

Role of metals loaded on a TiO₂ surface in the oxidation of xylene in air using an electron beam irradiation/catalytic process

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ARTICLE INFO

Article history:

Received 8 October 2008

Received in revised form 20 January 2009

Accepted 21 January 2009

Available online 29 January 2009

Keywords:

Non-thermal plasma

TiO₂

Metal-loaded TiO₂

Electron beam

Xylene

ABSTRACT

Catalytic oxidation of xylene in air was performed under electron beam (EB) irradiation using pure TiO₂ as well as TiO₂ loaded with Ag, Pt, Au, or Mn to clarify the role of loaded metal in the enhancement of oxidation of xylene and its irradiation byproducts to CO₂ in EB-induced non-thermal plasmas. EB irradiation experiments were performed with the catalyst bed placed in both irradiated and non-irradiated spaces. The highest conversion percentage of decomposed xylene to CO₂ was obtained by irradiation/catalytic oxidation using an Ag/TiO₂ bed placed in a non-irradiated space. The greater enhancement of CO₂ production on an Ag/TiO₂ pellet surface compared to that on other metal-loaded TiO₂ pellet surfaces was due to the synergetic effect of strong adsorption of the byproducts on the Ag loaded on TiO₂ and production of active oxygen from decomposition of O₃ in the presence of Ag.

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1. Introduction

Many studies have investigated the degradation of volatile organic compounds (VOCs) using non-thermal plasmas (NTPs) generated by corona discharge [1–3]. Various combinations of such NTPs with in situ heterogeneous catalysts have been tested to improve oxidation of byproducts, the selectivity of CO₂ production, and the energy efficiencies of the NTP process [4–8]. In particular, TiO₂ and metal-loaded TiO₂ such as Ag/TiO₂ and Pt/TiO₂ have been tested as such catalysts [9–12]. The efficiencies of VOC decomposition and the selectivity of CO₂ production were enhanced by loading Ag on the surface of the TiO₂ pellets [11,12]. In our previous studies, we examined the oxidation of xylene using TiO₂ and Ag/TiO₂ placed in or downstream of electron-beam (EB)-induced NTPs [13,14]. The higher conversion yield of the byproducts to CO₂ obtained using this combination is similar to that achieved by a corona-discharge NTP/catalytic process. Furthermore, the CO₂ conversion yield increased with the content of Ag loaded on the surfaces of the TiO₂ pellets. Thus, the presence of loaded metals in the NTP/catalytic process strongly influenced the catalytic oxidation of organics on the catalyst pellets. However, the mechanism of this oxidation enhancement is not clear.

In this study, we examined the role of metals loaded on the TiO₂ surface based on quantitative analysis of catalytic oxidation using TiO₂ loaded with Ag, Pt, Au, or Mn, placed in or downstream of EB-induced NTPs.

2. Experimental

2.1. Catalysts and a non-catalyst

For a metal-loaded TiO₂ (hereafter M/TiO₂) catalyst, we used titanium (IV) oxide loaded with various metals, each at a 5 wt% content. The metals used were Ag, Pt, and Au, which displayed larger electron affinities, and Mn, which had significant O₃ decomposition ability. Spherical TiO₂ pellets (diameters 3.3 ± 0.2 mm, 100% anatase form) were purchased from Sakai Chemical Industry Co. Ltd. The TiO₂ pellets were impregnated with solutions of AgNO₃, H₂PtCl₆·(H₂O)₆, H₂AuCl₄·(H₂O)₄, or MnCl₂·(H₂O)₄ (chemical purity higher than 98 wt%) to create Ag/TiO₂, Pt/TiO₂, Au/TiO₂, or Mn/TiO₂ pellets, respectively. The M/TiO₂ pellets were prepared by calcination of the resulting salt-loaded TiO₂ in carbon-free air at a temperature of 773 K for 10 h. The chemical form of loaded Ag and Mn appears to be mainly Ag₂O and MnO₂. The average surface area of the TiO₂ and M/TiO₂ pellets was measured by a dynamic BET method [15] with an automatic surface area analyzer (Mountech Co., Ltd., Macsorb^{TR} HM Model-1201). The results are summarized in Table 1.

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Table 1Average specific surface area of TiO₂ and metal-loaded TiO₂ pellets.

Catalysts	Specific surface area (m ² /g)
TiO ₂	68
5 wt% Ag/TiO ₂	60
5 wt% Pt/TiO ₂	59
5 wt% Au/TiO ₂	55
5 wt% Mn/TiO ₂	47

To reduce the volume of the irradiated space, we used spherical stainless steel pellets (SUS-304, hereafter SUS pellets) with a diameter of 3.0 mm as dummy pellets. The surfaces of the SUS pellets were polished to a mirror finish, and their average surface area was less than the minimum value detectable by the BET method ($\sim 10^{-2}$ m²/g).

2.2. EB irradiation/catalytic process using catalysts

As shown in Fig. 1(A), electrons accelerated to a kinetic energy of 53 keV in the vacuum EB generation tube of an EB generator entered the atmospheric sample gases via an irradiation window. Their deposited energy per unit of air thickness decreased linearly with the distance from the irradiation window. For irradiation of a sample gas in the absence of a catalyst, a stainless steel vessel was connected to the EB generation tube in order to cover the irradiation window, as shown in Fig. 1(A). The sample gas was air containing 50 ppmv *o*-xylene (C₆H₄(CH₃)₂) and 1 v% water vapor with a flow rate of 10.0 L/min (298 K and 0.10 MPa). We introduced this sample gas into the irradiation vessel after preheating at 373 K (flow rate: 12.5 L/min). As shown in Fig. 1(B) and (C), a catalyst bed with a volume of 12.2 cm³ (thickness: 8 mm) was placed at various distances from the irradiation window. This distance, measured as the linear distance between the irradiation window and the upper face of the catalyst bed, was fixed at 7, 17, 27, and 47 mm, respectively. Preliminary tests for EB irradiation of the sample gas using catalysts demonstrated that the catalytic activity for the oxidation of xylene to CO₂ decreased gradually at room temperature because the surface of the catalysts was covered with co-existent water and semi-volatile irradiation products of xylene and air components. This catalytic-oxidation activity was maintained for several hours by heating the catalysts to temperatures higher than 373 K. On the basis of these preliminary tests, in the present study, the temperature of the sample gas and the catalyst bed was maintained at 373 ± 3 K during irradiation. Thermal decomposition of xylene was not observed on the inner wall of the irradiation vessel and the catalyst pellet surface at this temperature. The gas hourly space velocity for both beds was calculated to be 6.15 × 10⁴ h⁻¹ at 373 K.

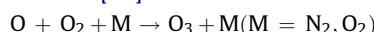
The average absorbed dose in the sample gas at 373 K was calculated from the concentration of O₃ produced by the

irradiation of pure O₂ gas introduced at a flow rate of 10.0 L/min at 298 K, as per previous studies [13,16]. In the cases where a catalyst bed is placed in an irradiated space, the kinetic energy of the incident electrons is delivered to both the sample gas and the catalyst bed (two media). When we placed the catalyst bed at distances greater than 27 mm (i.e., in a non-irradiated space), most of the electron energy was delivered to the sample gas (one medium).

The sample gas was analyzed using a Fourier transform infrared (FTIR) spectrometer (PerkinElmer, Spectrum One) equipped with a gas cell with an optical length of 4.8 m and a mercury cadmium telluride detector. We determined the concentrations of xylene, CO₂, CO, and O₃ in the sample gas downstream of the irradiation vessel using the relevant absorbance peaks in the FTIR spectra.

3. Oxidation scheme of xylene in air under EB irradiation

When ambient air is irradiated with EB, various oxidizing species such as OH radicals, O atoms, and O₃ are produced from air components through ionization and dissociation [17,18]. Most O atoms react rapidly with O₂ and produce O₃ through the following reaction [19]:



In general, the oxidation of organics by O₃ will be negligible compared to that by OH radicals and O atoms because of the lower reaction rate constants of the former reaction. Accordingly, OH radicals play an important role in initiating the oxidation of gaseous organics such as xylene in air. In an EB-irradiation space, xylene is attacked by OH radicals and changed into organic acids and aldehydes as irradiation byproducts. These irradiation byproducts are oxidized into CO₂ and CO in the EB-irradiated gas phase by OH radical attack in the irradiation space.

4. Results and discussion

Our previous study using Ag/TiO₂ suggested that Ag loaded on TiO₂ pellets produced active oxygen from O₃ decomposition [14]. Other metals that are loaded on the TiO₂ pellets also appear to have the ability to produce such active oxygen. Prior to the application of M/TiO₂ catalysts to EB irradiation, we examined the decomposition of O₃ in irradiated air (without any xylene). Subsequently, the oxidation of xylene and its irradiation byproducts using M/TiO₂ catalysts was studied along with the results for TiO₂.

4.1. Decomposition of EB-induced O₃ using TiO₂ and M/TiO₂

We detected ozone at a concentration of 63 ppmv in 0.17-mA-irradiated air at 373 K (without xylene), corresponding to an average dose of 10 kGy. The decomposition of O₃ in this gas was examined using a catalyst bed placed at a distance of 27 mm (in a

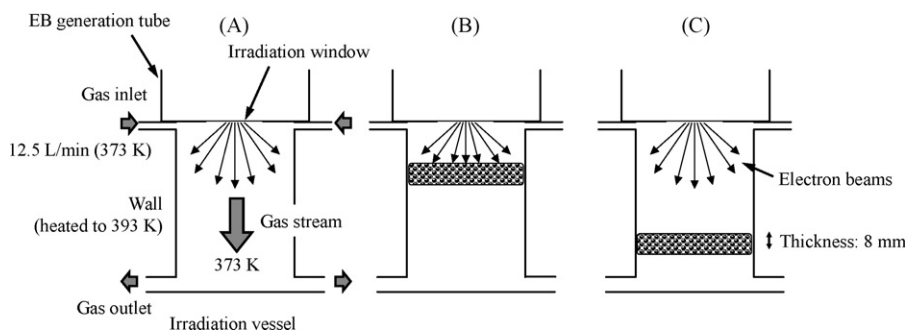


Fig. 1. Electron beam irradiation of a sample gas with and without a catalyst bed: in the absence of the catalyst (A) and in the presence of a catalyst bed whose upper face was placed at distance of 7 mm (B) and 47 mm (C) from the irradiation window of the EB generator.

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