept within unity and an adsorbed methanol molecule is allowed barely to have a limited number of neighbors. In consideration of the highly developed network structure of MS, the situation can be approximated to a dilute solution where solvent is immovable. Therefore, an attempt was made to use a kinetic treatment usually applied to dilute solution so as to interpret the experimental results obtained in the present heterogeneous systems. The formation of molecular hydrogen will be explained by the following reactions:

$$\mathrm{MS} \rightsquigarrow \mathrm{MS}^+ + e^-, \qquad (1)$$

$$e^- + \mathrm{MS}^+ \longrightarrow \mathrm{MS}^*, \qquad (2)$$

$$e^- + \mathrm{CH_3OH_{ad}} \longrightarrow \mathrm{CH_3O}^- + \mathrm{H}, \qquad (3)$$

$$\mathrm{H} + \mathrm{CH_3OH_{ad}} \longrightarrow \mathrm{H_2} + \mathrm{CH_2OH}, \qquad (4)$$

where CH_3OH_{ad} represents an adsorbed methanol molecule and MS^+ designates a positive hole. In this system, electrons produced in Reaction 1 will be consumed by Reactions 2 and 3. Thus the following equation is derived:

$$1/G(H_2)=1/G_e(1+k_2[MS^+]/k_3[CH_3OH_{ad}]). \qquad (I)$$

As shown in Fig. 6, plots of $1/G(H_2)$ vs. $1/[CH_3OH_{ad}]$ give a straight line with a slope of 1.56×10^{-3}, an intercept of 0.371, and a correlation coefficient of 0.9683, if correction is made for the adsorbed amount of CH_3OH ineffective in the formation of H_2 by shifting the origin of Fig. 1 to (1×10^{-3}, 0.13). From the intercept, G_e is obtained to be 2.7, which is close to the $G(N_2)$ of 2.8 obtained in the MS-N_2O system. This indicates that methanol reacts with N_2O-scavengeable electrons to produce H_2. The slope gives the ratio, $k_2[MS^+]/k_3$, of 4.2×10^{-3} mol g^{-1}.

In the presence of N_2O, the following reaction occurs:

$$e^-+N_2O \longrightarrow N_2O+O^-. \qquad (5)$$

For the MS-CH_3OH-N_2O system, therefore, $G(H_2)$ will be expressed by

$$1/G(H_2)=1/G_e(1+k_2[MS^+]/k_3[CH_3OH_{ad}] + k_5[N_2O]/k_3[CH_3OH_{ad}]). \qquad (II)$$

Plots of $1/G(H_2)$ vs. $[N_2O]$ with data shown in Fig. 2 should give a straight line. As shown in Fig. 7, however, they give a curve dependent on the amount of N_2O. In a limited region below 1.5×10^{-5} mol g^{-1} N_2O where the formation of hydrogen is effectively suppressed by N_2O, a straight line with a slope of 1.03×10^4, an intercept of 0.556, and a correlation coefficient of 0.9954 is obtained. At amounts above 1.5×10^{-5} mol g^{-1}, the decrease in $G(H_2)$ is slowed down and $G(H_2)$ becomes constant. The partial depression will be interpreted in terms of either a precursor of hydrogen other than electron or decrease in effective amount of N_2O on MS due to the coexistence of methanol. In the MS-N_2O system, $G(N_2)$ was observed to be 2.8 at amounts of N_2O above 2×10^{-4} mol g^{-1} and a partial depression of $G(N_2)$ by SF_6 or CCl_4 was observed similarly with the present case of $G(H_2)$. If a precursor of hydrogen other than electron exists and N_2O does not react with it, a good agreement between the saturated $G(N_2)$, 2.8, and the G_e estimated by extrapolation of plots of $1/G(H_2)$ vs. $1/[CH_3OH_{ad}]$, cannot be interpreted. Furthermore, CCl_4 was observed to behave similarly to N_2O with respect to the partial depression of the hydrogen formed from methanol, in spite of the fact that it lowers only a part of $G(N_2)$ in the MS-N_2O system. These results suggest that the partial depression of hydrogen formation is caused by decrease in effective amount of scavenger due to competition with methanol for limited adsorption sites. From the linear relation between $1/G(H_2)$ and $[N_2O]$ obtained in the region of small amount of N_2O, G_e can be estimated. Since the intercept is equal to $1/G_e(1+k_2[MS^+]/k_3[CH_3OH_{ad}])$ and $k_2[MS^+]/k_3$ is 4.2×10^{-3} mol g^{-1} as described above, 2.6 is obtained as G_e, which is consistent with that obtained in the MS-CH_3OH and MS-N_2O systems. Thus, the ratio of rate constants, k_5/k_3, is estimated to be 2.5×10^2 from the slope, which is equal to $1/G_e(k_5/k_3 \cdot [CH_3OH_{ad}])$.

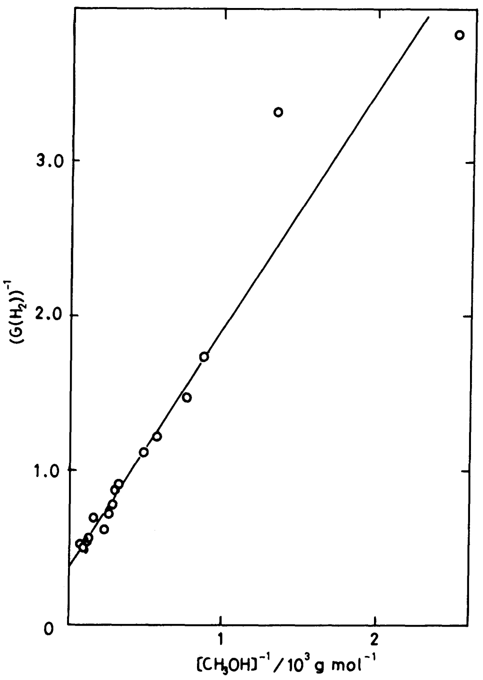

Fig. 6. $1/G(H_2)$ vs. $1/[CH_3OH]$. $[CH_3OH]$ and $G(H_2)$ are corrected by moving the origin of Fig. 1 to (1×10^{-3}, 0.13), respectively.

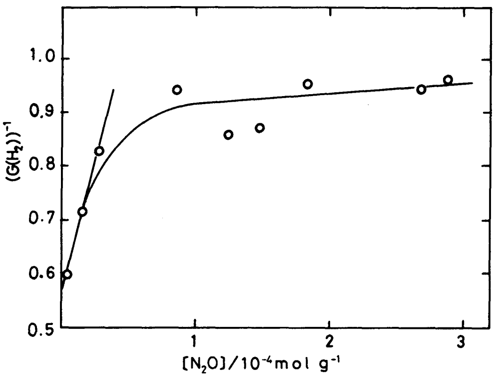

Fig. 7. $1/G(H_2)$ vs. $[N_2O]$. Calculated from the data shown in Fig. 2.

In the MS-MeOH-CCl_4 system, the same kinetic treatment is also applicable if the following reaction is considered:

$$e^-+CCl_4 \longrightarrow \text{product}. \qquad (6)$$

Plots of $1/G(H_2)$ vs. $[CCl_4]$ give the curve as shown in Fig. 8. From the experimental data in the limited amount region, G_e is obtained as 2.9 and the ratio of rate constants, k_6/k_3, as 2.0×10^2. It should be noticed

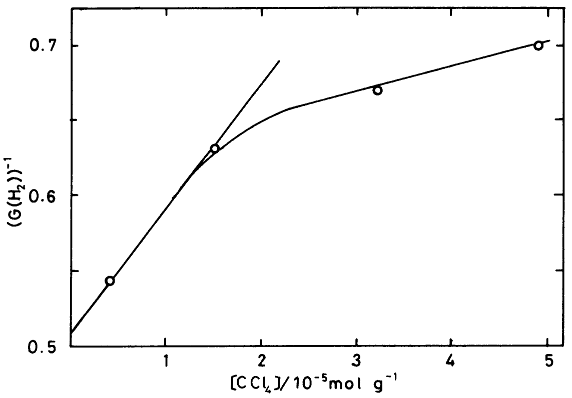

Fig. 8. $1/G(H_2)$ vs. $[CCl_4]$. Calculated from the data shown in Fig. 3.

that the ratio of k_6/k_5, 0.8, is quite different from that obtained in the MS-N_2O-CCl_4 system, 12.8.[14] The ratio obtained in the present system is close to that obtained for electrons generated in nonpolar liquid such as hexane or cyclohexane rather than in 2,2-dimethylpropane. This suggests that an energy state of excess electrons in MS, probably the conduction band of MS, may be affected by the adsorption of methanol. If the rate constant of electron for its reaction with N_2O in hexane, 1.09×10^{12} dm^3 mol^{-1} s^{-1}, or in cyclohexane, 2.4×10^{12} dm^3 mol^{-1} s^{-1},[15] is applied to k_5, 4.4×10^9 or 9.6×10^9 dm^3 mol^{-1} s^{-1} is obtained, respectively, as the rate constant of methanol for its reaction with the electron produced in MS.

The formation of formaldehyde and ethylene glycol may be explained by a mechanism which has been composed of Reactions 1, 4, 7, 8, and 9 by assuming processes similar to those of the radiolysis of liquid methanol:

$$MS^+ + CH_3OH_{ad} \longrightarrow MS + CH_3OH^+, \qquad (7)$$

$$CH_3OH^+ + CH_3OH \longrightarrow CH_3OH_2^+ + \cdot CH_2OH, \qquad (8)$$

$$2\cdot CH_2OH \longrightarrow HCHO + CH_3OH \qquad (9a)$$

$$\longrightarrow (CH_2OH)_2. \qquad (9b)$$

From these reactions we obtain

$$2\{G(FA) + G(EG)\} = G_e + G(MS^+), \qquad (III)$$

where $G(FA)$ and $G(EG)$ designate the G-values for the formation of formaldehyde and ethylene glycol, respectively. Since electrons and positive holes which have escaped from Reaction 2 produce these products and the G-value for such electrons or positive holes can be taken as $G(H_2)$, the relation expressed by Eq. III holds. The above mechanism appears to be very simple despite the complexity of adsorbed state. However, the formation of methane was observed to be negligible (G-value below 0.1) and no other products including carbon have been found. Furthermore, the yield of ethylene glycol decreases in the presence of N_2O, whereas formaldehyde increases as shown in Fig. 5. The result may be explained by addition of Reaction 10 to the above reactions:

$$O^- + \cdot CH_2OH \longrightarrow HCHO + OH^-. \qquad (10)$$

At 4.2×10^{-4} mol g^{-1} N_2O, $G(FA)$ of 1.87 and $G(EG)$ of 0.57 were obtained. If the ratio of Reactions 9a to 9b is not affected by N_2O, the formaldehyde produced through Reaction 9a is 0.57 and hence 1.3 is estimated as the G-value for the formaldehyde through Reaction 10. Therefore, the G-value for $\cdot CH_2OH$, which is a precursor radical of formaldehyde and ethylene glycol, is calculated to be 3.58. On the other hand, $\cdot CH_2OH$ is produced through Reactions 4 and 8. Thus $G(\cdot CH_2OH)$ is equal to the sum of $G(H_2)$ in Reaction 4 and $G(MS^+)$ in Reaction 7. In the presence of ca. 10^{-2} mol g^{-1} methanol and 4.2×10^{-4} mol g^{-1} N_2O, Reaction 2 may be neglected. Therefore, the total $G(\cdot CH_2OH)$ is calculated to be 3.8. This is considerably close to the value calculated on the basis of $G(FA)$ and $G(EG)$. The above mechanism, therefore, seems to be reliable.

The formation of N_2 is hard to understand in the presence of methanol. $G(N_2)$ increases with increasing amount of N_2O even in the region where $G(H_2)$ reaches a plateau value. It amounts to 3.4 at ca. 5×10^{-4} mol g^{-1} N_2O in spite of the incomplete suppression of H_2 formation. Although these results suggest that a short chain mechanism works, it needs another study to find a consistent mechanism.

References

1) J. M. Caffrey, Jr. and A. O. Allen, *J. Phys. Chem.*, **62**, 33 (1958).

2) J. W. Sutherland and A. O. Allen, *J. Am. Chem. Soc.*, **83**, 1040 (1961).

3) L. Abrams and A. O. Allen, *J. Phys. Chem.*, **73**, 2741 (1969).

4) R. I. Zalevskaya and Yu. D. Tsvetkov, *Kinet. Catal.*, **8**, 468 (1967).

5) G. R. Joppien and J. E. Willard, *J. Phys. Chem.*, **76**, 3158 (1972).

6) N. H. Sagert, J. A. Reid, and R. W. Robinson, *Can. J. Chem.*, **48**, 17 (1970).

7) J. W. Sutherland and R. Goodrich, *J. Am. Chem. Soc.*, **89**, 6779 (1967).

8) P. K. Wong and J. E. Willard, *J. Phys. Chem.*, **72**, 2623 (1968).

9) N. H. Sagert and R. W. Robinson, *Can. J. Chem.*, **46**, 2075 (1968).

10) H. Ogura, Y. Tachika, Y. Suzuki, C. Nakazato, M. Kondo, T. Sawai, and T. Sawai, *J. Nucl. Sci. Technol.*, **12**, 167 (1975).

11) H. Ogura, M. Hinata, C. Nakazato, M. Kondo, T. Sawai, and T. Sawai, *J. Nucl. Sci. Technol.*, **15**, 433 (1978).

12) H. Ogura, C. Nakazato, M. Kondo, T. Sawai, and T. Sawai, *J. Nucl. Sci. Technol.*, **16**, 57 (1979).

13) C. Nakazato and T. Masuda, *Chem. Lett.*, **1984**, 731.

14) C. Nakazato and T. Masuda, *Bull. Chem. Soc. Jpn.*, **59**, 2237 (1986).

15) A. O. Allen and R. A. Holroyd, *J. Phys. Chem.*, **78**, 796 (1974).