XAFS Characterization of Oxide-supported Mn_4 Clusters for Photocatalytic Oxidation

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[Introduction]

In biological systems, Mn_4 clusters are suggested to be active for photosynthesis and various Mn_4 oxoclusters with different cluster backbones and oxidation states were prepared as models for photosynthesis. However, their catalytic activities were quite low, and there are no reports on effective photocatalysis using their oxo species. We have designed supported Mn_4-cluster catalysts on oxide surfaces by selective reactions with surfaces and several Mn_4 precursors for photocatalytic oxidation. The structures of supported Mn clusters on oxide surfaces were investigated by XAFS.

[Experimental]

(A) $Mn_4O_6(tacn)_4(ClO_4)_4$ (tacn: triazacyclononane), (B) $Mn_4O_4(OOPPh_2)_6$, and (C) $[Mn_4O_2(CH_3COO)_7(bpy)_2](ClO_4)\cdot 3H_2O$ were impregnated with SiO_2 and γ-Al_2O_3 calcined at 773 K for 2 h, followed by the evacuation at 473 K for 2 h. XAFS measurements of the Mn_4 precursor and the supported Mn clusters were performed at a BL01B1 station in a transmission mode at 298 K.

[Results and Discussion]

The three Mn_4 precursors have different backbone structures of their Mn_4O_x cores, (A) adamantane type, (B) cubane type, and (C) butterfly type, whose EXAFS analysis agreed with the structures determined by XRD.

All the Mn_4 complexes maintained their original Mn_4 core structures after the impregnation on both oxide surfaces. Final evacuation at 573 K promoted the elimination of a part of their ligands, monitored by in-situ FT-IR. The adamantane-type Mn_4O_6 complex (A) converted to monomeric Mn species on γ-Al_2O_3 surface at 473 K, whose EXAFS spectra are shown in Fig. 1. On the other hand, Mn-Mn bonds in cubane-type (B) and butterfly-type (C) retained on the oxides, and distorted active Mn_4 complexes were created.

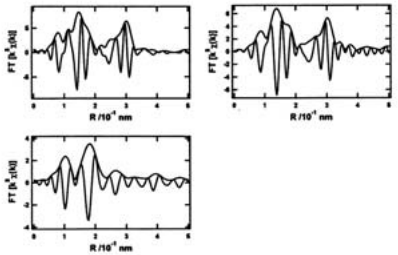

Fig. 1 Mn K-edge EXAFS spectra for (A) (top, left), Al_2O_3-impregnated catalyst of (A) (top, right), and supported catalyst (A) after evacuation at 473 K (bottom).

Quick XAFS Study on Reduction Behavior of Pt supported on TiO_2 at Room Temperature

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Quick XAFS (QXAFS) enables us to analyze dynamic behavior of catalytic active site in a short data-collection time by the continuous energy scanning. Fluorescence measurement, which is needed for diluted samples like supported catalysts, is possible in QXAFS technique, on the contrary to energy-dispersive XAFS spectra (DXAFS) in only use of transmission mode.

In the present study, we investigated the dynamic behavior of nano-sized platinum cluster formation using QXAFS technique. The interface of platinum and metal oxides (support material or semiconductor photocatalyst) was found to be important for the remarkable enhancement of catalytic activity and photocatalytic activity. However, the detailed mechanism about the formation of the platinum nanoclusters on metal oxides surface remains unclear.

Platinum was loaded on TiO_2 (JRC-TIO-4) by an impregnation with an aqueous solution of H_2PtCl_6 at 353 K. The impregnated sample was dried at 353 K and followed by calcination at 773 K in the air. Quick XAFS measurements were performed at BL01B1, SPring–8. The self-supporting wafer of the sample (PtO_2/ TiO_2) was mounted in an in-situ flow cell.

QXAFS measurement for low loaded 1.5 wt% PtO_2/TiO_2 was performed in fluorescence mode. The Si(111) monochromator was moved from 10.3° to 8.9° in 10 min. During 5% H_2 flow, the supported platinum oxide was reduced to platinum nanocluster. The structural change was taking place in the time scale of minutes. Therefore, there was the time delay in a spectrum between the first data and the last data points.

Figures 1 and 2 show QXAFS spectra of highly loaded 5.0 wt% PtO_2/TiO_2 in transmission mode. The Si(111) monochromator was moved from 10.3° to 8.9° in 1 min. Time dependent structural change of platinum oxide to metal cluster was successfully recorded.

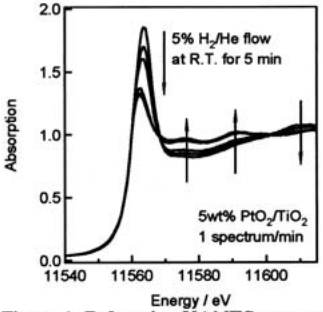

Figure 1. Pt L_3-edge XANES spectra of 5wt% PtO_2/TiO_2 measured in a 5% H_2 flow.

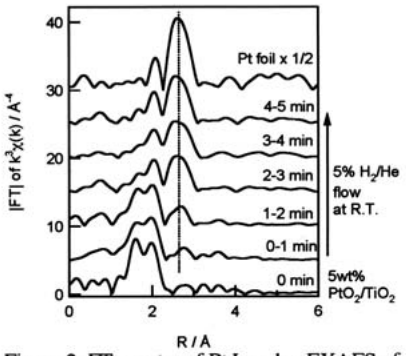

Figure 2. FT spectra of Pt L_3-edge EXAFS of 5wt% PtO_2/TiO_2 measured in a 5% H_2 flow.