

Structural changes in supported manganese oxides during ozone decomposition

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Introduction

We herein report the X-ray absorption fine structure (XAFS) spectroscopic studies to investigate the structural changes in alumina-supported manganese oxide catalysts during ozone decomposition reactions. The presence of water, ubiquitous constituent in effluent gas stream and formed in VOC decomposition, causes the structural changes in Mn oxide structures during the ozone decomposition. The used catalyst can be regenerated by the heat treatment in an O₂ flow at 723 K.

Experimental

Alumina-supported manganese oxides were prepared by the impregnation of γ -Al₂O₃ (Catalysis Society of Japan, JRC ALO-4, S_{BET} 170 m² g⁻¹) with the aqueous solution containing appropriate amount of Mn(CH₃COO)₂•4H₂O. Catalyst samples were dried at 383 K and then calcined at 773 K for 3 h in air.

XAFS measurements were carried out on the Photon Factory beam line BL-7C. Catalyst samples were 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 a flow-type reaction system. XAFS spectra were recorded at a temperature of 296 K. Reaction gases were prepared by N₂ and O₂ in cylinders by using the sets of thermal mass flow controllers. Ozone was synthesized from O₂ by a silent discharge ozone generator.

Results and discussion

Fig. 1 shows the Mn-K edge XANES spectra of the MnOx/Al₂O₃ catalyst. The absorption edge of XANES spectra was gradually shifted to higher energy with time on stream and a pre-edge peak newly appeared at 6540.6 eV, when ozone was fed into the cell with water vapor (water concentration: 0.55%). No such spectral changes occurred during ozone decomposition when water vapor was absent.

Linear relationship is observed between the energy shift of the Mn-K absorption edge and the oxidation state of the Mn-oxide samples. The absorption edge of MnOx/Al₂O₃ sample is close to that of Mn₃O₄, which consists of Mn^{II} and Mn^{III} species with the average oxidation state of 2.67. The shift of absorption edge to higher energy indicates that Mn oxidation state was changed to higher oxidation state. The appearance of a pre-edge band at 6540.6 eV, which is characteristic of that for MnO₂, implies the formation of Mn^{IV} species. The Mn-K edge EXAFS Fourier transforms of the used sample (line c) is compared with fresh catalyst with (line b) and without water vapor (line a) in Fig. 2. The band at

R=1.5 Å increased in its intensity after the ozone decomposition with water vapor. The increased band was ascribed to the coordination of water to Mn sites.

The coordination of water to Mn site was caused by the bond cleavage of Mn-O-Al bond. Although the bond cleavage of Mn-O-Al was not reflected in XAFS spectra, it is evidence by the fact that Mn ions were extracted from the catalyst surface by washing the used catalyst with water. This finding indicates that Mn was isolated from catalyst support to become a free Mn ion to which water is coordinated. The catalyst color was also changed slightly from brown to brownish pink. Heat treatment in O₂ flow at 723 K gave the same spectrum with that for fresh catalyst sample (line d), indicating that the catalyst was regenerated by the treatment.

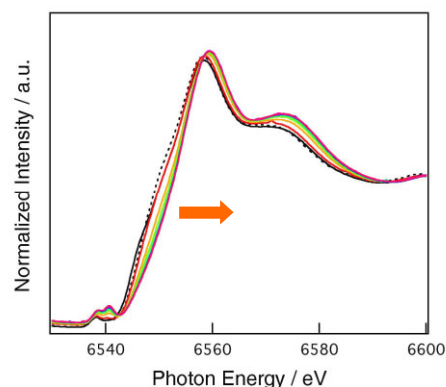


Fig. 1 Changes in Mn-K edge XANES spectra of Mn/Al₂O₃ sample during ozone decomposition.

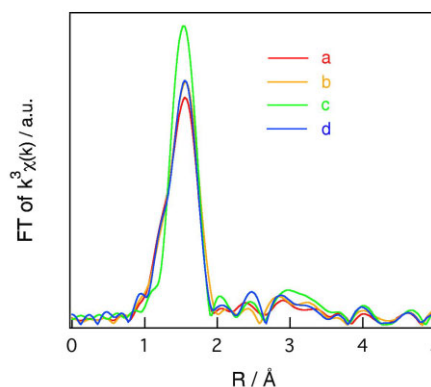


Fig. 2 Mn-K edge EXAFS Fourier transforms of Mn/Al₂O₃ sample.

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