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The Effect of Gamma-ray on the Catalytic Activity of Anatase, Degussa P25 and Bentonite in TCE and PCE Decomposition

Jinho Jung, Dae Hyun Yoo and Myun Joo Lee

Korea Atomic Energy Research Institute
P.O.Box 105 Yusung, Taejon 305-600, Korea

Abstract

Radiation treatment in the presence of catalysts such as anatase, P25 and bentonite showed an efficient removal of TCE and PCE compared with gamma-irradiation only. The gamma-ray pretreatment of P25 and bentonite enhanced the decomposition of TCE and PCE, respectively. The change of the catalysts by gamma-ray was characterized by EPR spectra. For anatase and bentonite, the peaks in the spectra increased significantly, but the pattern of the spectra changed in the case of P25. The relationship between the peaks and the pollutant decomposition should be further clarified due to the complexity of the spectra.

I. Introduction

Groundwater contamination with chlorinated ethylenes such as TCE (trichloroethylene) and PCE (perchloroethylene) is becoming a serious problem in industrialized areas of Korea. As a result, the government has limited TCE and PCE concentrations in groundwater less than 0.03 and 0.01 mg/L, respectively, since 1993. However, the contamination of groundwater was not reduced due to increasing industrialization and poor groundwater conservation. Thus, many techniques have been proposed for the reclamation of groundwater. Among them, adsorption onto activated carbon and air-stripping are found to be efficient and economic, however, they just do remove the contaminants but do not destroy them.¹

An attractive solution for the groundwater contamination is radiation treatment. Gehringer *et al.* showed that TCE and PCE were completely decomposed by gamma-ray or electron-beam, and the decomposition was more efficient in the presence of ozone.^{2,3} However, there

are few reports that investigate the effect of catalysts on the decomposition of TCE and PCE, and no report that evaluates the effect of the pretreatment of the catalysts by gamma-ray. Electron paramagnetic resonance (EPR) spectroscopy is a powerful tool to characterize paramagnetic metal ions and defects in oxide catalysts.^{4,5} In this work, EPR was used to characterize the gamma-ray treated catalyst and the efficiency of the catalyst in the decomposition of TCE and PCE was investigated.

II. Experimental

Catalysts used in this work were anatase (Aldrich), P25 (Degussa) and bentonite (Aldrich). For the gamma-ray treatment of the catalysts, irradiation was performed at room temperature (around 20 °C) 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 70 kGy. Pollutant stock solutions (about 100 mg/L) were prepared by dissolving spectrophotometric grade 99.5 % TCE and 99 % PCE (Aldrich) in distilled and deionized water. For the decomposition of TCE and PCE, irradiation was performed at room temperature (around 20 °C) in a low-level ⁶⁰Co source (Paranomic, UK). The radioactivity of the source is around 270 Ci. Irradiation samples were prepared in 45 mL glass bottles with the pollutant stock solution and the catalyst powder. TCE and PCE contents were measured by a Younglin M600D (Korea) gas chromatograph equipped with an electron capture detector. The column was a 30-m DB-624 from J & W. The EPR spectra of the catalyst powder were recorded in the X-band on a Bruker EMX spectrometer at 77 K.

III. Results and Discussion

EPR study : EPR spectroscopy was used to characterize the change of anatase, P25 and bentonite by gamma-ray. Figure 1 shows the EPR spectra of anatase powder recorded at 77 K. Four peaks in the spectra increased up to 15 % by gamma-ray. The peaks with $g = 1.951$ and $g = 1.972$ can be assigned as the axial defect (Ti^{3+}), $g = 2.005$ as an electron trapped at an oxygen vacancy (F-center) and $g = 1.991$ as Ti^{3+} in TiO_2 formed after degassing at 200 °C or reduction with 50 Torr of H_2 at the same temperature.⁶

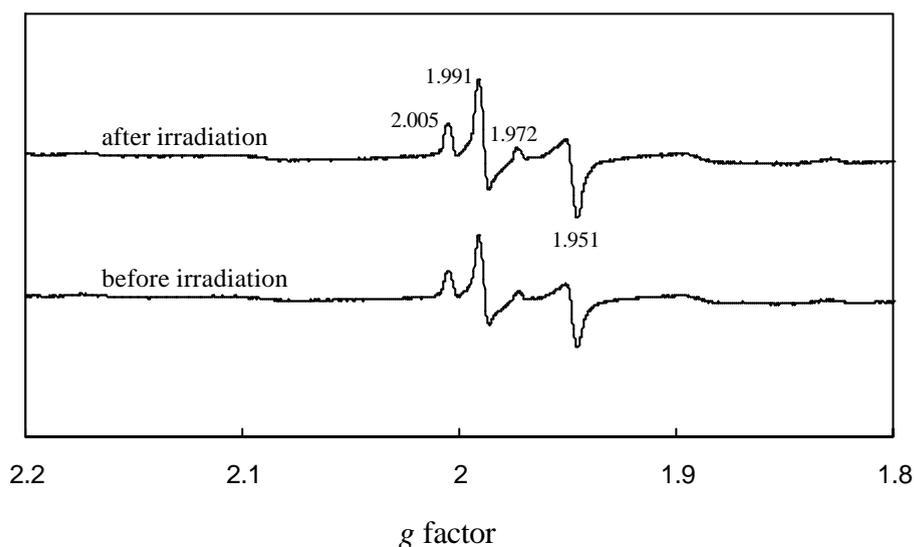


Figure 1. EPR spectra of anatase powder before and after gamma-irradiation.

EPR spectra of P25 are given in Figure 2. The peaks with $g = 2.036$, $g = 2.022$ and $g = 2.017$ can be assigned as oxygen radicals (O^-). The difference of the g values is probably due to the change in the spin distribution of the oxygen radical, which is caused by gamma-ray.⁷ The peak with $g = 1.980$ is attributable to Ti^{3+} , and this peak did not change.

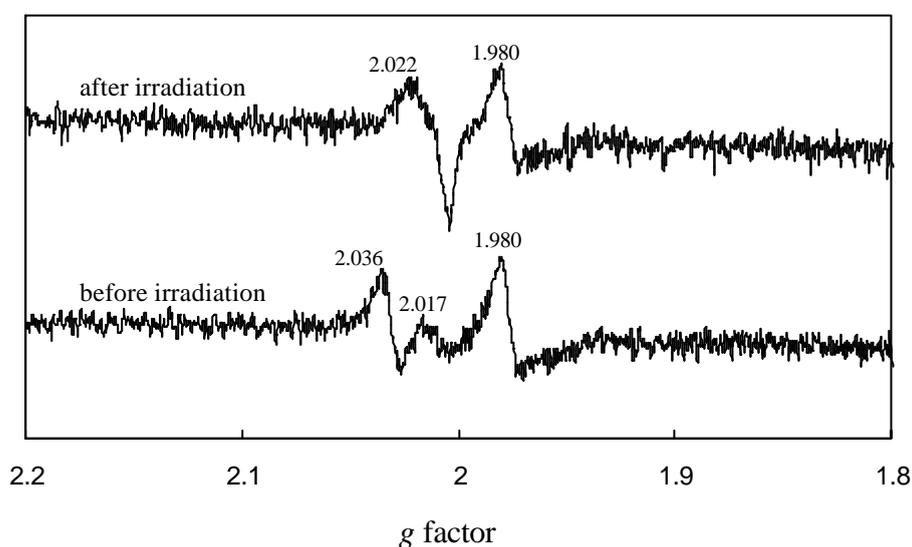


Figure 2. EPR spectra of P25 powder before and after gamma-irradiation.

EPR spectra of bentonite are given in Figure 3. The peaks with $g = 2.005$ arises from natural irradiation, which induces the formation of radicals or trapped electrons and holes.⁴ The six narrow peaks (marked by asterisks) in the spectra is attributed to free Mn^{2+} ions located at

some imperfections. Though the Mn^{2+} peaks did not change significantly, the peak with $g = 2.005$ increased markedly by gamma-ray.

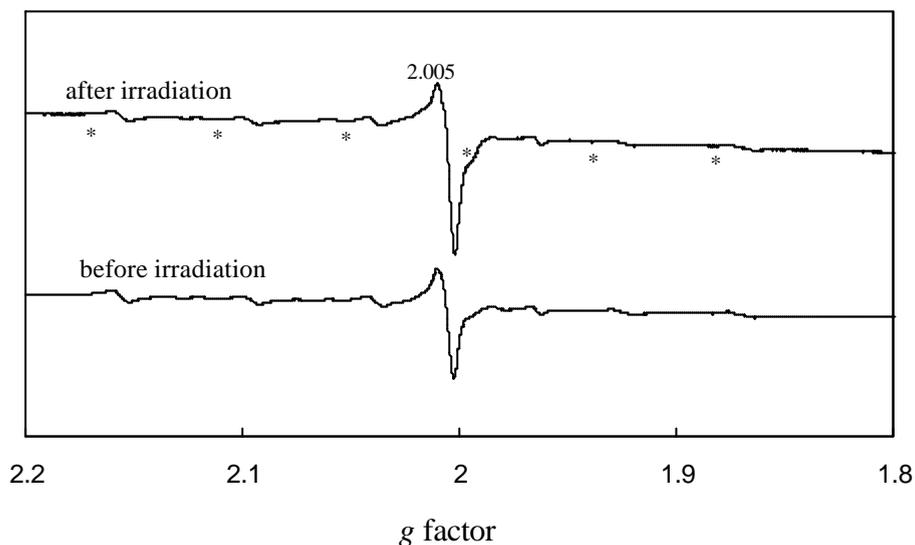


Figure 3. EPR spectra of bentonite powder before and after gamma-irradiation.

TCE and PCE decomposition : The removal of TCE and PCE by gamma-ray in the presence of catalysts is given in Figure 4. Without the catalyst, TCE and PCE were decomposed up to 53 % and 86 %, respectively, at a dose of 60 Gy. For the TCE decomposition, 10 to 25 % of increase was achieved with the catalysts, but there is no significant difference between the catalysts. Except P25, the pretreatment of the catalysts by gamma-ray reduced the TCE decomposition. Contrary to the TCE decomposition, there is no significant increase of the PCE decomposition by the catalysts, even decreased the decomposition in the case of P25 and bentonite. However, the gamma-ray treated bentonite showed the most efficient catalytic activity.

The enhancement of TCE and PCE decomposition in the presence of the catalysts may be caused by the formation of electron/hole pairs and/or defects (activated centers) in the catalysts by gamma-ray.^{8,9} As indicated in the EPR study, the pretreatment of the catalysts gave the significant change of the activated centers, but the effects of the change on the TCE and PCE decomposition was not clear with the above data. The relationship between the peaks and the pollutant decomposition should be further clarified.

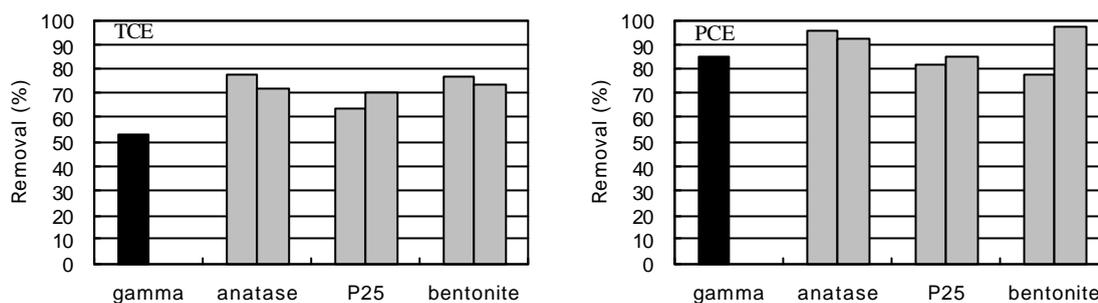


Figure 4. TCE and PCE decomposition by gamma-ray without and with catalyst. Conditions: catalyst 0.02 g; solution 40 mL; dose 60 Gy. Legends: Black, γ -ray only; vertical, γ -ray/raw catalyst; horizon, γ -ray/treated catalyst.

Acknowledgement

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