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ScienceDirect

Radiation Physics and Chemistry 77 (2008) 585–590

Radiation Physics and Chemistry

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Application of ozone decomposition catalysts to electron-beam irradiated xylene/air mixtures for enhancing carbon dioxide production

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Received 25 June 2007; accepted 10 September 2007

Abstract

The electron beam (EB) oxidation of gaseous xylene in air, appearing as ventilation gases emitted from painting factories, was investigated under various experimental conditions. Thereby, the implementation of an ozone decomposition catalyst, MnO_2, into EB-induced oxidation of xylene/air mixtures strongly contributed in the achievement of a better purification degree.

Keywords: Oxidation; Aromatic hydrocarbons; Electron beam; Decomposition; O_3; Xylene; CO_2

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1. Introduction

Various volatile organic compounds (VOCs) have been widely used in the industry, e.g. as solvents, basic material for chemical synthesis, etc. Because of their light volatility, they appear frequently as air pollutants and cause environmental problems when released into the atmosphere (Wiederkehr, 1984).

Electron beam (EB) technology is one of the advanced technologies for treating environmental pollutants in gases and water. This technology is based on oxidation reactions of pollutants with oxidizing species produced from such media by the irradiation. When irradiated to air, various oxidizing species such as OH radicals, O atoms, and O_3 are produced from air components (N_2, O_2, and H_2O) through their ionization and dissociation (Mätzing, 1991). Among these species, OH radicals can oxidize gaseous pollutants such as VOCs and NO_x/SO_2 in air. However, most of the O atoms rapidly react with 21 vol% O_2 in air and produce O_3 with the assistance of a third body, M ($=N_2/O_2$). The resulting O_3 can hardly oxidize gaseous VOCs in the gas phase within a few seconds because of its lower reactivity than that of OH radicals (Atkinson et al., 1982). If the O_3 remaining in the irradiated VOCs/air mixtures can be utilized for the oxidation of VOCs or their irradiation byproducts, the absorbed dose of irradiation required for purification of the VOC/air mixture will be reduced.

In the water phase, O_3 has been known as strong and active oxidizing species for oxidation of organic contaminants. The synergetic effect has been reported for implementation of O_3 to radiation-induced degradation of pollutants in water because of the attack of active species from radiolysis of water and that of injected O_3 and its originated radical anions (Getoff, 2002; Popov and Getoff, 2006). The degradation pathway of organic pollutants has been clarified (Getoff, 1996).

On the other hand, in the gas phase, a promising method for the activation of inactive O_3 seems to be the application of O_3 decomposition catalysts to irradiated VOCs/air mixtures. The oxidation of VOCs at concentrations of a few thousand ppmv by exposing both VOCs/air mixtures and injected O_3 to O_3 decomposition catalysts at temperatures in the range of 298–723 K has been studied (Li and Oyama, 1996, 1997; Naydenov and Mehandjiev, 1993; Ragaini et al., 1993; Gervasini et al., 1994). The oxidation

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doi:10.1016/j.radphyschem.2007.09.008

of VOCs is initiated through the reaction of the active oxygen, such as O atoms, O^-, O_2^-, and O_3 transients, produced by the O_3 decomposition on the surface of the catalysts. Catalysts for both O_3 decomposition and VOC oxidation include MnO_2, MgO, MoO, and Co_3O_4. Manganese dioxide is the most active O_3 decomposition catalyst among the transition metal oxides (Dhandapani and Oyama, 1997).

The aim of the present paper concerns the EB-induced oxidation of xylene occurring as an air pollutant at painting factories in Japan. The experiments embrace the application of MnO_2 to an irradiated xylene/air mixture containing remaining O_3 in the frame of EB treatment of polluted air.

2. Experimental

The experimental setup for the preparation of sample gases, the EB irradiation of them, the catalytic process, and the analysis of the irradiated them with and without the catalytic process is described in the following sections.

2.1. MnO_2

Manganese dioxide (obtained from Mitsui Mining and Smelting Co., Ltd.) containing Mn and Cu contents by 52 ± 5 and 3 wt%, respectively, was used as an O_3 decomposition catalyst. MnO_2 is in the form of pellets (diameter, 4 mm; length, 4–10 mm). The average surface area of the MnO_2 pellet was measured to be 205.6 m^2/g by an automatic surface area analyzer (Mountech Co., Ltd., Macsorb HM Model-1201) using a dynamic Brunauer–Emmet–Teller (BET) method (Brunauer et al., 1938).

2.2. EB irradiation of xylene/air mixture

Air containing 100 ppmv *o*-xylene ($C_6H_4(CH_3)_2$) and 1.0×10^4 ppmv water vapor, hereafter referred to as the xylene/air mixture, was prepared as a sample gas. The concentration of xylene in the gas mixture was evaluated by a gas chromatograph (Shimadzu Co. Ltd., GC-8A) (GC) equipped with a flame ionization detector (FID). Air containing 1.0×10^4 ppmv water vapor, hereafter referred to as air, was also prepared for use as an experimental reference.

A compact EB generator with a maximum accelerating voltage of 55 kV and maximum current of 0.5 mA (Hakoda et al., 2006) was used as a radiation source for irradiating the air and xylene/air mixture as shown in Fig. 1. The xylene/air mixture and air were introduced into the irradiation cup at a flow rate of 5.0 L/min and irradiated with an EB of 53 keV. The temperatures of air and xylene/air mixture were maintained at 298 K during irradiation by the circulation of cooling water outside the cup. The average absorbed dose in the gas sample was estimated from the concentration of O_3, which is produced by the irradiation of pure O_2 gas at a flow rate of 5.0 L/min at 298 K, using the G value of 0.62 μmol/J for the generation of O_3 (Namba et al., 1989).

Xylene in air was oxidized into gaseous and particulate byproducts besides CO_2 and CO under EB irradiation (Hakoda et al., 2006). An irradiated xylene/air mixture containing no particulate byproducts was also prepared by removing 98 wt% (carbon concentration) of particulate byproducts from the gas phase by performing filtration using quartz fibers. This was done to examine the chemical form (gaseous and particulate forms) of the byproducts, which are oxidized into CO_x through the catalytic process.

2.3. Catalytic processing of irradiated air and xylene/air mixture

The MnO_2 pellets with a total weight of 3.1 and 15.5 g in a quartz cylinder (i.d., 23 mm; length, 140 mm) were placed in an oven and maintained at a constant temperature. The MnO_2 pellets weighing 3.1 and 15.5 g can decompose 50% and 100%, respectively, of 150 ppmv O_3 in air at room temperature; this O_3 is generated by an UV-type O_3 generator. This MnO_2 pellet layer was placed downstream of the irradiation cup as shown in Fig. 1. The time taken for the irradiated air and xylene/air mixture (5.0 L/min) to travel from the irradiation cup to the upper surface of the MnO_2 layer was 0.20 s. The irradiated air and xylene/air mixture were preheated to different temperatures, 303, 353,

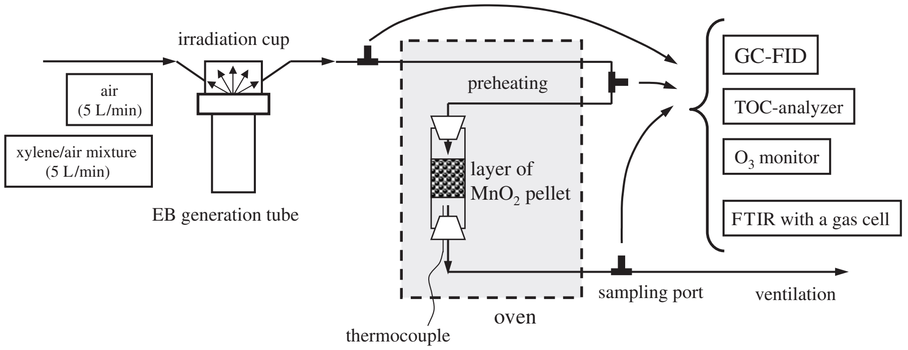

Fig. 1. Apparatus for electron beam irradiation of air and xylene/air mixture, their catalytic process using MnO_2, and analysis of these gases before and after the catalytic process.