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Efficiency of Hydroxyl Radical Production of Gamma-ray Treated Bentonite

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Abstract

Bentonite was treated by gamma-rays in various conditions, and the change of the catalyst was characterized by EPR spectroscopy. EPR spectra of bentonite gave a peak with $g = 2.005$. The intensity of the peak was inversely proportional to the efficiency of hydroxyl radical production, and non-treated bentonite showed the most efficient production. Decomposition of PCE (tetrachloroethylene) was largely dependent on the efficiency of hydroxyl radical production.

I. Introduction

Radiation treatment using gamma-rays or electron-beams is based on the production of highly reactive species such as hydroxyl radicals ($\cdot\text{OH}$), hydrogen peroxide (H_2O_2), perhydroxyl radicals ($\text{HO}_2\cdot$), hydrated electrons (e_{aq}^-) and hydrogen atoms ($\cdot\text{H}$).¹ Among them, hydroxyl radicals are known to be dominant species in the oxidative decomposition of organic pollutants.^{2,3} However, there are few reports that evaluate the effect of catalysts on the radiation treatment in terms of hydroxyl radical production efficiency. In this work, electron paramagnetic resonance (EPR) spectroscopy that is a powerful tool to characterize

paramagnetic metal ions and defects in oxide catalysts was used to characterize the change of bentonite by gamma-rays.^{4,5} The combination of EPR and spin-trapping method was also used to detect unstable hydroxyl radicals.⁶

II. Experimental

Catalyst preparation and characterization : The catalyst used in this work was bentonite from Aldrich. Besides raw catalyst powder, three kinds of suspensions were made. Acidic and alkaline suspensions were prepared by adding HNO₃ and NaOH, respectively. The equilibrium pH of the suspensions was adjusted to around 2.5 and 10.5, respectively. The third suspension was prepared by adding 100 mg/l of Cu(NO₃)₂ and the pH of the suspension was adjusted to around 6.5. The raw catalyst powder and suspensions were irradiated in a high-level ⁶⁰Co source (AECL IR-79, Canada). The radioactivity of the source is around 100,000 Ci. The total absorbed dose was around 450 kGy. After gamma-irradiation, the suspensions were dried at 110 °C and finely ground. EPR spectra of the catalyst samples were recorded in the X-band on a Bruker EMX spectrometer at 77 K.

Hydroxyl radical measurement : A nitron spin-trapping reagent DMPO (5,5-dimethyl-pyrroline-N-oxide) was purchased from Aldrich. The catalysts prepared in the previous section were suspended in distilled and deionized water and stabilized for one day. The suspensions were mixed with DMPO in phosphate buffer (0.1 M, pH 7.4) just before gamma-irradiation. Irradiation was performed in a low-level ⁶⁰Co source (Paranomic, UK). The radioactivity of the source is around 270 Ci. The total absorbed dose was around 100 Gy. Immediately after irradiation, around 25 µl of the sample solution was transferred into a capillary tube, and EPR spectra were recorded in the X-band on a Bruker EMX spectrometer at room temperature.

PCE decomposition : Pollutant stock solution (about 100 mg/l) was prepared by dissolving spectrophotometric grade 99 % PCE (Aldrich) in distilled and deionized water.

For the decomposition of PCE, irradiation was performed at room temperature in the low-level ^{60}Co source. The samples for irradiation were prepared in 45 ml glass bottles with the pollutant stock solution and catalyst powders. PCE content was measured by a Younglin M600D (Korea) gas chromatograph equipped with an electron capture detector. The column of GC was a 30-m DB-624 from J & W.

III. Results and Discussion

Characterization of catalysts : EPR spectroscopy was used to characterize the change of bentonite by gamma-rays. Figure 1 shows the EPR spectra of bentonite recorded at 77 K.

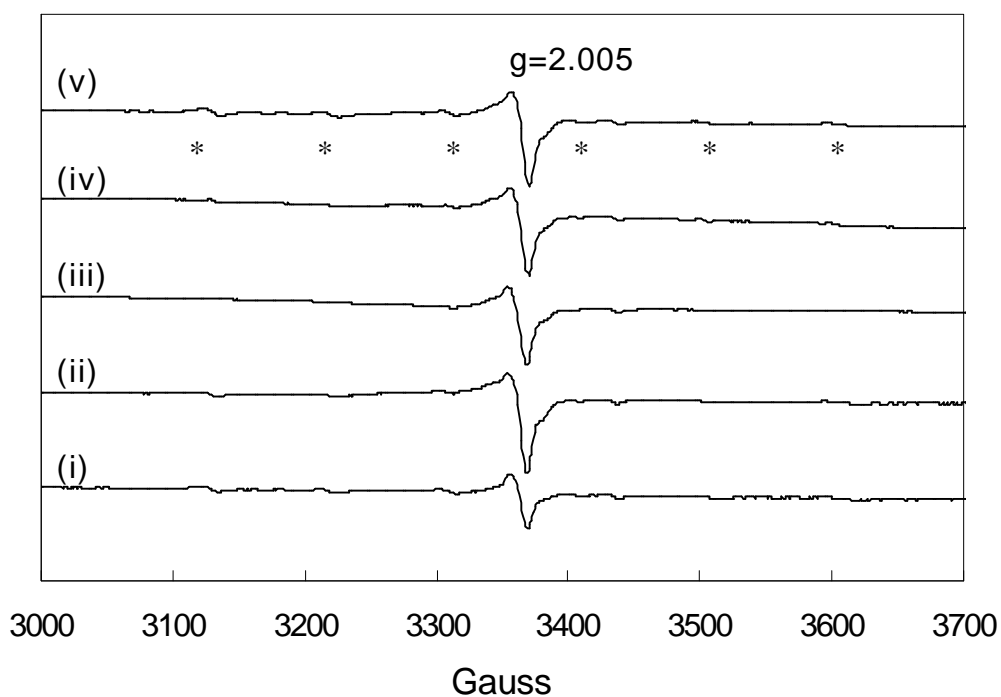


Figure 1. EPR spectra of bentonite at 77 K. The catalyst treatments were (i) none, (ii) gamma-irradiation, (iii) gamma-irradiation in the presence of copper ions, (iv) gamma-irradiation in acidic condition and (v) gamma-irradiation in alkaline condition.

The peak with $g = 2.005$ arises from natural irradiation, which induces the formation of radicals or trapped electrons and holes.⁴ The intensity of the peak was varied with treatment conditions. The six narrow peaks (marked by asterisks) in the spectra are attributed to free Mn^{2+} ions located at some imperfections. Unlike the typical EPR spectra of Cu(II) solid species, Cu(II)-added bentonite did not give a broad signal in front of the peak. This indicates that Cu(II) ions exist not as aggregates but as ion-exchanged species. Considering the cation exchange capacity of bentonite, the copper ions are mainly attached to the bentonite surface by ion-exchange.

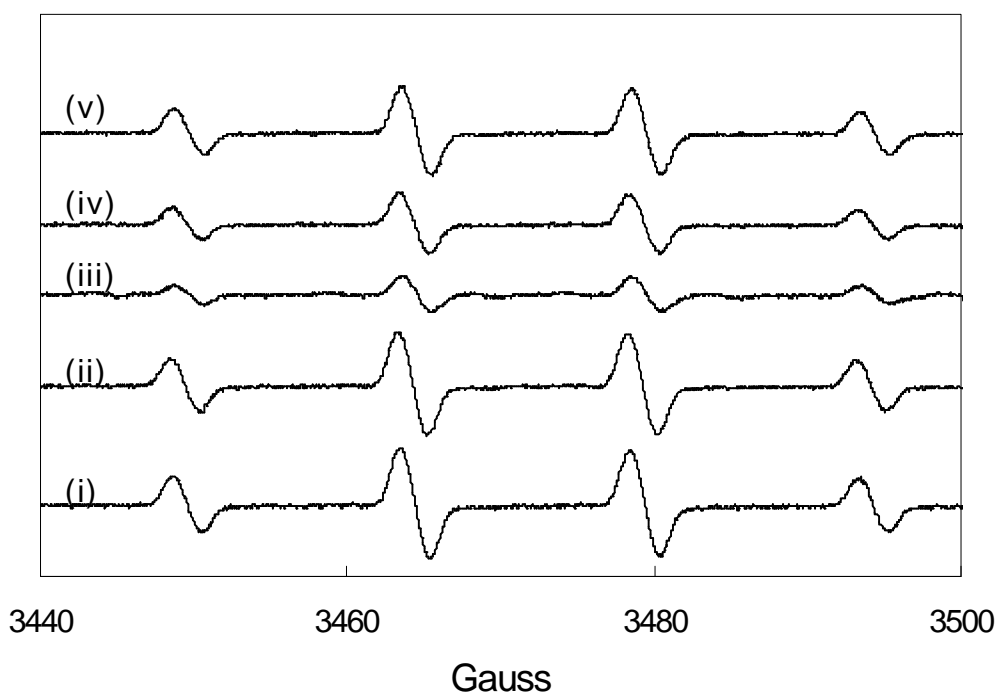


Figure 2. EPR spectra of DMPO-OH adduct at room temperature formed during gamma-irradiation in the presence bentonite. The catalyst treatments were the same as the legend of Figure 1. The concentrations of DMPO and catalyst were 100 mM and 4 mg/ml, respectively.

Efficiency of catalysts : An EPR/spin-trapping method was used to determine hydroxyl radicals produced during gamma-irradiation. Figure 2 shows the typical EPR spectrum of DMPO-OH adduct that was composed of quartet lines having peak height ratio of 1:2:2:1.⁷ This was confirmed by the fact that a hydroxyl radical scavenger such as ethanol significantly decreased the signal (data not shown). Gamma-ray treatments of bentonite in various conditions reduced the DMPO-OH adduct signal, and the signal intensity was largely suppressed in the presence of Cu(II). This indicates that non-treated bentonite is the most efficient hydroxyl radical producer, and the catalytic activity of bentonite in the radiation treatment of PCE becomes reduced along with gamma-irradiation.

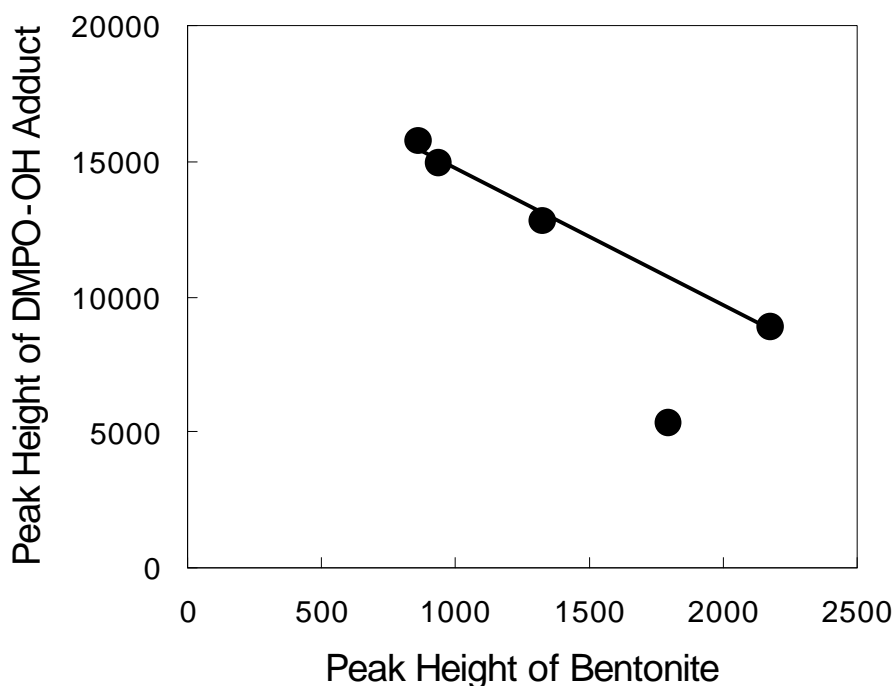


Figure 3. Relationship between peak height of bentonite and signal height of DMPO-OH adduct.

The relative intensity of DMPO-OH adduct signal was compared with the relative intensity of the bentonite peak in order to evaluate the relationship between them. As indicated in Figure 3, the intensity of the DMPO-OH signal linearly decreased with the increase of bentonite peak intensity. This means that the increase of defect site in bentonite decreases the efficiency of hydroxyl radical production. However, Cu(II)-added bentonite did not fit with the above linearity because the ion-exchanged copper ions additionally inhibit hydroxyl radical production.

The relationship between the DMPO-OH signal intensity and PCE decomposition is given in Figure 4. PCE decomposition was largely dependent on the signal intensity, in other words, on hydroxyl radical concentration. This indicates that the hydroxyl radicals are a dominant species in the oxidative decomposition of PCE by gamma-rays.

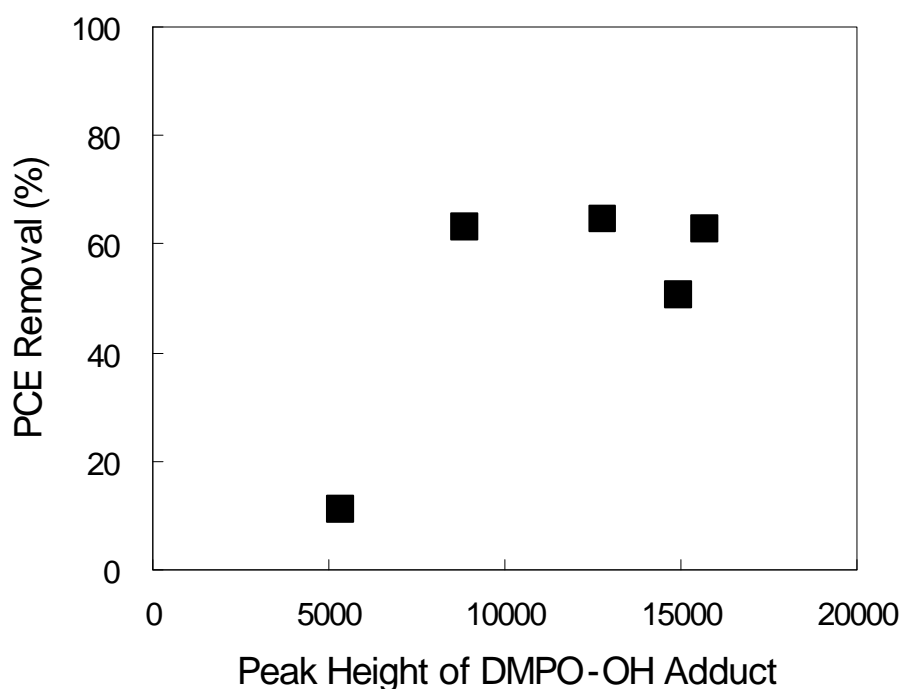


Figure 4. Relationship between signal height of DMPO-OH adduct and PCE removal. Conditions used in PCE decomposition: PCE, 10 mg/l; catalyst, 0.02 g; dose, 60 Gy.

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