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GAMMA-RAY IRRADIATION EFFECT ON AQUEOUS PHENOL SOLUTIONS DISPERSING TiO_2 OR Al_2O_3 NANOPARTICLES

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Abstract. Gamma-ray radiolysis of aqueous phenol solutions dispersing TiO_2 or Al_2O_3 nanoparticles was investigated. Organic compounds, including phenol and aromatic intermediates induced by the radiolysis, were effectively removed from the aqueous phase in the presence of the nanoparticles, and the Al_2O_3 showed higher efficiency. Generation of inorganic gases was, however, suppressed in the presence of the nanoparticles. The removal of the organic compounds from the aqueous phase is partly explained by the adsorption of the aromatic intermediates to the nanoparticles. For the removal of the organic compounds, addition of the nanoparticles before the gamma-ray irradiation was more effective than addition after the irradiation. A reaction that enhances the removal of organic compounds seemed to proceed in the presence of the nanoparticles.

1. INTRODUCTION

Radiolysis and photocatalysis of aqueous solutions containing various toxic organic compounds have been studied as a possible technique applicable to water treatment process [1-4]. In general, organic compounds are directly decomposed by ionizing radiation, but usually far higher efficiency is required for commercial use [1,2]. Photocatalytic decomposition of the organic compounds also has been well studied. As the main advantage of the photocatalytic reaction is the utilization of solar energy, semiconductor materials such as TiO_2 are exclusively studied as a photocatalyst [3,4]. The UV photon is able to activate the photocatalyst. However, penetration length of UV photons into the solution is too short to utilize large reactor.

We have reported that some kinds of nanoparticles, e.g. TiO_2, Al_2O_3, dispersed in water drastically enhance the hydrogen gas evolution yield induced by γ-ray irradiation in comparison with that caused by pure water radiolysis [5-10]. We have proposed a hypothetical mechanism taking account both of radiolysis and photocatalytic effects [9], in which reactions that enhance the hydrogen yield proceed on the nanoparticle's surface. Higher energy of γ-photon could activate even Al_2O_3 usually classified as an insulator. This photocatalytic process seemed to proceeds regardless of the chemical species of the nanoparticle.

In this paper, we report on the radiolysis of aqueous solutions containing TiO_2 or Al_2O_3 nanoparticles using γ-ray. High efficiency of removing toxic organic species from the solution is anticipated by the radiation enhanced decomposition of organic compounds induced by γ-ray and photocatalysis occurring on nanoparticle's surface. Phenol was taken as a model compound of toxic organic compounds, because it is water soluble and the simplest aromatic compound. A dramatic efficiency of removing organic species from aqueous phase, if any, would

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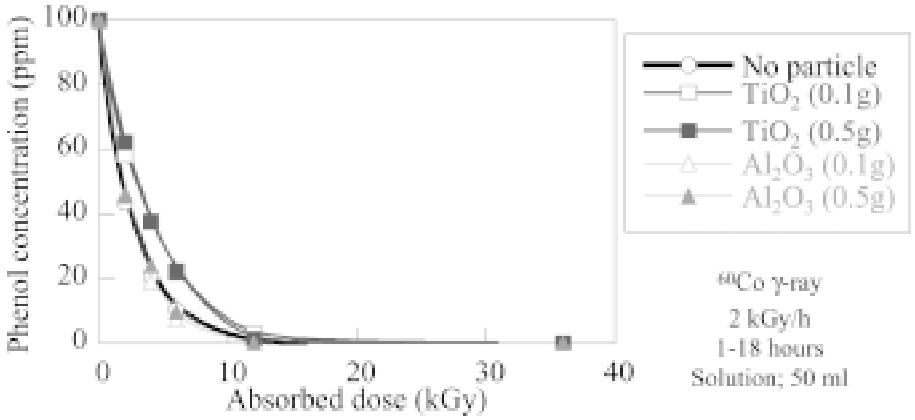

Fig. 1. Effect of absorbed dose on phenol concentration.

lead to a process which makes full use of radiation energy emitted from the high level radioactive waste.

2. EXPERIMENTAL

Materials examined in this work were nanoparticles of TiO_2 and Al_2O_3 obtained from Nanophase Tech. Corp. (NanoTek), and their nominal average size were 30 and 33 nm, respectively. Their size distributions, agglomerated particle's size and TEM micrographs have been reported elsewhere [6,7,9]. X-ray diffraction measurements indicated that TiO_2 was mainly of anatase and few % of rutile, and Al_2O_3 was of γ–Al_2O_3. All phenol solutions examined in this work were prepared as 100 wt. ppm. The particles of 0.1 or 0.5 g were dispersed in the phenol solution of 50 g, to which ^{60}Co γ-ray was irradiated at room temperature. Dose rate of the γ-ray was 2 kGy/h and irradiation time was 1–18 hours. During the irradiation the dispersion was shaken by rotating a disk on which vials were mounted [7]. After the irradiation, CO_2, CO and CH_4 gas evolved and confined in the free space of the vial was sampled with a syringe and analyzed by a gas chromatograph with flame ionization detector (GC-FID, HITACHI G-3500). In advance to the analysis of aqueous phase, the dispersion was centrifuged with centrifugal machine (KUBOTA 3K30C) to remove the nanoparticles. Various organic compounds should be generated as intermediates, and some of which are qualitatively analyzed by a gas chromatograph with mass-spectrometer (GC-MS, SHIMADZU GCMS-QP5000). Concentration of phenol was measured with GC-FID, and the amount of total organic carbon (TOC) was evaluated by a total carbon analyzer (SHIMADZU TOC5000A). The adsorbed amount of phenol and other aromatic compounds, which should be generated as intermediates, onto the nanoparticle surface was also evaluated. Those solutions of 100 wt. ppm were prepared and 1 wt. % of TiO_2 and Al_2O_3 nanoparticles were added to the solution. The dispersions were stirred for 3 hours without γ-ray irradiation, and centrifuged before the analysis as well. Dose absorbed by the sample dispersion was evaluated as those absorbed by the pure water, because mass of the particle and dissolved phenol is far smaller than that of water.

3. RESULTS AND DISCUSSION

Fig. 1 shows the phenol concentration plotted against the absorbed dose. It is noticed that phenol could be fully degraded by γ-ray irradiation, even without nanoparticles. TiO_2 nanoparticles seem to suppress the phenol degradation slightly, while Al_2O_3 did not.

Fig. 2 shows the TOC concentration plotted against the absorbed dose. It was indicated that the TOC concentration was effectively reduced in the presence of the TiO_2 and Al_2O_3 nanoparticles, and the latter showed higher effciency. Larger amount of nanoparticles showed higher efficiency for the TOC removal.

It was reported that the first step of the phenol decomposition by radiolysis and photocatalysis is an oxidation of phenol forming various aromatic intermediates such as hydroquinone, cathecol, pyrogallol and hydroxyhydroquinone [2,4]. The process is schematically expressed in Fig. 3. Subsequent degradation processes lead to the generation of in-

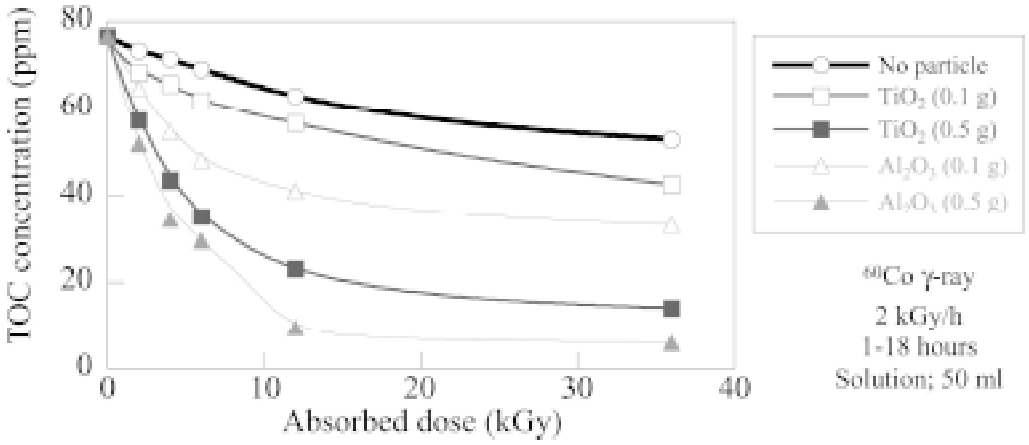

Fig. 2. Effect of absorbed dose on TOC concentration.

organic gases such as CO and CO_2. In our study, the formation of hydroquinone and catechol was qualitatively confirmed in aqueous phase of the irradiated solution both with and without nanoparticles. Table 1 shows the adsorption ratio of those aromatic compounds to the nanoparticles, indicating that the adsorption of phenol to the nanoparticles is negligible. It is noticed that the adsorption ratio increases with increasing number of OH groups in these aromatic compounds. The reduction of TOC concentration by the nanoparticles shown in Fig. 2 is explained by the adsorption of those aromatic compounds onto the nanoparticle's surface.

To investigate whether the decomposition reaction is enhanced by existence of the nanoparticle, 1 wt. % of Al_2O_3 nanoparticles were added to the irradiated phenol solution, and the results are shown in Fig. 4. Concentration of TOC is plotted against the absorbed dose. The TOC concentration was reduced by addition of nanoparticle even after the irradiation, which is obviously due to the adsorption of the intermediates to the nanoparticles. It should be noticed, however, that the TOC removal was much more enhanced when the nanoparticles exist during irradiation. This result implies a reaction that accelerates the removal of TOC proceeds in the presence of nanoparticles.

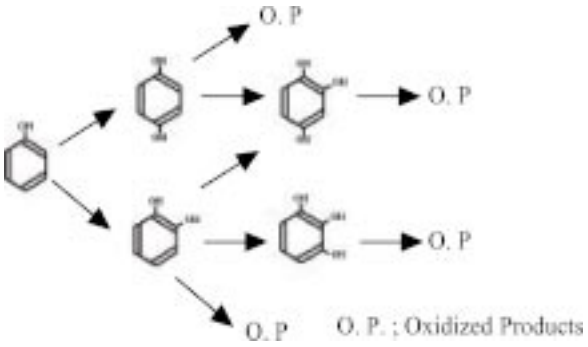

Fig. 3. Initial process of phenol degradation.

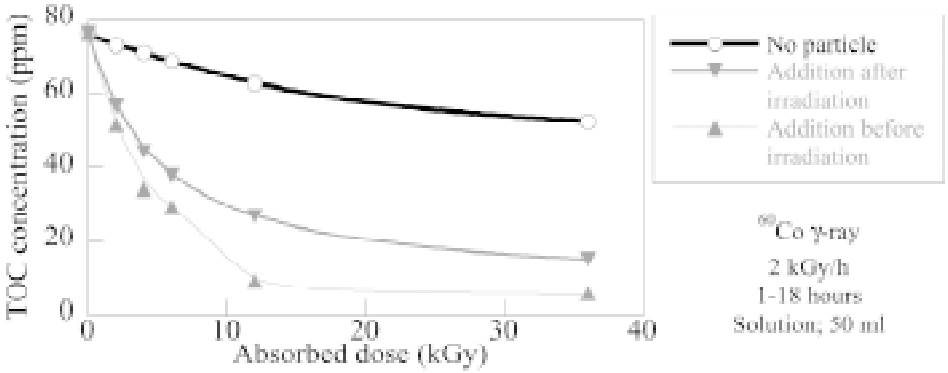

Fig. 4. Effect of Al_2O_3 nanoparticle on TOC concentration. (Nanoparticles were added before and after the irradiation).

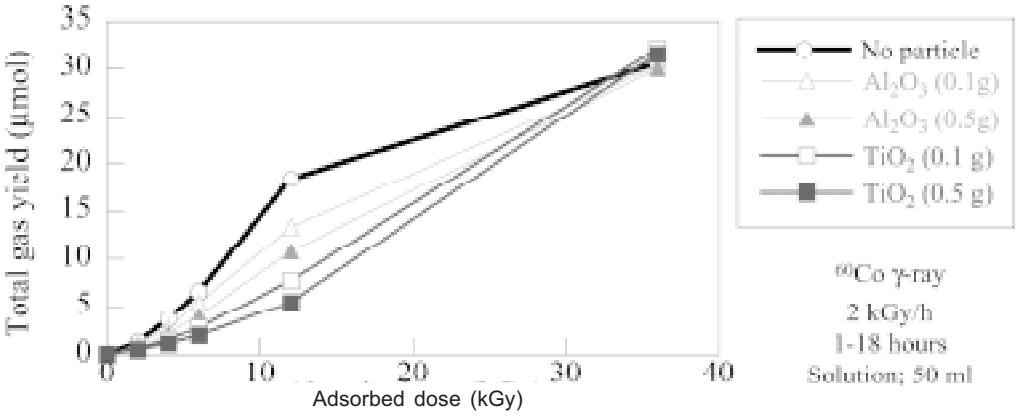

Fig. 5. Effect of absorbed dose on total gas evolution yield. (Total gas involves CO_2, CO and CH_4 gas).

Fig. 5 shows the total gas evolution yield plotted against the absorbed dose. Total gas involves CO_2, CO and CH_4 gas. The CO_2 gas was the major component with a yield about one and two order higher than those of CO and CH_4 gas, respectively. The yields were suppressed in the presence of TiO_2 and Al_2O_3 nanoparticles, and the suppression with the latter was remarkable. The yields decreased with increasing nanoparticle's amount. This fact seems to be inconsistent with the result shown in Fig. 2 and Fig. 4. Adsorption of intermediates to the nanoparticles might have prevented the radiolysis of intermediates proceed in the aqueous phase. Quantitative analysis of intermediates is required to understand the total decomposition mechanism.

4. SUMMARY

In the radiolysis of aqueous phenol solution, organic compounds were effectively removed by dispersing TiO_2 or Al_2O_3 nanoparticles, and the latter was more effective. The removal of TOC is partly explained by the adsorption of aromatic intermediates to the nanoparticles. Reactions that accelerate the TOC removal seemed to proceed in the presence of nanoparticles. However, inorganic gas evolution yield was not enhanced by the nanoparticles.

REFERENCES

[1] R. M. Quint, H. R. Park,P. Krajnik, S. Solar, N. Getoff and K. Sehested // *Radiat. Phys. Chem.* **47** (1996) 835.

[2] S. Hashimoto, T. Miyata, M. Washino and W. Kawakami // *Environ. Sci. Technol.* **13** (1979) 71.

[3] K. Bekbolt, A. S. Suphandag and C. S. Uyaguner // *J. Photochem. Photobiol. A* **148** (2002) 121.

[4] K. Okamoto, Y. Yamamoto, H. Tanaka, M. Tanaka and A. Itaya // *Bull. Chem. Soc. Jpn.* **58** (1985) 2015.

[5] T. A. Yamamoto, S. Seino, M. Katsura, K. Okitsu, R. Oshima and Y. Nagata // *Nanostructured Materials* **12** (1999) 1045.

[6] S. Seino, R. Fujimoto, T. A. Yamamoto, M. Katsura, S. Okuda and R. Oshima // *Radioisotopes* **49** (2000) 354, in Japanese.

[7] S. Seino, R. Fujimoto, T. A. Yamamoto, M. Katsura, S. Okuda, K. Okitsu and

Table 1. Adsorption ratio of phenol and aromatic intermediates on nanoparticles.

Name / *Formula*	*Phenol* C_6H_5OH	*Hydroquinone* $C_6H_4(OH)_2$	*Catechol* $C_6H_4(OH)_2$	*Pyrogallol* $C_6H_3(OH)_3$	*Hydroxyhydroquinone* $C_6H_3(OH)_3$
TiO_2	~ 0%	14%	61%	89%	95%
Al_2O_3	~0%	12%	41%	90%	94%

(Initial concentration: 100 ppm , Nanoparticle: 1 wt %, Stirred for 3 hours without irradiation)

R. Oshima // *Mat. Res. Soc. Symp. Proc.* **608** (2000) 505.
[8] S. Seino, T. A. Yamamoto, R. Fujimoto, K. Hashimoto, M. Katsura, S. Okuda, K. Okitsu and R. Oshima // *Scripta Materialia* **44** (2001) 1709.
[9] S. Seino, T. A. Yamamoto, R. Fujimoto, K. Hashimoto, M. Katsura, S. Okuda and K. Okitsu // *J. Nucl. Sci. Technol.* **38** (2001) 636.
[10] S. Seino, T. A. Yamamoto, R. Fujimoto, K. Hashimoto, M. Katsura, S. Okuda and K. Okitsu // *Mat. Res. Soc. Symp. Proc.* **676** (2001) Y3.43.1.