Catalytic activity of clay from tidal flat sediments in the decomposition of perchloroethylene by gamma-rays

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In the decomposition of perchloroethylene (PCE) by gamma-rays, clay from tidal flat sediments showed an efficient catalytic activity. Moreover, the clay thermally treated at 700 °C in air enhanced the PCE removal efficiency better than that of the well known catalyst Degussa P-25 TiO_2. The change of the clay by the thermal treatment was identified by electron paramagnetic resonance (EPR) spectroscopy. The intensity of the signal that arises from the natural radiation defect was decreased with increasing thermal treatment temperature, and inversely dependent on the PCE removal efficiency.

KEY WORDS: clay; PCE; gamma-rays; EPR; TiO_2

1. Introduction

All chlorinated organic compounds, including PCE, are hazardous compounds. Hence, many technologies such as aeration, conventional oxidation (commonly ozonation), activated carbon absorption and advanced oxidation technology have been attempted and the effective methods have been desired to treat these chlorinated organic contaminants [1–3]. Among them, the most promising method seems to be radiation treatment with gamma-rays or electron beams. But, as it was shown [4], water radiolysis alone is not sufficient for effective degradation of chlorinated pollutants in water. Therefore, seeking for some apt promoters such as a catalyst to increase the efficiency of water radiolysis seems to be one of the most actual tasks. Thus, we investigated the gamma-ray decomposition of PCE using clay from tidal flat sediments as catalyst in this study. Moreover, the catalytic activity of clay in the PCE removal was characterized by EPR spectroscopy that is a powerful tool to characterize paramagnetic metal ions and defects in oxide catalysts [5,6].

2. Experimental

2.1. Clay treatment and characterization

The clay used in this work was taken from tidal flat sediments at Yeosu, South Korea. It contains, expressed as a weight percentage mass, 29% silicon, 10% aluminum, 3.8% iron and 2.3% potassium analyzed using energy dispersive X-ray spectrometer (EDS).

The clay was washed with distilled water several times, and dried at 110 °C after sedimentation and filtration and then finely ground. After this treatment, the thermal treatments of clay were carried out in air at 300, 500, 700 and 900 °C for 2 h. EPR spectra of clays before and after the thermal treatment were recorded in the X-band on a Bruker EMX spectrometer at 77 K.

2.2. PCE decomposition

Pollutant stock solution (about 0.6 mmol) was prepared by dissolving spectrophotometric grade 99% PCE (Aldrich) in distilled and deionized water. TiO_2 was obtained from Degussa and used without further treatment. Experiments were performed with 0.06 mmol PCE solution in the presence of 0.1 wt% TiO_2 (Degussa P-25) or thermally treated clays in a ^{60}Co-irradiation source (Paranomic, UK, around 270 Ci) at room temperature (around 20 °C). All samples were prepared in 50 ml pyrex glass bottles and filled up to 30 ml. PCE contents were measured by a Younglin M600D gas chromatograph equipped with a ^{63}Ni-electron capture detector.

3. Results and discussion

Figure 1 shows the PCE removal by gamma irradiation at a dose of 100 Gy with and without catalysts. The PCE removal for gamma irradiation alone, P-25 and the thermally treated clay at 700 °C was 76.0, 83.0 and 96.6%, respectively. The PCE removal efficiency of the clay was much better than that of TiO_2, which is known to enhance the radiation-induced decomposition [7].

The effect of thermal treatment on the catalytic activity of clay in PCE removal was investigated and the result is shown in figure 2. The PCE removal efficiency abruptly increased between 300 and 500 °C. The clay treated at 110 and

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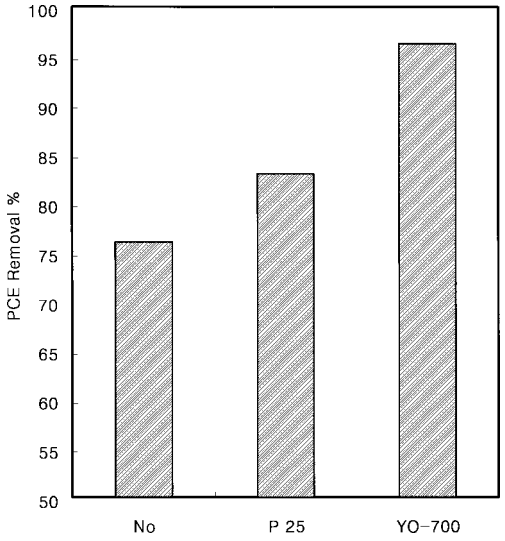

Figure 1. PCE decomposition with and without catalysts (No: gamma irradiation alone; P-25: Degussa TiO_2; and YO-700: thermally treated clay at 700 °C).

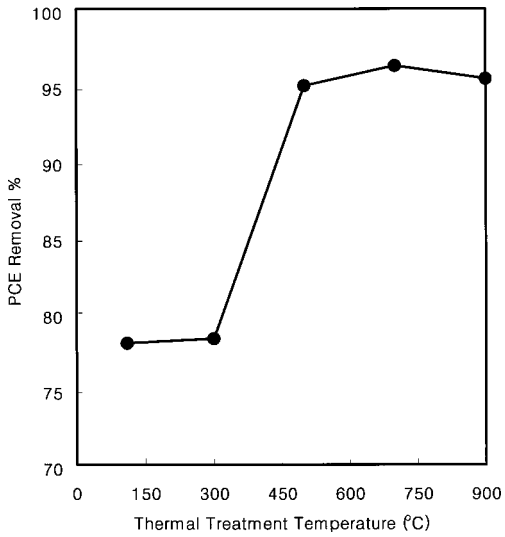

Figure 2. PCE decomposition as a function of thermal treatment temperature of clay.

300 °C showed a removal efficiency of below 80%, but the clay treated above 500 °C gave a much higher removal efficiency of approximately 95%. The highest PCE removal was obtained with the clay treated at 700 °C (96.6%).

EPR spectroscopy was used to characterize the change of clay by thermal treatment temperature. Figure 3 shows EPR spectra of clays that were thermally treated from 110 to 700 °C. They showed three distinct signals. Signal I at $g = 4$ comes from localized Fe^{3+} in the structure, broad signal II at $g = 2$ is attributable to Fe(III) oxy/hydroxide species and narrow signal III $g = 2$ is assigned as the natural radiation defect that induces the formation of radicals or trapped electrons and holes [5,8,9].

The intensity of signal I increases while the intensity of signal III decreases with increasing thermal treatment temperature. These trends of signal I and signal III may be

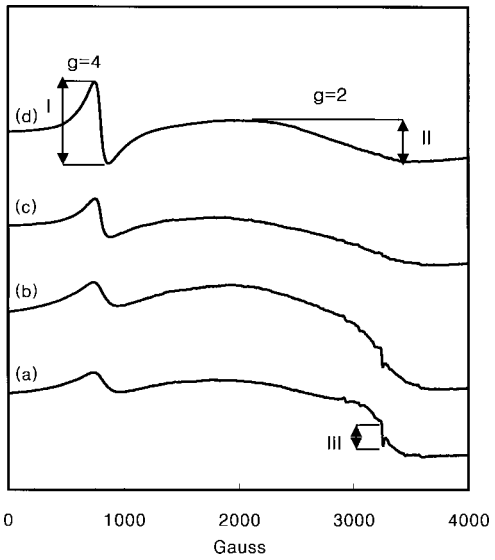

Figure 3. EPR spectra of clay thermally treated at (a) 110, (b) 300, (c) 500 and (d) 700 °C.

deeply related to the PCE removal efficiency, because the decomposition of PCE was largely dependent on thermal treatment temperature. According to the result of Jung *et al*., the intensity of signal III is inversely proportional to the production of hydroxyl radicals that are dominant oxidizing species in the decomposition of PCE by gamma-rays [10–12]. However, the relationship between the signal I and the decomposition of PCE has not been identified, thus this should be further characterized.

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