

Investigation of active sites on manganese supported on zeolite Y for catalytic oxidation with ozone

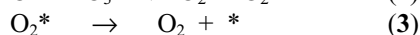
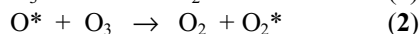
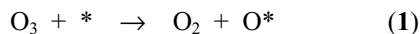
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Introduction

Manganese oxide catalysts are useful for ozone decomposition and catalytic oxidation of VOC with ozone in gas streams. Oyama and his co-workers have reported that the mechanism for O₃ decomposition on manganese oxide supported on γ -Al₂O₃ (denoted by MnOx/Al₂O₃), and that the reaction proceeds through two irreversible steps, the adsorption of ozone on the catalyst surface and the desorption of molecular oxygen (eqs. (1)-(3)), where * denotes the surface site on the catalyst [1-3].



Thus, Mn acts as the catalytic active site for oxidation reaction by forming oxygen species active for VOC oxidation. These reactions can be applied to the oxidation of various types of organic compounds [4, 5].

Recently, we found that Mn ion-exchanged zeolite Y (denoted by MnY) showed higher activity for the catalytic oxidation of benzene with ozone compared with supported manganese oxide catalysts, MnOx/Al₂O₃ and MnOx/SiO₂. However, no information has been obtained on the catalytic active sites for the reaction. We herein report the X-ray absorption fine structure (XAFS) spectroscopic studies to investigate the Mn structures supported on Y-type zeolites.

Experimental

XAFS measurements were carried out on the Photon Factory beam line BL-7C and BL-9A. MnY was prepared by a conventional ion-exchange method from an aqueous solution containing Mn-acetates and NaY (Zeolyst, Si/Al= 5.1). Catalyst samples were dried at 383 K and pressed into thin self-supporting wafers with 20 mm ϕ in diameter and set in an in situ cell with polyimide film (Du Pont-Toray Co., Ltd. Kapton 200H), which was connected to the flow-type reaction system. XAFS spectra were recorded at a temperature of 296 K in N₂ flow. Data reduction was carried out by using Rigaku REX-2000.

Results and Discussion

Figure 1 shows the Mn-K edge EXAFS Fourier transforms for the MnY catalyst before and after heat treatment at 723 K in N₂ flow. Only the peak for Mn-O was observed for the sample before the heat treatment,

indicating that Mn was highly dispersed in the zeolite catalyst. On the other hand, the peak probably ascribed to Mn-Mn contribution appeared after the heat treatment at 723 K, along with the decrease of the peak due to Mn-O contribution. Thus, highly dispersed species are diminished and aggregated species were formed. The EXAFS spectra were unchanged after subsequent heat treatment at 723 K in O₂ flow. This catalyst showed steady-state activity for the oxidation of benzene to COx without the release of organic byproducts under moderate condition (343 K). We recently reported the structural changes of manganese supported on alumina during ozone decomposition [6]. Therefore, further investigation is now in progress to clarify the structures of catalytic active sites on MnY catalyst and their changes for during ozone decomposition.

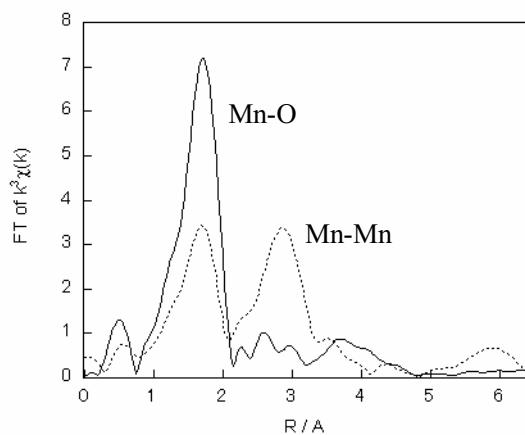


Figure 1 Mn-K edge EXAFS Fourier transforms of MnY catalyst. (solid line) as prepared; (dashed line) after heat treatment at 723 K in N₂ flow.

References

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