



Catalytic properties of copper-manganese mixed oxides supported on SiO₂ for benzene oxidation with ozone



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ABSTRACT

Catalytic oxidation of benzene was carried out over SiO₂-supported manganese oxides and manganese-containing mixed oxides at 333–373 K. The catalysts were prepared by impregnation methods from metal nitrate precursor and calcined at 673–873 K. The addition of Cu, Ni, and Fe to Mn oxides suppressed the decrease of benzene oxidation activity and improved the steady state activity for benzene oxidation at 343 K, whereas the addition of Co decreased the activity. The highest activity was obtained for Cu-Mn/SiO₂ catalysts with the molar ratio of Cu-Mn 1:1. XRD studies revealed that Cu₃Mn₃O₈ and CuMn₂O₄ spinel phases were formed in the Cu-Mn/SiO₂ catalysts. The catalytic activity of Cu-Mn mixed oxides increased with the increase in their calcination temperature, in accordance with the increase in the spinel type Cu-Mn mixed oxide phases.

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1. Introduction

Catalytic oxidation process by using ozone is one of the effective processes for the abatement of air polluted with volatile organic compounds (VOCs) [1]. The process has the advantages over catalytic combustion process in that the reaction proceeds at relatively lower temperatures and the apparent activation energy decreases by the presence of ozone. The process is effective for VOC removal at low concentration region, whereas the catalytic combustion process is effective for VOC removal at high concentration levels. In addition, inexpensive metal oxides such as manganese oxides are effective active species and noble metals are unnecessary for the reaction [2–6].

Our precedent studies have revealed that supported manganese oxides exhibit higher activity for catalytic oxidation of benzene and cyclohexane than the oxides of other transition metals in the first transition series. Catalytic properties of manganese oxides for catalytic ozonation process have been also reported [7–18], and the factors for obtaining highly active supported manganese oxide catalysts were investigated. The reaction rate does not depend on the kinds of catalyst support and but on the catalyst surface area. On the other hand, the decomposition ratio of ozone to VOC, the character of the ozone utilization, was the lowest for SiO₂-supported manganese oxides among the supported manganese

oxide tested in the reaction. Thus, SiO₂-supported manganese oxides with high surface area are good candidates for catalytic ozonation from the standpoint of activity and the efficiency for ozone utilization.

SiO₂-supported manganese oxides were generally prepared by impregnation technique using two kinds of precursors, manganese nitrate and manganese acetate. The dispersion and the structure of manganese oxides on supporting materials can be controlled by changing these precursors [11,19,20]. Highly dispersed manganese oxides can be deposited on SiO₂ by using manganese acetate [11,20], whereas aggregated manganese oxides are formed on SiO₂ when manganese nitrate was used for the preparation [11]. Our precedent studies have shown that both highly dispersed and aggregated manganese oxide species act as the active sites for benzene oxidation with ozone [15].

In this study, we investigated the catalytic properties of SiO₂-supported manganese oxides and manganese-containing mixed oxides prepared by impregnation methods using manganese nitrate precursor and factors controlling their catalytic properties. The addition of transition metals, such as Cu, to SiO₂-supported manganese oxides is effective for improving their catalytic properties. Cu-Mn mixed metal oxides supported on SiO₂ calcined at 873 K especially exhibited higher activities for catalytic oxidation of benzene with ozone than the SiO₂-supported manganese oxide catalysts under briefly heated condition (343 K). The effects of catalyst composition and preparation conditions of the catalysts on their catalytic properties were investigated in detail.

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2. Experimental

2.1. Catalyst preparation

SiO₂-supported manganese oxides and manganese-containing mixed oxides were prepared by impregnation of SiO₂ (Fuji Silisia Q-6) with metal nitrates, Mn(NO₃)₂, Fe(NO₃)₂, Co(NO₃)₂, Ni(NO₃)₂ and Cu(NO₃)₂ (Wako Pure Chem. Ind.). The supported catalysts were dried and calcined at 673–873 K in air. The total amount of metal on SiO₂ was 3.64 mmol per 1.0 g of SiO₂, which corresponds to 20 wt% loading for Mn/SiO₂.

2.2. Catalyst characterization

The surface area of a sample was determined by BET method from N₂ adsorption isotherm at 77 K with Belsorp mini (BEL Japan Co. Ltd.). X-Ray diffraction patterns were obtained by using JEOL RINT2200 diffractometer using CuK α line. FTIR spectra of the catalysts were obtained by using Jasco FTIR 480 Plus spectrometer equipped with a diffuse reflectance accessory.

2.3. Catalytic oxidation with ozone

Catalytic oxidation of benzene was carried out with a fixed bed flow reactor. Details of the reaction system for benzene oxidation were reported in the previous papers [14–18]. Reaction gases for the catalytic reactions were prepared by benzene in N₂, N₂ (>99.9995%, total hydrocarbon < 1 ppm) and O₂ (>99.9995%, total hydrocarbon < 1 ppm) in cylinders. Ozone was synthesized from pure O₂ by using an ozone generator. Prior to the benzene oxidation with ozone, catalyst was heated at 573 K in O₂ flow for 1 h, and then thermostated at a reaction temperature (343 K) with a water bath or a heating apparatus. Benzene concentration 150 ppm, ozone 2250 ppm, O₂ 10%, gas flow rate 500 ml min⁻¹ (N₂: 300 ml min⁻¹, C₆H₆: 150 ml min⁻¹, O₂: 50 ml min⁻¹), catalyst weight 0.10 g. Gas sample was analyzed by using an FTIR spectrometer (PerkinElmer Spectrum One) equipped with a 2.4 m optical length gas cell (volume 100 ml). In this system, homogeneous gaseous reaction of benzene with ozone can be neglected. The reaction rate for benzene oxidation was determined under the condition where conversions were linear to the W/F values.

TPO measurements were carried out for the catalysts that had been used for benzene oxidation with ozone using the flow reactor described above. After catalytic ozonation of benzene was carried out, the reaction gas was changed to N₂-O₂ with the flow rate of 500 ml min⁻¹. Then, the used catalyst was heated at a rate of 10 K min⁻¹ to 773 K. The products in the effluent gases from the reactor were analyzed by using the FTIR spectrometer with the optical length gas cell.

3. Results and discussion

3.1. Catalytic properties of manganese oxides on SiO₂

It has been reported that the structure of manganese oxides on supporting materials is affected by the precursor complex when they are deposited by conventional impregnation technique [19,20]. The use of manganese nitrate with Al₂O₃ [14] and SiO₂ [20] resulted in aggregated crystalline phases of manganese oxides. Fig. 1 shows the XRD patterns of SiO₂-supported manganese oxides (Mn/SiO₂) catalysts prepared by impregnation technique using metal nitrate precursors and calcined at 673–873 K (Fig. 1(a)). Manganese oxide phase MnO₂ was observed for the Mn/SiO₂ catalyst calcined at 673 K. The oxides transformed to Mn₂O₃ by calcination at higher temperature: the mixture of MnO₂ and Mn₂O₃ was

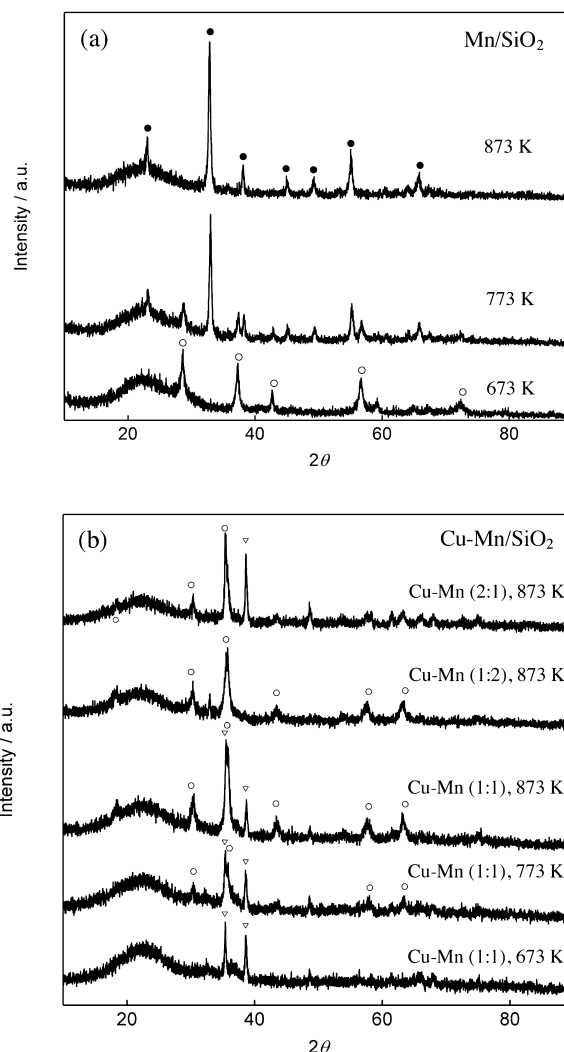


Fig. 1. XRD patterns of SiO₂ supported catalysts. (a) Mn/SiO₂; (○) and (●) refer to the phases of MnO₂ and Mn₂O₃, respectively. (b) Cu-Mn/SiO₂; (▽) and (○) refer to the phases of CuO and Cu₃Mn₃O₈, respectively.

formed at 773 K and Mn₂O₃ was only observed at 873 K. Catalyst surface area was independent of the calcination temperature (Table 1).

Catalytic properties of Mn/SiO₂ depended on their calcination temperatures. As shown in Table 1, benzene oxidation rate at steady-state increased with the increase in catalyst calcination temperature. The main products were CO₂ and CO and small amount of formic acid was detected in the reaction. The CO₂/CO ratio was around 2 and was independent of catalyst calcination temperature. The ozone/benzene ratio was ca 9.0 and was not also affected by the calcination temperature. These findings indicate that the formation of aggregated Mn₂O₃ exhibited higher activity for benzene oxidation with ozone than MnO₂ on SiO₂, whereas product distribution and efficiency for ozone utilization were not affected by the manganese oxide structures.

3.2. Catalytic activities of Mn-containing mixed oxides on SiO₂

Fig. 2 shows the time course profiles for benzene oxidation with ozone over the Mn/SiO₂ and Mn-containing mixed oxide catalysts calcined at 873 K. With the Mn/SiO₂ catalyst, benzene conversion decreased with time on stream. The decrease in benzene conversion was ascribed to the build-up of byproduct compounds on the catalyst, which covered the catalysts surface sites and inhibited

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