

Structural Analysis of Active Sites for Catalytic Ozonation of Benzene on Alumina-supported Manganese Oxides

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Introduction

Manganese oxides have been used for various types of chemical reactions such as oxidation reactions, catalytic combustion of volatile organic compounds (VOCs), nitrous oxide decomposition, selective catalytic reduction of NO with NH₃, and ozone decomposition. They are also effective for the catalytic oxidation of VOCs with ozone (catalytic ozonation) in air. We have reported that the combination of silent discharge reactor and manganese oxide catalysts facilitates the benzene oxidation [1]. Although the mechanism and the structure of active sites for ozone decomposition have been studied [2-4], there is no known relationship between the structures of manganese oxides and the activities for the catalytic ozonation of benzene. In this study, we investigated the structure of Mn-O species on alumina-supported manganese oxides with different Mn loading by EXAFS studies. Our findings provide us the information on the structure of active sites for the catalytic ozonation.

Experimental

Alumina-supported manganese oxides were prepared by the impregnation of γ -Al₂O₃ (Catalysis Society of Japan, JRC ALO-8) with the aqueous solution containing the appropriate amount of Mn(CH₃COO)₂·4H₂O (Wako Pure Chemical Industries, Ltd. >99.9%). Catalyst samples were dried at 383 K and then calcined at 773 K for 3 h in open air. Mn₃O₄ was purchased from Aldrich Chemical Company, Inc. and used as received.

The samples were pressed into 20 mm ϕ self-supporting wafers and loaded into a flow-cell for EXAFS measurements. Mn-K edge EXAFS spectra were collected in a transmission mode at BL-7C.

Results and Discussion

Figure 1 shows the Mn-K edge EXAFS Fourier transforms for the alumina-supported manganese oxides with different Mn loading level. The spectra were obtained after heating in O₂ flow at 723 K for 2 h and then cooled down to the ambient temperature. For the catalyst sample with low loading (2.5 wt%), a peak due to the bond of Mn-O is observed, while no obvious peaks for Mn-Mn bond are observed. The intensity of Mn-Mn increases with increasing the Mn loading, while the peaks for Mn-O are almost unchanged in their intensities. These findings reveal that Mn is highly dispersed on the

alumina support at low loadings and the amounts of the Mn-O-Mn moieties increase with increasing the loading level.

Figure 1 also shows the Fourier-transform of Mn₃O₄. The peak positions of Mn-O and Mn-Mn in the high Mn loading catalysts resemble with those of neat Mn₃O₄. Thus, Mn₃O₄ structures are formed on the catalyst at high loading level. This is consistent with the observations that crystalline Mn₃O₄ was detected for the sample by XRD.

The rate for the catalytic ozonation of benzene did not depend on Mn loading (the data are not shown), although Mn was indispensable to obtain the catalytic activities. It is likely that both the highly-dispersed Mn-O and Mn₃O₄ species are the active sites for the catalytic ozonation.

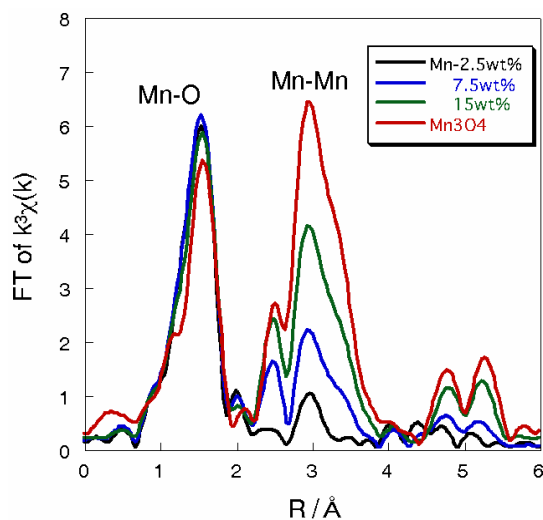


Fig. 1 Fourier transforms of Mn-K edge for alumina-supported manganese oxides and Mn₃O₄ in O₂ flow at room temperature.

References

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