Structural analysis of manganese oxides supported on SiO$_2$ for benzene oxidation with ozone

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ABSTRACT

Catalytic oxidation of benzene with ozone was carried out over SiO$_2$-supported manganese oxides (Mn/SiO$_2$) prepared by impregnation methods using two kinds of manganese precursors, manganese nitrate and acetate. The structure of manganese oxides were characterized by X-ray diffraction and X-ray absorption measurements and effects of the manganese oxide structures on their catalytic properties were investigated. EXAFS studies revealed that by using manganese nitrate precursor in catalyst preparation, aggregated manganese oxides Mn$_2$O$_3$ were formed, whereas highly dispersed manganese oxides were formed when manganese acetate precursor was used. In both cases, the structures were not strongly affected by the manganese loading levels. The average oxidation state estimated form the absorption edge in the XANES region was also almost unchanged by changing the manganese loading for both catalysts. The catalytic activities of Mn/SiO$_2$ for benzene oxidation with ozone at 343 K were much higher for the catalysts prepared from manganese acetate precursors than those prepared from manganese nitrate precursor at any given manganese loading levels, indicating that highly dispersed manganese oxides on SiO$_2$ exhibited much higher activities for the reaction than the aggregated manganese oxides on SiO$_2$. The product distribution and the efficiency for ozone utilization were not so much affected by the manganese oxide structures.

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1. Introduction

Manganese is one of the most frequently used constituents in catalytic materials, and due to its redox abilities, manganese-based catalysts are effective for the various kinds of reactions including decomposition of hydrogen peroxide [1], partial oxidation with hydrogen peroxide [2], oxidation of CO [3–5], methane [6], aromatic compounds [7], aqueous phenol in aqueous solution [8], NO–CO reaction [9], and chemical-looping combustion processes [10]. Catalytic properties of manganese oxides generally depend on their structures, oxidation states and surface areas. To improve the catalytic properties of manganese oxides, therefore, these properties should be controlled. The structures of manganese oxides are generally controlled by changing the preparation conditions, whereas they are supported on supporting materials with high surface area for improving their surface areas.

Manganese oxides have been used for catalytic oxidation with ozone (catalytic ozonation) for control of volatile organic compounds in gas phase [13–20]. We have investigated the catalytic

properties of supported manganese oxides for catalytic ozonation processes [21–25] and reported that the supported manganese oxides are effective for catalytic oxidation of aromatic compounds and alkanes using ozone at relatively low temperature and especially at their low concentration levels. Catalytic properties of supported manganese oxides strongly depended on the supporting materials. The rate for benzene oxidation is linearly correlated with catalyst surface area and did not depend on the kinds of supporting materials, whereas the ratio of the amount of ozone decomposed to that of benzene oxidized was the lowest for SiO$_2$-supported manganese oxides [23]. Thus, SiO$_2$-supported manganese oxides with high surface area are effective for the reaction from the standpoint of activity and the efficiency for ozone utilization.

In the case of supported manganese oxide catalysts, the structure of manganese oxides can be controlled by changing the preparation methods. When the supported manganese oxides were prepared by a conventional impregnation technique, the manganese oxide structures strongly depended on precursor materials and manganese oxide loadings [24,26–28]. The use of manganese nitrate for the preparation of γ-Al$_2$O$_3$-supported manganese oxides gave the aggregated manganese oxides, whereas the use of manganese acetate gave highly-dispersed manganese oxides at low loading levels and aggregated manganese oxides at high loading

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levels. We also investigated the catalytic properties of γ-Al$_2$O$_3$-supported manganese oxides for benzene oxidation with ozone and clarified that both the highly-dispersed Mn oxides and the aggregated manganese oxides were the active sites for benzene oxidation with ozone.

In this study, we prepared SiO$_2$-supported manganese oxides (Mn/SiO$_2$) by impregnation method using manganese nitrate and acetate precursors to investigate the effect of precursor and manganese loading on the structures of manganese oxides with XRD, EXAFS, and XANES studies. By using a SiO$_2$ support with high surface area, two kinds of manganese oxide, aggregated Mn$_2$O$_3$ species and highly dispersed manganese oxides were separately prepared on SiO$_2$ support with manganese nitrate and acetate precursors. We carried out catalytic ozonation of benzene in gas phase with the two kinds of Mn/SiO$_2$ catalysts and compared the catalytic properties in terms of activity, product distribution, and efficiency for ozone utilization.

2. Experimental

2.1. Catalyst preparation

SiO$_2$-supported manganese oxides were prepared by impregnation of the SiO$_2$ (Fuji Silysia Chem. Ltd. CariACT Q-6) with aqueous solutions containing Mn complex precursors, Mn(CH$_3$COO)$_2$·4H$_2$O (Wako Pure Chemical, Japan, >99.9%) or Mn(NO$_3$)$_2$·xH$_2$O (Wako Pure Chemical, >99%). The catalyst samples were then dried at 373 K for 24 h and calcined at 873 K for 5 h in air. BET surface area of the SiO$_2$ support was 472 m^2 g^{-1} after calcination at 873 K. Manganese oxides, MnO, Mn$_2$O$_3$, Mn$_3$O$_4$, and MnO$_2$ were obtained from Sigma-Aldrich Co. LLC. and used as reference samples.

2.2. Catalyst characterization

XRD patterns were taken with a Rigaku XRD diffractometer RINT-2200 using Cu-$K\alpha$ radiation. The X-ray tube was operated at 30 kV and 100 mA. Surface areas of SiO$_2$-supported manganese oxides were determined by BET method from N$_2$ adsorption isotherm at 77 K, which were measured by BELSorp-mini series (BEL Japan Inc.).

EXAFS spectra were taken at the Photon Factory beam line BL-7C in High Energy Accelerator Research Organization (KEK-PF). Catalyst samples were pressed into thin self-supporting disks with 10 mmϕ in diameter. Data reduction of experimental absorption spectra was carried out with a REX2000 software according to the method recommended by the Standards and Criteria Committee of the International XAFS Society [29]. The EXAFS oscillations, $\chi(k)$, were extracted from the data using a smoothing spline and normalized to the edge height. The k^3-weighted EXAFS data ($k^3\chi(k)$) were Fourier transformed to R-space over 3.0–12.0 Å^{-1}. To obtain the coordination numbers (CN), bond distances (R), Debye–Waller factor (σ^2), and energy shift (ΔE), the inverse Fourier transformation to k-space was employed and the experimental data were fitted to the theoretical backscattering amplitude and phase shift functions calculated by the program FEFF8 [30]. For the curve-fitting, a maximum number of free parameters did not exceed the number n, which was estimated according to the Nyquist theorem [31]: $n = (2\Delta k \Delta r/p) + 1$, where Δk and Δr, are the k (where k is the wave vector) and r (where r is the distance from the absorber atom) ranges, respectively. The validity of the theoretical parameters was checked by running the MnO, Mn$_3$O$_4$, Mn$_2$O$_3$ and MnO$_2$ reference samples.

XANES spectra were obtained after background-corrected and normalized spectra were transformed to the first derivatives. The
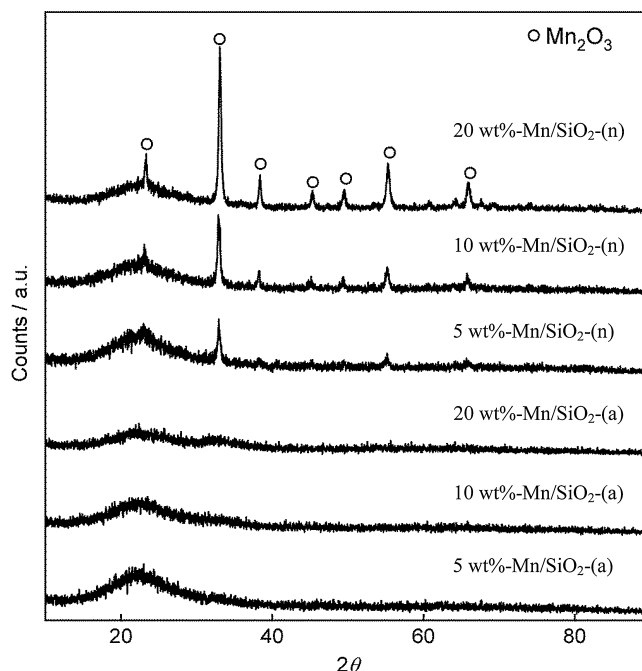

Fig. 1. XRD patterns of Mn/SiO$_2$ catalysts.

absorption edge was estimated from the inflection points of the spectra [25].

2.3. Catalytic ozonation of benzene

Catalytic ozonation of benzene in gas phase was carried out with a fixed bed flow reactor. Details of the reaction systems are described elsewhere [21]. Ozone was synthesized from O$_2$ by a silent discharge ozone generator. Prior to the catalytic reaction, the catalyst sample in a Pyrex glass reactor was heated at 573 K in O$_2$ flow. Then, the catalyst was cooled and thermostated at 343 K. Gas samples were analyzed with a Fourier-transform infrared spectrophotometer (Perkin-Elmer Spectrum One) equipped with a 2.4 m optical length gas cell (volume 100 mL). The catalytic reactions were conducted under the condition where homogeneous benzene oxidation with in gas phase can be neglected.

3. Results and discussion

3.1. Structure of manganese oxides on SiO$_2$ supports

The structure and dispersion of manganese oxides on supporting materials significantly depended on the preparation methods, precursor compounds, and the kinds of supporting materials. When SiO$_2$-supported manganese oxides were prepared by impregnation technique using manganese acetate, manganese oxides can be deposited on SiO$_2$ with high dispersion. On the other hand, manganese nitrate was used for the catalyst preparation, aggregated manganese oxides were mainly formed on SiO$_2$. Fig. 1 shows the XRD patterns of SiO$_2$-supported manganese oxides prepared from manganese nitrate (denoted by Mn/SiO$_2$-(n)) and those prepared from manganese acetate (MnO$_x$/SiO$_2$-(a)) with various manganese loading. The textural properties of MnO$_x$/SiO$_2$-(n) and MnO$_x$/SiO$_2$-(a) catalysts are summarized in Table 1. For Mn/SiO$_2$-(n) catalysts, the diffraction patterns of crystalline Mn$_2$O$_3$ phases were observed along with broadening peak of SiO$_2$ support at $\theta = 22°$. No other crystalline phases, such as MnO, MnO$_2$ and Mn$_3$O$_4$ were observed, suggesting that Mn$_2$O$_3$ phases were mainly formed in the Mn/SiO$_2$-(n) catalysts. The peak intensities for Mn$_2$O$_3$