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journal homepage: www.elsevier.com/locate/radphyschemDecomposition of hydrogen peroxide by γ -ray irradiation in mixture of aqueous solution and Y-type zeolite

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HIGHLIGHTS

- H_2O_2 was efficiently decomposed by irradiation in a water–zeolite mixture.
- A kinetic model calculation of the water–zeolite system was performed.
- Radiolytic decomposition of H_2O_2 adsorbed on the zeolite was proposed.
- The zeolite had little effect on H_2 production in the H_2O_2 solutions.

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ABSTRACT

Radiolysis of aqueous hydrogen peroxide (H_2O_2) solutions in the presence of Y-type zeolite was studied to clarify the radiation-induced reactions of H_2O_2 in water–zeolite heterogeneous systems. The mixtures of the solutions with the zeolite were irradiated by γ -rays. H_2O_2 decomposed remarkably in the presence of the zeolite. Numerical calculations using a kinetic model were performed and compared with the experimental results. A reaction that decomposes H_2O_2 adsorbed on the zeolite was proposed and introduced into the kinetic model as an effect of the zeolite. The decomposition of adsorbed H_2O_2 was formulated as a reaction induced by energy deposition on the zeolite. The kinetic model calculations satisfactorily explained the measured H_2O_2 decomposition by adopting a high yield for the introduced reaction, $1.4 \times 10^{-6} \text{ mol J}^{-1}$. Moreover a comparison of the calculations with the measured production of oxygen (O_2) indicates that reduction and oxidation of adsorbed H_2O_2 proceeded at comparable yields during decomposition. Further, measurements of hydrogen (H_2) suggest that the zeolite had little effect on H_2 production at high H_2O_2 concentrations.

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1. Introduction

Hydrogen peroxide (H_2O_2) is one of the products of water radiolysis. Reactions induced by ionizing radiations that produce or decompose H_2O_2 are related to various influences of radiations on radioactive liquids, slurries, and solids with high water content. The generation of H_2O_2 in particular is important in redox chemistry and the corrosion of materials. Therefore, an understanding of the reactions of H_2O_2 is indispensable to estimating the influences of radiations. The radiation-induced reactions of H_2O_2 in water have been intensively investigated (Elliot and Bartels, 2009). However, in heterogeneous systems of solid materials and water, the radiation-induced reactions differ considerably from those in homogeneous aqueous solutions. Recent work has revealed significant effects of solid materials with high specific

surface areas on the production of H_2O_2 (Liu et al., 1997; Milosavljevic et al., 2004; Le Caër et al., 2007; Roth et al., 2011; Yamada and Kumagai, 2012). The reactions of H_2O_2 in heterogeneous systems are still insufficiently understood.

Zeolite–water mixtures are important heterogeneous systems in nuclear engineering. Zeolites are porous crystalline aluminosilicate materials having selective cation exchange properties. Zeolites were used to decontaminate radioactive water generated in the accident at Three Mile Island by removing radioactive cations from the contaminated water (Quinn et al., 1984; Henrie et al., 1986). In addition, the ion-exchange method using zeolites has been applied to water treatment at the Fukushima Dai-ichi Nuclear Power Station. For stable water treatment operation and safe storage of the spent zeolite adsorbents, the influences of ionizing radiations on zeolite–water systems need to be adequately understood and controlled. An understanding of the reactions of H_2O_2 will serve as a basis for estimations of the influences of radiations due to H_2O_2 generation. Concurrently, it will also deepen the understanding of gas generation in zeolite–water systems, because accumulated H_2O_2 , hydrogen (H_2),

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and oxygen (O₂) under ionizing radiations affect each other through reactions with radical transients.

Some studies pointed out significant effects of zeolites on the radiolysis of water molecules adsorbed in their pore structures. Pulse radiolysis studies by Thomas and coworkers showed that energy deposition on zeolites containing adsorbed water molecules produced radical transients at very high efficiencies (Liu et al., 1997, 1995; Lu et al., 1993). Their work also revealed that the reactions of the transients were slowed by the limited diffusion in the frameworks of the zeolites. In case of molecular products, studies of H₂ showed that the irradiation of zeolites containing adsorbed water molecules produced H₂ (Nakashima and Tachikawa, 1987; Nakashima and Aratono, 1993; Nakashima and Masaki, 1996). The studies suggest that the radiation energy deposited on the zeolites decomposed the adsorbed water molecules. These reports imply that the radiolytic production and subsequent reactions of H₂O₂ may also be affected by zeolites.

Hence, the radiation-induced reactions of H₂O₂ in aqueous solutions mixed with Y-type zeolite was investigated in this study. The focus was on the decomposition of H₂O₂ because our previous work on H₂ production suggests that the presence of zeolites inhibits the accumulation of H₂O₂ (Kumagai et al., 2013). Mixtures of aqueous H₂O₂ solutions and zeolite were irradiated by γ -rays, and the decomposition of H₂O₂ was measured. Then, model calculations of the chemical kinetics were performed to obtain an interpretation of the effect of zeolite on H₂O₂ decomposition.

2. Experimental

2.1. Materials

The zeolite used in this study is Y-type zeolite (5.5 SiO₂/Al₂O₃ ratio) containing sodium as the charge-balancing cation purchased from Wako Pure Chemical Industries. The zeolite is hereafter denoted as NaY. Y-type zeolite is a synthesized zeolite material with a high SiO₂/Al₂O₃ ratio and is isostructural to the natural mineral faujasite. NaY was selected from the commercially available zeolites because it has a negligible effect on the stability of H₂O₂. As a preliminary test to select a suitable zeolite for the irradiation experiments, the spontaneous decomposition of H₂O₂ was checked in the mixture of water with several zeolites at room temperature. NaY scarcely accelerated the spontaneous decomposition of H₂O₂.

During sample preparation, the weight of the NaY was measured at 80 ± 2% relative humidity and 22 ± 3 °C. NaY was conditioned in the atmosphere until the variation in the weight due to moisture adsorption became negligible. The humidity was controlled by the saturated salt solution method using ammonium chloride (NH₄Cl) (Greenspan, 1977). The water content of the moisture-adsorbed NaY was measured by thermogravimetric analysis (TG-50, SHIMADZU). The water content was determined to be 25.0 ± 0.2 wt% from the weight loss by heating to 500 °C under a dry nitrogen atmosphere.

Aqueous solutions were prepared with water purified by distillation and ion exchange with a pure water system (SA-2100E1, EYELA). The electrical resistivity of the pure water was 18 M Ω cm. Potassium bromide (KBr) and H₂O₂ were used as reagents to prepare the aqueous solutions. KBr (99%) was purchased from Wako Pure Chemical Industries, and H₂O₂ (35 wt% aqueous solution) was purchased from Mitsubishi Gas Chemical Company.

2.2. Irradiation and product analysis

The NaY-aqueous solution mixtures were irradiated by γ -rays from a ⁶⁰Co radiation source at the Takasaki Advanced Radiation

Research Institute, Japan Atomic Energy Agency. Before irradiation, the samples were stored in a refrigerator overnight to equilibrate the NaY with the aqueous solutions. After storage, the pH of the supernatants of the samples became 9.0 ± 0.2. The samples were then de-aerated by argon (Ar) gas before irradiation. The samples were irradiated in glass vials sealed with septa at room temperature (ca. 20–25 °C). During irradiation, the samples were not agitated; therefore, they separated into two layers, a sediment layer of NaY below and a supernatant layer above. The sample vials also contained headspace gases.

After irradiation, first, the headspace gases were analyzed to measure the concentrations of H₂ and O₂ using a gas chromatograph (GC-14 A, SHIMADZU) equipped with a molecular sieve 5 A column and a thermal conductivity detector. Next, the supernatant solutions were analyzed by liquid chromatography to measure the concentrations of H₂O₂ using a high-performance liquid chromatography (HPLC) system (Agilent 1100 series, Agilent Technologies) equipped with a silica-based column (Inertsil CX, GL Science) and an electrochemical detector (ED623, GL Science). Before they were injected into the HPLC system, the supernatant solutions were filtered with hydrophilic polytetrafluoroethylene filters with 0.2 μ m pores to remove the NaY powders from the solutions. The filtration did not affect the measurement of H₂O₂.

2.3. Dosimetry

The absorbed doses were measured by a dichromate dosimeter (Mai et al., 1998). The absorbed doses of the samples were calculated from the measured doses and the mass energy-absorption coefficients of the materials for 1.25 MeV photons (Hubbell and Seltzer, 1995). The absorbed doses of the aqueous solutions and the water adsorbed on NaY were calculated using the coefficient for water, 2.97 × 10⁻² cm² g⁻¹. The coefficient for NaY was calculated to be 2.65 × 10⁻² cm² g⁻¹ from the composition formula Na₄Al₄Si₁₁O₃₀. The composition formula was assumed from the SiO₂/Al₂O₃ ratio of NaY, 5.5. The absorbed doses of the samples were then obtained as the averages weighted by the weight fractions of the aqueous solution, adsorbed water, and NaY.

2.4. Measurement of H₂O₂ adsorption

The adsorption behavior of H₂O₂ on NaY was measured separately from the γ -ray irradiation experiments in order to calculate the adsorbed quantities of H₂O₂ from the measured concentrations in the supernatants. Aqueous H₂O₂ solutions of different concentrations were mixed with NaY, and the mixtures were continuously stirred to disperse NaY in the solutions at 22 ± 3 °C. Small aliquots of the suspensions were sampled intermittently, and the solutions were separated from the suspensions by filtering to measure the H₂O₂ concentrations.

3. Numerical calculation

3.1. Kinetic model

Numerical calculations of the chemical kinetics were performed to obtain an interpretation of the results of the irradiation experiments. The calculation model was spatially separated into headspace, supernatant, and sediment regions, as illustrated in Fig. 1. The kinetic model in the supernatant region considered the water radiolysis, chemical reactions, and diffusion. In the sediment region, effects of NaY were additionally introduced into the kinetic model. The mathematical modeling of effects of NaY will be discussed later on the basis of the experimental results. The headspace region was included in the model to take account of

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