9A, 7C/2001G115

XAFS studies on the local structures of visible-light responsive zeolite photocatalysts: Cr-containing mesoporous silica (Cr-HMS)

Hiromi YAMASHITA*[1], Satoshi OHSHIRO[1], Keiko KIDA[1],
Katsuhiro YOSHIZAWA[1], Masakazu ANPO[1]
[1]Dept. Appl. Chem., Osaka Prefecture University, Gakuen-cho 1-1, Sakai, Osaka 599-9531, Japan

Introduction

The highly dispersed transition metal oxides incorporated within the framework of microporous and mesoporous silica zeolites show unique reactivities for several photocatalytic reactions. However, these metal oxides can operate as the photocatalysts only under UV light irradiation. To establish the clean photocatalysis system it is vital to develop the photocatalysts which can operate efficiently under visible light irradiation.

In the present study, the photocatalytic reactivities of Cr-containing mesoporous silica zeolite (Cr-HMS) have been investigated and the local structures of active sites were studied using XAFS analysis [1-3].

Experimental

Cr-HMS mesoporous molecular sieves (Si/Cr=50, 100, 500) were synthesized using tetraethylorthosilicate and $Cr(NO_3)_3.9H_2O$ as the starting materials and dodecylamine as a template. The catalysts were heated in O_2 at 723 K before use. XAFS spectra were obtained at the BL-9A and -7C facility of the Photon Factory at the National Laboratory for High Energy Physics (KEK-PF) in Tsukuba. The Cr K-edge absorption spectra were recorded in the fluorescence mode at 295 K with a ring energy of 2.5 GeV and the Fourier transformation was performed on k^3-weighted EXAFS oscillations by a procedure described in previous literature [1-3].

Results and discussion

Figure 1 shows the XAFS spectra of the treated Cr-HMS and imp-Cr/HMS. Cr-HMS exhibits a sharp and intense preedge peak which is characteristic of Cr-oxide moieties in tetrahedral coordination having terminal Cr=O. In the FT-EXAFS spectrum, only a single peak due to the neighboring oxygen atoms (Cr-O) can be observed showing that Cr ions are highly dispersed in Cr-HMS. In the curve fitting analysis of the FT-EXAFS spectrum, the best fitting was obtained with two oxygen atoms (Cr=O) in the shorter atomic distance of 1.57 Å and two oxygen atoms (Cr-O) in the long distance of 1.82 Å. The imp-Cr/HMS exhibits a weak preedge peak in the XANES spectra and an intense peak due to the neighboring Cr atoms (Cr-O-Cr) in the FT-EXAFS spectra, indicating that the catalyst consists of a mixture of tetrahedrally and octahedrally coordinated Cr-oxide species (Cr_2O_3-like cluster).

In the presence of NO, Cr-HMS exhibited photocatalytic reactivity for the decomposition of NO into N_2, O_2, N_2O not only under UV light irradiation and but also visible light λ>450 nm) irradiation. Especially, under visible light irradiation, the higher selectivity for N_2 formation was observed [2]. In the presence of propane and O_2, a complete oxidation proceeded under UV light irradiation. While partial oxidation proceeded under visible light irradiation to produce acetaldehyde with a high selectivity. The photoepoxidation of propene with O_2 and the photopolymerization of ethylene also proceeded under visible light on Cr-HMS [3]. The charge transfer excited state of the tetrahedral Cr-oxide moieties and the large pores of the mesoporous zeolite play a significant role in the photocatalytic reactions.

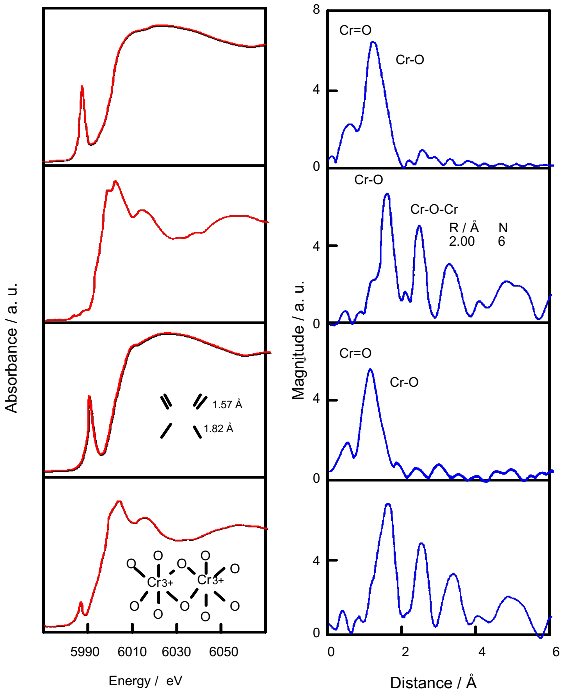

Fig. 1. Cr K-edge XANES spectra (A-D) and Fourier transforms of EXAFS spectra (a-d). (a) CrO3, (b) Cr2O3, (c) Cr-HMS (Si/Cr=50), (d) imp-CrHMS (Si/Cr=50). R: atomic distance (Å), N: coordination number.

References

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*yamashita@chem.osakafu-u.ac.jp