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Hydrogen Gas Evolution from Water Included in a Silica Gel Cavity and on Metal Oxides with γ-Ray Irradiation

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Hydrogen gas evolution from water induced with γ–ray irradiation of silica gels and metal oxides dispersed in water is studied by examining the hydrogen gas evolved. Hydrogen gas is detected by gas chromatography after ^{60}Co γ–ray irradiation of the sample solution in a closed vial at room temperature. Water adsorbed on the surface of metal oxides shows more evolution of hydrogen gas than pure water. Hydrogen gas evolution is maximized in the silica gels when the size of a silica gel cavity is about 2 nm, being on the order of spur size. The most active surface toward the decomposition of water upon γ–ray irradiation is that of SiO_2 dried at 100 °C after sample preparation.

1. Introduction

The radiolysis of water is one of the most important factors affecting the chemical condition of the coolant in nuclear reactors, and the *G*–values of water decomposition products and rate constants of the atomic reactions for these species are required for a thorough analysis of the process. To date, there is much data for the *G*–values and rate constants only at ambient temperature. In nuclear reactors, fast neutrons show smaller net–water decomposition than γ–rays.[1] Radiolysis due to β–decay of tritium–bearing wastes causes evolution of tritiated gas. Such hydrogen evolution is also an important problem in the packaging of radioactive waste in cement or asphalt. In these cases, the radiolysis of water has been studied from the standpoint of the depression of γ–ray decomposition of water, and the amount of hydrogen evolution has been generally evaluated with respect to the $G(H_2)$–value for pure water. Furthermore, hydrogen (H_2) is expected to become a major energy source in the future. Current steam reforming of hydrocarbons produces large amounts of carbon dioxide that is a cause of global warming, and the substrate supplies are finite. Safe and economically competitive H_2 technologies should be developed to meet future energy needs. Since the study of the so–called Honda and Fujishima Effect was published,[2] many studies on hydrogen evolution using light have been carried out.[3] This reaction mechanism consists of a photocatalytic reaction which is caused by photosensitized oxidation and reduction due to electrons and hole pairs generated in an illuminated n–type semiconductor. Kato et al. report effective and continuous evolution of hydrogen gas from water with light irradiation using nano particles of $NaTaO_3$.[4] They succeeded in producing hydrogen gas at a rate of 19.8 mmol h^{-1} for longer than 400 h. Hydrogen can be produced from γ–ray radiolysis of water, similar to photocatalysis with ultraviolet or visible light. Kohn suggested that enhanced decomposition was observed in the radiolysis of molecular substances in the adsorbed state.[5] Therefore, an understanding of the radiolysis of adsorbed water becomes important for evaluating hydrogen gas evolution due to γ–ray radiolysis of water. Of note is the possibility of using radiation emitted by the unstable fission products contained in spent nuclear fuel elements.

Nakashima and Tachikawa irradiated three types of silica gel in tritiated water vapor and reported that energy transfer from the silica gel to the water plays an important role in the decomposition of water.[6] They reported about 40 times larger $G(H_2)$ at $p = 0.05$ for tritiated water than for pure water. Here, p is W_{H_2O}/W_{SGOH}, where W_{H_2O} and W_{SGOH} are the weight of physisorbed HTO(gas) and the weight of silica gel with surface hydroxyl(gas), respectively. Sunaryo et al. studied the γ–radiolysis of water with ^{60}Co γ–rays.[1] The method is based on the combination of three kinds of aqueous solution containing: (a) 2×10^{-3} mol kg^{-1} $NaNO_2$; (b) 10^{-3} mol kg^{-1} acetone + 10^{-2} mol kg^{-1} methanol; (c) 10^{-3} mol kg^{-1} $HClO_4$ + 10^{-2} mol kg^{-1} methanol. The values of G_{H_2}, G_H, G_{e^-}, G_{OH}, and $G_{H_2O_2}$, for the γ–radiolysis of water were determined to be 0.45, 0.63, 2.75, 3.12, and 0.58, respectively. In addition, the values for fast neutron radiolysis of water were determined at room temperature. The rate constants for the reactions $2(\cdot CH_2OH) \rightarrow (CH_2OH)_2$, $2(\cdot CH_2OH) \rightarrow CH_2O + CH_3OH$, and $\cdot CH_2OH + H_2O_2 \rightarrow CH_2O + H_2O + \cdot OH$ were determined to be 2.25×10^9, 1.5×10^8, and 5×10^4 $M^{-1}s^{-1}$, respectively. This reveals that the fast neutron radiolysis brought smaller radical yields, larger molecular yields and smaller net water decomposition due to the high LET of the fast neutrons. Wada et al. began a photoelectrochemical study which used γ–radiation instead of visible light to generate electrons and hole pairs, and reported that hydrogen gas evolution was about 60 times that of the blank when TiO_2 Ru (deposited on the surface) was used as a catalyst.[7] However, $G(H_2)$ for the blank is reported to be 0.012, which is not in accord with the accepted value, 0.45. Yamamoto et al. used nanoparticles of TiO_2 and α– and γ–Al_2O_3, and their surface–treated nanoparticles, and reported that hydrogen gas evolution induced by γ–ray irradiation of α– and γ–Al_2O_3 in aqueous solution was much higher, 7 – 8 times that of the background.[8] Cecal et al. reported the enhancement of hydrogen gas evolution in γ–ray irradiated water containing ZrO_2, TiO_2, BeO, and SiO_2.[9] Jung et al. studied the effect of the addition of methanol or EDTA on hydrogen gas evolution in the γ–ray irradiation of water containing TiO_2 and reported that the addition of EDTA increased hydrogen gas evolution.[10] Comparison of the activities of the catalysts described above for hydrogen gas evolution is difficult because the data are obtained with different ratios of catalyst weight/water volume

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and different irradiation conditions. In this paper the activities of nanoparticles of SiO_2 and TiO_2 for hydrogen gas evolution are examined to develop the high yields of hydrogen via γ–ray irradiation of water. Here, G–values are defined as the number of species formed or destroyed per 100 eV of energy absorbed. The symbol G with a subscript (such as G_{H_2}) shows the primary yield, while a G with parentheses (such as $G(H_2)$) indicates the experimentally evaluated yields of the product.

2. Experimental

Three types of silica gels (Fuji Davison) varying in diameter of cavity, *e.g.*– Silica gel A (diameter of cavity: 20 Å), B(40 Å), and ID(150 Å), were used. Three types of nano particles of SiO_2 were also prepared, using different drying temperatures. To a mixed solution of 14 mL of 25% ammonia solution and 20 mL of ethanol, 10 mL of TEOS (tetraethylorthosilicate) was slowly poured. The precipitates were washed with ethanol several times and a portion was dried at 100 ˚C for 2 h (this sample is abbreviated as SiO_2 100 ˚C). Second portion was dried at 150 ˚C for 2 h (SiO_2 150 ˚C) and another at 230 ˚C for 2 h (SiO_2 230 ˚C).

Two types of nano particles of TiO_2 were prepared, also using different drying temperatures. Titanium tetraisoperoxide (TTIP) was used as a starting material for the TiO_2 nano particles and the coupling agent (isopropyltris(dioctyl pyrophosphate)titanate) was supplied from Ajinomoto Fine Techno. Co. To a mixed solution of 10 mL of TTIP and 50 mL of ethanol was slowly poured a mixed solution of 1.1 mL of conc. HCl and 30 mL of ethanol. The mixture was allowed to stand overnight, and a pale yellow liquid was obtained after evaporating with the coupling agent at 80 ˚C. After one day, the liquid was washed with methanol and hexane, centrifuged, washed with hexane, and dried to obtain a powder of TiO_2. A part of the powder was dried at 500 ˚C for 2 h (TiO_2 500 ˚C). The surface area of the particles was measured via the BET method. The particle sizes were estimated to be 400 – 500 nm for SiO_2 and 40 – 50 nm for TiO_2 based on the surface area and the assumption that the particles are in cubic form.

About 200 mg of the particles were dispersed in degassed water(about 300 mg) in a 3 mL vial under nitrogen atmosphere. γ–Ray irradiation was performed at room temperature with a ^{60}Co γ–ray source at Kyushu University. The dose rate of the γ–ray was set to 374 Gy h^{-1} and irradiation time was about 30 h. No detectable leakage of hydrogen gas out of the vials was confirmed by an independent method: A defined volume of mixed gas (hydrogen/air) was sealed into an unirradiated vial for a week, and then the contents were evaluated using gas chromatography. After irradiation, gas which had accumulated in the free space in the vial was also analyzed by gas chromatography (Shimadzu; GC–8A, TCD). Molecular sieve (13X, 60/80) was packed in a column (diameter 3 mm × length 2.5 m) and Ar gas was used as the carrier. Injection temperature was 90 ˚C and column temperature, 120 ˚C. The amount of hydrogen gas dissolved in water was negligible in comparison with the amount accumulated. The $G(H_2)$–values of hydrogen gas production from water were obtained as the average value of three measurements.

3. Results and Discussion

Absorption dose D is defined as

$$D = 0.877 \times D_r \times (\mu / \mu_{air}) \times 100$$

where D_r is irradiation dose, μ mass absorption coefficient of a particular material, and μ_{air} mass absorption coefficient of air. The values of mass absorption coefficient μ are dependent on the number of electrons constituting the material. The absorption of energy for a heterogeneous system is calculated from the weight average presented by the weight ratio of mass absorption coefficients for each element constituting the material. Furthermore, the fact that the energy absorbed by the catalysts may contribute to the decomposition of physisorbed/chemisorbed water must be considered. That is, the energy absorbed by catalysts may be consumed more effectively in the formation of hydrogen gas than the energy absorbed by bulk water. Energy transfer phenomena have been observed in radiolysis of molecular silica gel[11] and porous glass.[12] It has been reported that this process involves transfer of energy, positive charge, and electrons, and that an electron or exciton is capable of long–range migration. For these reasons, it is difficult to evaluate exact $G(H_2)$–values in this experiment. Bond–dissociation energies of molecular hydrogen and oxygen are 432 and 493.6 kJ mol^{-1}, respectively, and that of H_2O averages 458.9 kJ mol^{-1}.

The $G(H_2)$–values of hydrogen gas production from water(y) measured for the silica gels, SiO_2, TiO_2, and TiO_2(500 ˚C) dispersed in water, are listed in Table 1. Figure 1 shows the surface area dependence of the $G(H_2)$–value. The experimental $G(H_2)$–value for pure water is 0.43, close to the reported value 0.45.[1] The $G(H_2)$–values listed in Table 1 should be considered raw data because the values are not corrected for the difference in the γ–ray absorption coefficients of the metal oxides and for that in the γ–ray absorption coefficients between the metal oxides and water. As discussed above, water adsorbed on the catalysts may accept energy from the catalysts. It is clear from Table 1 that the SiO_2 and TiO_2 have certain effects on the enhancement of hydrogen gas evolution. The plots of Figure 1 can be fit to $y = 0.0012x + 0.424$, where y is

TABLE 1: G–Values of Hydrogen Gas Production from Water for Metal Oxides Dispersed in Water

Catalyst	Surface Area/m^2g^{-1}	Dose/kGy	$G(H_2)$–value	All H_2/μL*	Remarks
Silica gel A (20 Å)	4.7×10^2	34.6	1.0	24.9	
Silica gel B (70 Å)	3.9×10^2	34.6	0.8	21.2	
Silica gel ID (150 Å)	2.2×10^2	34.6	0.6	16.4	
SiO_2 (100 ˚C)	8	18.2	2.9	37.1	
SiO_2 (150 ˚C)	7	17.9	2.8	35.7	
SiO_2 (230 ˚C)	4	24.3	1.5	26.5	
TiO_2	6.6×10	8.99	0.88	9.82	
TiO_2	6.6×10	8.99	0.86	10.93	pH 5 with HCl
TiO_2	6.6×10	8.99	1.05	14.03	pH11 with KOH
TiO_2 (500 ˚C)	1.2×10	8.99	0.58	6.42	
TiO_2 (500 ˚C)	1.2×10	8.99	0.52	6.54	pH 5 with HCl
TiO_2 (500 ˚C)	1.2×10	8.99	0.52	6.99	pH11 with KOH

* Experimental error is about 15%.

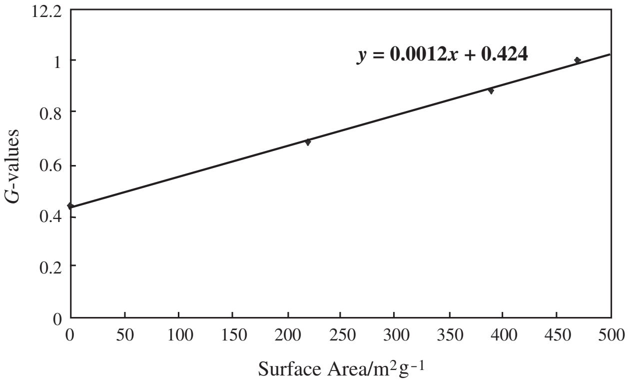

Figure 1. Plots of hydrogen gas evolution vs. the surface areas of the silica gels.

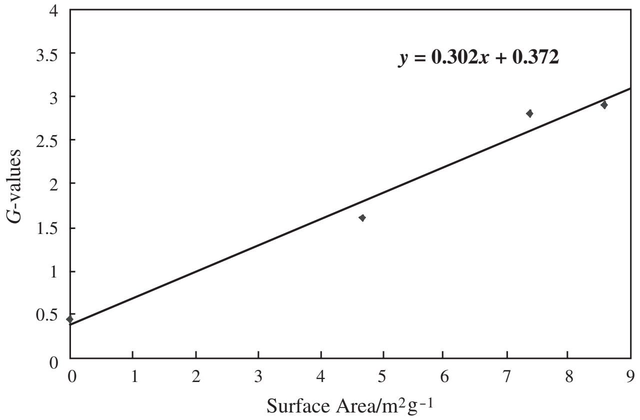

Figure 2. Plots of hydrogen gas evolution vs. the surface areas of the SiO_2.

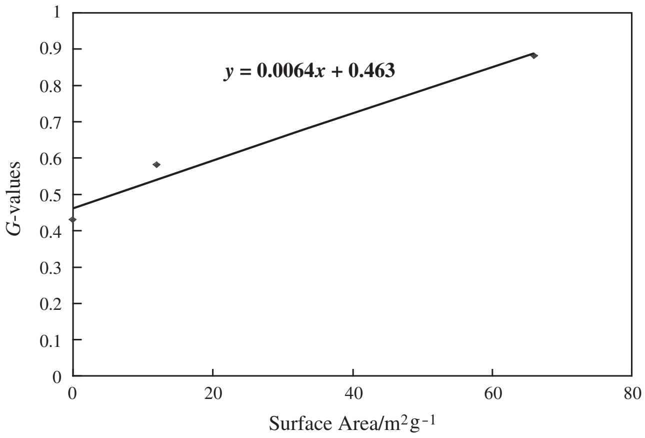

Figure 3. Plots of hydrogen gas evolution vs. the surface areas of the TiO_2.

the $G(H_2)$–value of hydrogen gas production of water and x the surface area of the metal oxides. The plots show that hydrogen gas evolves mainly on the surface of the silica gels and that water adsorbed on the surface of the metal oxides is more easily decomposed by γ–ray irradiation than pure water. This conclusion is reliable even though the $G(H_2)$–values are calculated on the assumption that the γ–ray absorption coefficients of the supported materials are equal to that of water. Nakashima and Tachikawa studied hydrogen gas evolution for a system of water vapor on silica gel and reported that the volume of hydrogen gas evolution can be expressed as a function of the surface coverage and the concentration of surface hydroxyls.[6] The liquid phase results here show that the volume of hydrogen gas evolution can be expressed as a function of the surface area, in accordance with the gas phase results. The size of the cavity of Silica gel A is 2 nm and that of the spur produced by γ–ray irradiation is reported to be 2 nm.[13] Therefore, the size of the cavity is similar to that of the reaction region for each interaction of a γ–ray with the materials.

Hydrogen gas evolution was measured for SiO_2 dispersed in water, and the $G(H_2)$–values for hydrogen gas production of water (y) are plotted versus the surface area of the SiO_2 (x) in Figure 2. The plots can be approximated by the relation $y = 0.302x + 0.372$. The coefficient for the SiO_2, 0.302 is larger than that for the silica gels. This fact supports the conclusion that the surface of SiO_2 is more active to the decomposition of water upon γ–ray irradiation than that of the silica gels. The difference in the activity between the silica gels and SiO_2 results in a difference in surface hydroxyl concentration, a difference in surface structure, or in a difference in the physical properties responsible for the surface structure. Which difference, however, is not clear from this experiment. The SiO_2 (100 °C) has larger surface area than the SiO_2 (230 °C). Therefore the SiO_2 (100 °C) is the most active among the varieties of SiO_2. The reactivity of the SiO_2 dispersed in water toward γ–ray irradiation may be not explained by the same mechanism as that for the decomposition of water by light because SiO_2 is not reported to be active in the decomposition of water by light. Under the influence of γ–rays, the catalysts experience an energetically activated state $[H_2O\ X]^*$, which produces ·H and ·OH radicals. Finally, hydrogen is produced. This radical process is one of the probable reactions for hydrogen production. Here, the ratios of hydrogen/oxygen were not evaluated because a trace amount of oxygen remained in the vials.

The results for the TiO_2 dispersed in water are shown in Figure 3 and the $G(H_2)$–values can be approximated by $y = 0.0064x + 0.463$. This result is similar to that for the silica gels. Cecal et al.[9] measured the hydrogen production yield with a total irradiation dose of 100 to1700 kGy: The rate of hydrogen gas production in the case of TiO_2 increases with the total irradiation doses. The activity for water decomposition of TiO_2 is less than that of SiO_2 in the range less than 100 kGy, and the difference obtained here between TiO_2 and SiO_2 for the activities of water decomposition are in accordance with theirs. The existence of Ti^{3+} produced by irradiation may be important to the water decomposition although we do not have any evidence to that effect.

To study the effect of the pH of the solution on hydrogen evolution, TiO_2 in water was irradiated in solutions of different pH. For TiO_2, slightly larger $G(H_2)$–values were observed for alkaline solution (Table 1). Dainton and Watt have reported that the $G(H_2)$–values in γ–radiolysis of water (0.04 M aqueous acrylamide solution) slightly increase with a decrease in the pH of solution.[14] Therefore, the difference in the experimental data here is within experimental errors if the effect of Cl^- on γ–ray decomposition is considered, although the interference of Cl^- in hydrogen gas evolution was not observed in a separate experiment.

It is considered that in order to produce hydrogen gas with high yield, electron–hole pairs produced by γ–ray irradiation should be separated rapidly, and the hydrogen gas produced must rapidly leave the reaction site before the revers–reactions with oxygen occurs.

4. Conclusion

SiO_2 catalysts enhanced the radiolytic decomposition of water and subsequent production of H_2 by γ–ray irradiation. Hydrogen gas evolution was maximized when the size of the cavity of the silica gels was about 2 nm, on the order of spur size. The most active surface toward the radiolytic decomposition of water was that of SiO_2 dried at 100 °C after preparation.

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