

XAFS analysis of tetrahedrally coordinated metal oxides assembled photocatalysts

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Introduction

The transition metal oxides (e.g. Ti⁴⁺-, V⁵⁺-, Cr⁶⁺-oxide) containing silica-based materials such as zeolites and mesoporous silicas show the unique properties as efficient catalysts for various photocatalytic reactions such as the decomposition of NO_x, oxidation of CO as well as partial oxidation of hydrocarbons [1]. Among them, Cr⁶⁺-oxide containing catalyst have attracted much attention due to their visible light sensitivity and fascinating catalytic activities [1,2].

In the present study, tetrahedrally coordinated Ti⁴⁺- and Cr⁶⁺-oxides assembled mesoporous silica was prepared by stepwise chemical vapor deposition (CVD) treatments and characterized by XAFS and other spectroscopic methods.

Experimental

Mesoporous silica (MCM-41) as a support was prepared by a hydrothermal synthesis method using tetramethoxysilane and hexadecyltrimethylammonium bromide as template. CVD treatment was performed using a specially manufactured vacuum line system equipped with titanium tetrachloride (TiCl₄), chromyl chloride (CrO₂Cl₂), H₂O and O₂ reservoir. Ti⁴⁺- and Cr⁶⁺-oxides assembled catalyst and single component anchored catalysts are denoted as Cr-Ti/MCM-41, Cr/MCM-41 and Ti/MCM-41, respectively.

Photocatalytic reactions, i.e. polymerization of ethylene and oxidation of CO, were carried out in a closed system using a quartz reactor under irradiation of UV and visible ($\lambda > 420$ nm) light at 293 K.

XAFS spectra at Ti K-edge and Cr K-edge were measured in the fluorescence mode at 298 K. Before the measurements, samples were degassed at 723 K for 1 h and then sealed within polyethylene film under an argon atmosphere. Obtained data were examined using the analysis program (Rigaku REX2000).

Results and discussions

Figure 1(a-d) shows the X-ray absorption near edge structure (XANES) spectra of Ti/MCM-41, Cr-Ti/MCM-41 and reference samples (titanium isopropoxide (TIP) and TiO₂(anatase)). The XANES spectrum of TIP showed the single pre-edge peak at around 4970 eV, which is attributed to the local structure of titanium atoms in a tetrahedral symmetry. This intense pre-edge peak is a consequence of the 1s to 3d transition. Ti/MCM-41 and Cr-Ti/MCM-41 exhibited a characteristic and intense single pre-edge peak. This peak was quite similar to that of TIP, showing the existence of Ti⁴⁺-oxide moieties with tetrahedral coordination.

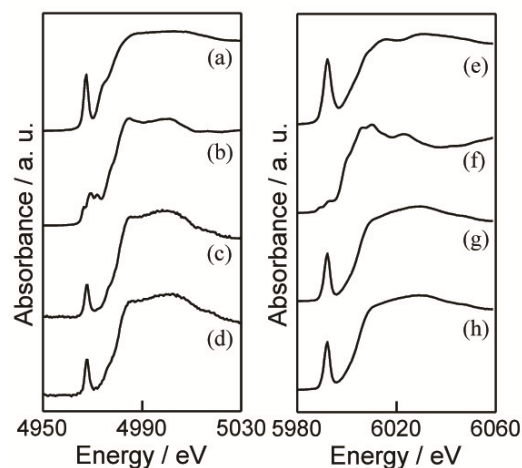


Figure 1. XANES spectra at Ti K-edge (a-d) and Cr K-edge (e-h) of (a) titanium isopropoxide, (b) TiO₂ (anatase), (c) Ti/MCM-41, (d,h) Cr-Ti/MCM-41, (e) CrO₃, (f) Cr₂O₃ and (g) Cr/MCM-41.

As shown in Fig 1 (e-h), XANES spectra of Cr-Ti/MCM-41 and Cr/MCM-41 showed a peak at around 5990 eV assignable to the 1s to 3d transition, which is similar to that of CrO₃ as a reference of tetrahedral Cr⁶⁺-oxide and completely differs from that of Cr₂O₃ as a reference of octahedral Cr³⁺-oxide clusters. The successful assembling of tetrahedrally coordinated Ti⁴⁺- and Cr⁶⁺-oxides on MCM-41 as main species without the formation of aggregated species by stepwise CVD treatments was confirmed from the results of XAFS measurements.

In the photocatalytic reactions, Cr-Ti/MCM-41 exhibited higher efficiency for the photocatalytic polymerization of ethylene as well as the oxidation of CO into CO₂ than those on single component Cr⁶⁺-oxide anchored MCM-41 under UV and visible light. The combination of Ti⁴⁺- and Cr⁶⁺-oxides were effective for enhancement of photocatalytic activities.

References

- [1] H. Yamashita, K. Mori, Chem. Lett., 36, 348 (2007).
- [2] T. Kamegawa, T. Shudo, H. Yamashita, Top. Catal., 53, 555 (2010).

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