© 1988 The Chemical Society of Japan *Bull. Chem. Soc. Jpn.*, *61*, 1899—1902 (1988)

Hydrogen Formation from Water Adsorbed on Zeolite during Gamma-Irradiation

Masayoshi Aoki, Chiyoko Nakazato, and Takahiro Masuda*
Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Fukasawa 2-1-1, Setagaya-ku, Tokyo 158
(Received December 9, 1987)

The γ-radiolysis of water adsorbed on synthetic zeolite, MS 13X (Molecular Sieve 13X), has been investigated by the product analysis method using gas chromatography. One of the main products is molecular hydrogen, the *G* value of which increases with increasing amount of water adsorbed on MS 13X and reaches a first plateau (0.42) at ca. 4 mmol of water per g of MS 13X. At ca. 6 mmol g^{-1} of water, it resumes the increase and finally approaches a second plateau (1.2) at ca. 9 mmol g^{-1}. The formation of hydrogen is depressed by an electron scavenger, while ammonia, a scavenger of positive hole, enhances the hydrogen formation. The result indicates that hydrogen is produced through a reaction of water with electrons generated in MS 13X. The rate constant for the reaction of electrons with water adsorbed on MS 13X is estimated to be $(2.6\pm0.3)\times10^8$ dm^3 mol^{-1} s^{-1}, on the assumption that rate constants for reactions of electrons with some electron scavengers determined in liquid cyclohexane can be applied to this system.

Enhanced yield in the radiolysis of a substance adsorbed on solid has been explained in terms of the energy transfer from adsorbent to adsorbate. Exciton, electron, and positive hole have been proposed as energy carriers.[1-6] Recently we found that N_2O adsorbed on synthetic zeolite (Molecular Sieve 13X; abbreviated to MS) is radiolyzed to produce N_2 with a *G* value of 2.8, which is saturated against the adsorbed amount of N_2O.[7] In the presence of a second electron scavenger, $G(N_2)$ decreases with increasing amount of the second scavenger. Relative reactivities of electrons generated in MS toward several kinds of scavengers suggest that these electrons are similar to those produced in liquid 2,2-dimethylpropane with respect to reactivity.[8,9] This implies that electrons generated in MS are possibly in a "quasi-free" state. On the other hand, we found that adsorption of methanol alters relative reactivities to those observed in liquid cyclohexane or hexane.[5] In the system with methanol, molecular hydrogen is produced as a main product and the formation of hydrogen is explained by a mechanism including a reaction of electrons with adsorbed methanol. The estimated rate constant for the reaction of electrons with adsorbed methanol is much higher than that determined in liquid methanol. These suggest that electrons generated in MS adsorbing methanol is "slightly solvated" in a way similar to excess electrons in cyclohexane or hexane.[8-10]

The radiolysis of water adsorbed on MS is of interest in the reactivity and state of electrons generated in the system and their reaction with adsorbed water, because the reaction of "nearly dry" electrons with water can be approximated to a reaction occurring at the initial stage of radiolysis of liquid water.

In this study, an attempt was made to clarify the state of electrons generated in the MS-H_2O system by determining the relative reactivity of the electrons toward some electron scavengers. Molecular hydrogen was found to form from water adsorbed on MS and stepwise increase in $G(H_2)$ was observed with increasing amount of water. The relative reactivity determined by competition kinetics showed that electrons produced in this system are similar to those in the MS-CH_3OH system rather than those in MS-N_2O. The rate constant for the reaction of electrons with water adsorbed on MS was estimated by assuming that rate constants for reactions of electrons with some electron scavengers are the same with those obtained in liquid cyclohexane.

Experimental

Zeolite (Molecular Sieve 13X) was purchased from Nippon Kuromatokogyo K. K. The specific surface area is 1030 m^2 g^{-1}. Dinitrogen monoxide, ammonia, and sulfur hexafluoride were obtained from Takachiho Kagakukogyo K. K. and purified by distillation under vacuum before use. Carbon tetrachloride was obtained from E. Merck, Ltd.

The procedure of pretreatment of MS and introduction of adsorbates were described elsewhere in detail.[7] Molecular hydrogen and nitrogen were analyzed by gas chromatography according to the method employed in a previous work on silica gel.[4] Water was triply distilled after treatment with alkaline permanganate.

Results and Discussion

Molecular hydrogen is produced from water adsorbed on MS during γ-irradiation. The *G* value for hydrogen formation increases with increasing amount of water stepwise as shown in Fig. 1. *G* values are calculated on the basis of total energy absorbed by MS and water. At amounts below 6.6×10^{-4} mol g^{-1}, formation of hydrogen was hardly observed. This may be explained by consumption of water due to chemisorption of water by some active site of MS or reaction of hydrogen molecule or atom with the site, as has been discussed with the MS-CH_3OH system.[5] The formation of hydrogen is effectively depressed by electron scavenger. Figure 2 shows the dependence of $G(H_2)$ on the amount of several electron scavengers in the presence of 4 mmol g^{-1} of adsorbed water. At ca. 10^{-4}

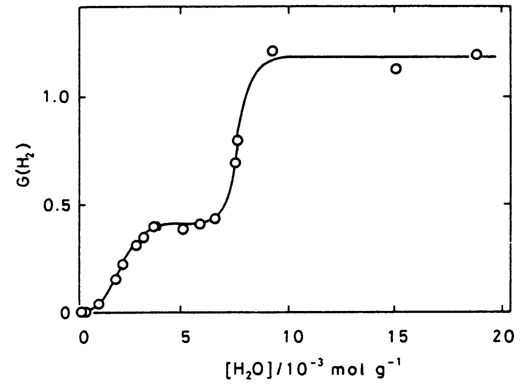

Fig. 1. Dependence of $G(H_2)$ on adsorbed amount of H_2O. Adsorbed amount is expressed as mol of H_2O per g of MS.

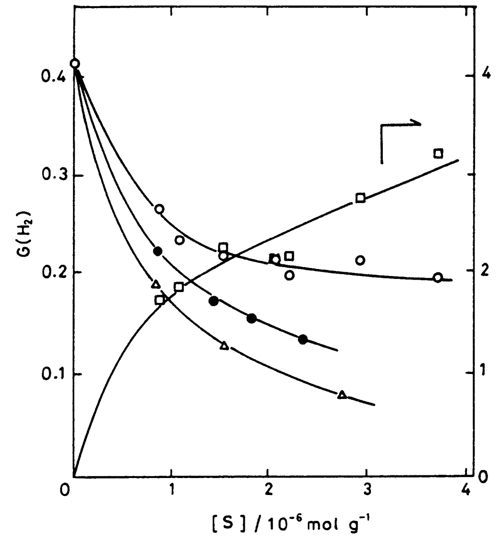

Fig. 2. Dependence of $G(H_2)$ and $G(N_2)$ on adsorbed amounts of scavengers. Adsorbed amount is expressed as mol of scavengers per g of MS. 4×10^{-3} mol g^{-1} of H_2O present. ○; N_2O, ●; CCl_4, △; SF_6, □; $G(N_2)$ produced from N_2O.

mol g^{-1} of scavengers, the formation of hydrogen is completely depressed in every case. Therefore, a precursor of hydrogen is thought to be eliminated by these electron scavengers. On the other hand, addition of ammonia, a positive hole scavenger, results in an enhancement of hydrogen formation. Since the formation of hydrogen from ammonia itself was hardly observed in the absence of water as shown in Fig. 3, the increase in $G(H_2)$ in the presence of water is caused by scavenging of positive hole. Therefore, molecular hydrogen is considered to be produced through a reaction of adsorbed water with electrons generated in MS. The formation of hydrogen is explained by the sequence of reactions

$$\mathrm{MS} \rightsquigarrow \mathrm{MS}^+ + e^-, \tag{1}$$

$$e^- + \mathrm{MS}^+ \longrightarrow \mathrm{MS}^*, \tag{2}$$

$$e^- + H_2O \longrightarrow H + OH^-, \tag{3}$$

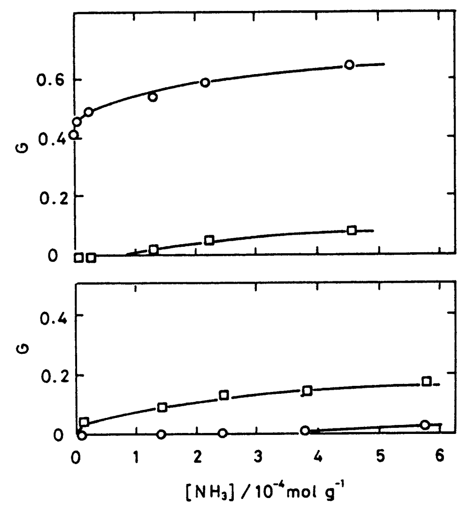

Fig. 3. $G(H_2)$ and $G(N_2)$ vs. $[NH_3]$. ○; $G(H_2)$, □; $G(N_2)$. Upper, 4×10^{-3} mol g^{-1} of H_2O present. Lower, H_2O absent.

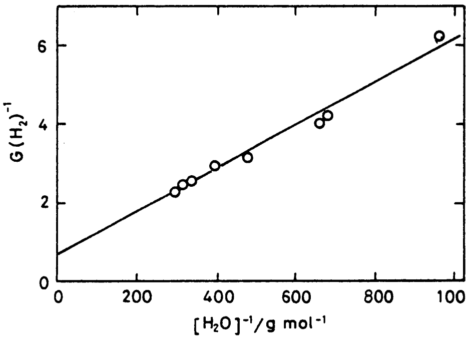

Fig. 4. $1/G(H_2)$ vs. $1/[H_2O_{ad}]$.

$$H + H \longrightarrow H_2. \tag{4}$$

In the presence of an electron scavenger or ammonia, Reaction 5 or 6 takes place:

$$e^- + S \longrightarrow \text{product(s)}, \tag{5}$$

$$\mathrm{MS}^+ + NH_3 \longrightarrow \text{product(s)}. \tag{6}$$

From the above reactions, the following equation can be derived:

$$1/G(H_2) = 2(1 + k_2[\mathrm{MS}^+]/k_3[H_2O_{ad}])/G_e \tag{I}$$

and

$$1/G(H_2) = 2\{1 + (k_2[\mathrm{MS}^+] + k_5[S])/k_3[H_2O_{ad}]\}/G_e \tag{II}$$

where $[H_2O_{ad}]$ represents adsorbed amount of water. By plotting $1/G(H_2)$ against $1/[H_2O_{ad}]$ or $[S]$, G_e and the ratio of rate constants, k_5/k_3, can be estimated. Figures 4 and 5 are examples of the plots, which show a good linear relation. From the intercepts and slopes of these straight lines, G_e and the ratio of rate constants are calculated. In Table 1, the values estimated for various systems are summarized. G-values of electron agree fairly well with each other and the value (3.06 ± 0.07) is obtained as the average. From the ratio

Table 1. Estimated Values of G_e and k_s/k_3 and Comparison of k_s/k_{N_2O}

System	G_e	k_s/k_3	k_s/k_{N_2O}		
			This work	Ref. 9	Ref.10
MS-H_2O	3.15				
MS-H_2O-N_2O	3.03	8.02×10^3	1	1	1
MS-H_2O-CCl_4	2.99	1.04×10^4	1.3	1.1	1.5
MS-H_2O-SF_6	3.01	1.71×10^4	2.1	1.7	2

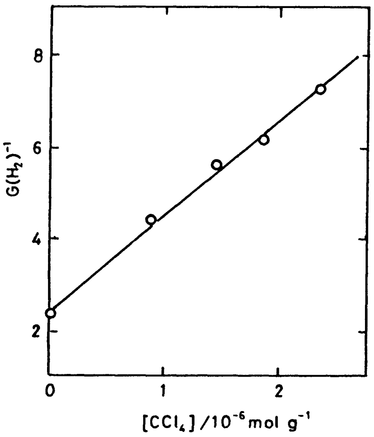

Fig. 5. $1/G(H_2)$ vs. $[CCl_4]$.

Table 2. Values of k_3 Calculated on the Basis of k_s Determined in Cyclohexane

Scavenger	$k_3/dm^3\ mol^{-1}\ s^{-1}$
N_2O	3.0×10^8
CCl_4	2.6×10^8
SF_6	2.3×10^8
Average	$(2.6\pm0.3)\times10^8$

of rate constants, k_5/k_3 relative rate constants based on k_{N_2O} can be calculated for CCl_4 and SF_6. In the last three columns, they are compared with those determined in liquid cyclohexane.[9,10] It is indicated that the electrons generated in water-adsorbing MS are similar to those in liquid cyclohexane with respect to the reactivity toward these scavengers. If the rate constants for these scavengers determined in cyclohexane are used as k_5, the rate constant for the reaction of the electrons with water adsorbed on MS is estimated to be $(2.6\pm0.3)\times10^8$ $dm^3 mol^{-1} s^{-1}$ as an average (Table 2). This is quite different from the rate constant for the reaction of hydrated electrons with water in aqueous systems. As mentioned above, $G(H_2)$ increases with increasing amount of water stepwise and the experiments of scavengers were carried out at the amount of water which corresponds to the first plateau. Molecular Sieve 13X includes sodium ion of 6.4 mmol g^{-1}, which is known as a counterpart of the negative charge located on aluminium atom. Since the sodium ion in the hexagonal prism of MS cannot get into contact with water molecule, the content of the sodium ion effective for the adsorption of water will be less than 6.4 mmol g^{-1}. It can be considered, therefore, that the amount of the water at the first plateau is approximately equal to the effective amount of sodium ion. Furthermore, it is reported that water is adsorbed predominantly on the Na^+ sites of synthetic zeolite to form $(Na_4)^{3+}$-$(H_2O)_x$ by trapping an electron.[11,12] These suggest that hydrogen atom is formed from water through the reaction with sodium atom. Reaction 3 may be rewritten to

$$e^- + Na^+ \longrightarrow Na, \tag{7}$$

$$Na + H_2O \longrightarrow Na^+ + OH^- + H. \tag{8}$$

This mechanism is consistent with the observed high reactivity of the electrons generated in the MS-H_2O system toward water molecule.

One of the authors previously found that scavengers of positive hole with ionization potentials below 11.1 eV decolorize a color center of silica gel, which is assigned to a positive hole produced by γ-irradiation.[3] While the color center of silica gel is stable at room temperature, no absorption is observed in the case of irradiated MS. However, the electron affinity of MS^+ is at least above 10.85 eV, because methanol (I_p=10.85) reacts with MS^+ to produce formaldehyde and ethylene glycol.[5] Since the ionization potential of ammonia is 10.2 eV, the proposed mechanism including the scavenging of MS^+ by ammonia is reliable.

As seen in Fig. 2, the G value for nitrogen formation is apparently larger than the decrease in $G(H_2)$, even if $G(N_2)$ is equal to $2G(H_2)$. A similar disagreement in stoichiometry was observed in hexane and cyclohexane when N_2O was used as an electron scavenger.[13,14] As reported in a previous paper, the $G(N_2)$ from N_2O adsorbed on MS is 2.8 at adsorbed amounts of N_2O above 5×10^{-4} mol g^{-1}. In the presence of CH_3OH, values from 2.6 to 2.8 are estimated as G_e by plotting $1/G(H_2)$ vs. $1/[CH_3OH]$ or [S], whereas $G(N_2)$ is ca. 3.4 and differs from the G value of the electron scavenged by N_2O. Estimated G values for electrons generated in various systems of MS seem to converge in the neighborhood of 2.8. However, the $G(N_2)$ in the MS-N_2O system differs from those in systems MS-CH_3OH-N_2O and MS-H_2O-N_2O. The relative reactivity of the electrons produced in these systems toward some electron scavengers can be classified into two types, one observed in liquid 2,2-dimethylpropane and the other in liquid hexane or cyclohexane. These results suggest a resemblance in the energy state of excess electrons between liquid hydrocarbons and MS. The disagreement of stoichiometry between $G(N_2)$ and G value of scavenged electron will, therefore, be related to the energy state of excess electrons generated in the irradiated systems.

References

1) P. K. Wong, *J. Phys. Chem.*, **75**, 201 (1971).

2) K. Sogabe, A. Hasegawa, Y. Yamada, and M. Miura, *Bull. Chem. Soc. Jpn.*, **45**, 3362 (1972).

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

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

5) C. Nakazato, R. Murayama, M. Aoki, and T. Masuda, *Bull. Chem. Soc. Jpn.*, **60**, 2775 (1987).

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

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

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

9) A. O. Allen, T. E. Gangwer, and R. A. Holroyd, *J. Phys. Chem.*, **79**, 25 (1975).

10) K. Mori, K. Ito, and Y. Hatano, *J. Phys. Chem.*, **79**, 209 (1975).

11) J. H. Shen, A. C. Zettlemoyer, and K. Kller, *J. Phys. Chem.*, **84**, 1453 (1980).

12) D. N. Stamires, "Molecular Sieves," Soc. Chem. Industry, London (1968), p. 328.

13) Y. Hatano, K. Takeuchi, and S. Takao, *J. Phys. Chem.*, **77**, 586 (1973).

14) Y. Hatano and J. L. Abboud, *Bull. Chem. Soc. Jpn.*, **47**, 236 (1974).