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## Characterization and photocatalytic reactivities of Cr-HMS mesoporous molecular sieves

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Investigations of the local structures and photocatalytic reactivity of Cr-containing mesoporous molecular sieves (Cr-HMS) have been carried out. Cr-HMS involves tetrahedrally coordinated Cr-oxide species which are highly dispersed and incorporated with terminal Cr=O groups in the framework of molecular sieves. On the other hand, the imp-Cr/HMS prepared by an impregnation method consists of both tetrahedrally and octahedrally coordinated Cr-oxide species. The Cr-HMS exhibits much higher photocatalytic reactivity under UV irradiation for the isomerization of cis-2-butene than the imp-Cr/HMS and Cr-silicalite microporous catalysts. The charge transfer excited state of the tetrahedrally coordinated Cr-oxide species plays a significant role in the photocatalytic reaction.

**Keywords:** Mesoporous molecular sieves, Chromium oxide species, Photocatalysis, Local structure, Photoluminescence

### 1. INTRODUCTION

Metalosilicates including various transition metal ions within the framework of zeolites and molecular sieves have been the subject of many recent studies due to their significant role in various efficient and selective catalytic reactions [1,2]. In this paper, the characterization of Cr-containing mesoporous molecular sieves (Cr-HMS) has been carried out by means of dynamic photoluminescence, XAFS, UV-VIS, and XRD measurements. Also, photocatalytic reactivities for the isomerization of cis-2-butene have been investigated. Special attention has been focused on comparisons of the results obtained with these Cr-HMS mesoporous molecular sieves, CrS-1 microporous zeolites and metal oxide-impregnated HMS catalysts in order to clarify the effects of the local structure of the active sites and the pore size of the cavities on determining the photocatalytic reactivity.

### 2. EXPERIMENTAL

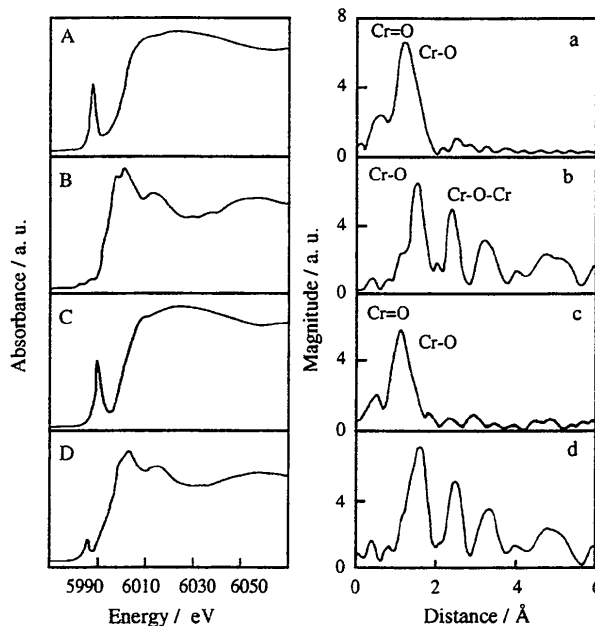
Cr-HMS mesoporous molecular sieves (0.2–2.0 wt% as Cr) were synthesized using tetraethylorthosilicate and

Cr(NO<sub>3</sub>)-9H<sub>2</sub>O as the starting materials, and dodecylamine (DDA) as a template [3], respectively. The Cr-silicalite (CrS-1) microporous zeolites (0.2 wt% as Cr) were hydrothermally synthesized using tetraethoxysilane and Cr(NO<sub>3</sub>)-9H<sub>2</sub>O starting materials, and tetrapropyl ammonium hydroxide (TPAOH) as a template, respectively. The imp-Cr/HMS catalyst (2.0 wt% as Cr) was prepared by impregnating HMS with an aqueous solution of Cr(NO<sub>3</sub>)-9H<sub>2</sub>O. Calcination of the sample was carried out in a flow of dry air at 773 K for 5 h. Prior to spectroscopic measurements and photocatalytic reactions, the catalysts were degassed at 723 K for 2 h, heated in O<sub>2</sub> at the same temperature for 2 h and then finally evacuated at 473 K for 2 h. The XAFS spectra were obtained at the BL-7C facility of the Photon Factory at the National Laboratory for High Energy Physics (KEK-PF) in Tsukuba with a ring energy of 2.5 GeV and some spectra were obtained at Pohang Acceleratory Laboratory. The Cr K-edge absorption spectra were recorded in the fluorescence mode at 295 K with an Si(111) two-crystal monochromator. The photocatalytic isomerization of cis-2-butene was carried out in a quartz reactor under UV irradiation at 273 K using a high pressure mercury lamp ( $\lambda > 270$  nm).

### 3. RESULTS AND DISCUSSION

The results of XRD analysis, UV-VIS absorption and ESR measurements indicated that the Cr-HMS mesoporous molecular sieve has the structure of the HMS molecular sieve having mesopores larger than 20 Å and the Cr-oxide species are highly dispersed in the framework, while no other phases are formed [4].

Figure 1 shows the XANES and FT-EXAFS 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 species in tetrahedral coordination having terminal Cr=O

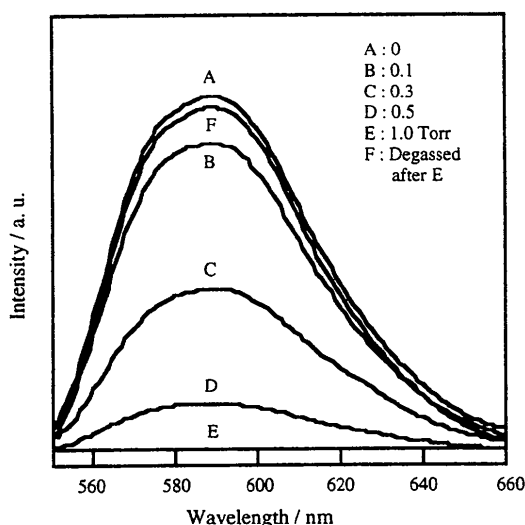


**Fig. 1.** The XANES (A–D) and FT-EXAFS (a–d) spectra of CrO<sub>3</sub> (A,a), Cr<sub>2</sub>O<sub>3</sub> (B,b), Cr-HMS (2.0 wt% as Cr) (C,c), and imp-Cr/HMS (2.0 wt%) (D,d).

groups [5]. 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. The curve-fitting analysis of the EXAFS spectra indicates that Cr-HMS consist of 4-coordinate Cr ions with two terminal Cr=O groups; the first shell with coordination number (CN) of 2.1 and atomic distance (R) of 1.57 Å and the second shell with CN of 1.6 and R of 1.82 Å, respectively. In the case of the imp-Cr/HMS catalyst, the intensity of the peak due to the neighboring Cr atoms (Cr-O-Cr) in the FT-EXAFS spectrum is strong, indicating that the catalyst consists of a mixture of tetrahedrally and octahedrally coordinated Cr-oxide species (Cr<sub>2</sub>O<sub>3</sub>-like cluster). From analysis of XANES and FT-EXAFS, we found that imp-Cr sample consists of 20 % of tetrahedral species and 80 % of octahedral species.

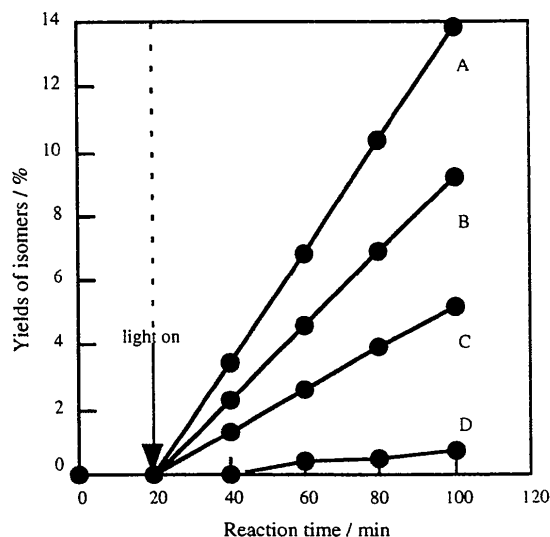
As shown in Fig. 2, the Cr-HMS catalyst evacuated at 473 K exhibits a photoluminescence spectrum at around 550-750 nm upon excitation of the absorption band at around 410 nm. These absorption and photoluminescence spectra were found to be similar to those obtained with well-defined highly dispersed Cr-oxides species anchored onto Vycor glass or silica [6] and can be attributed to the charge transfer processes on the tetrahedrally coordinated Cr-oxide species involving an electron transfer from O<sup>2-</sup> to Cr<sup>6+</sup> and a reverse radiative decay, respectively. These results indicate that the Cr-HMS mesoporous molecular sieve involves the Cr-oxide species in tetrahedral coordination having terminal Cr=O groups, being in good agreement with the results obtained by XAFS and UV-VIS measurements.

UV irradiation of Cr-HMS in the presence of cis-2-butene led to an efficient photocatalytic isomerization of cis-2-butene into trans-2-butene. As shown in Fig. 3, the reactions are found to proceed only under UV irradiation and the yields increase with a good linearity against the irradiation time,



**Fig. 2.** The photoluminescence spectrum of Cr-HMS (a) (2.0 wt% as Cr) at 77 K and the effect of the addition of cis-2-butene (b-f) on the intensity of the photoluminescence.

indicating that the reaction proceeds photocatalytically. The Cr-HMS exhibits significantly higher photocatalytic reactivity than the imp-Cr/HMS and CrS-1 having mesopores and micropores, respectively. As shown in Fig. 2, the addition of cis-2-butene onto the Cr-HMS leads to an efficient quenching of the photoluminescence of the catalyst, its extent depending on the amount of added butenes. These results indicate that the excited state of the tetrahedrally coordinated Cr-oxide species easily and efficiently interact with the added butene. And the large mesoporous cavities are suitable for achieving efficient photocatalytic reactions.



**Fig. 3.** The time profiles of the photocatalytic isomerization of cis-2-butene into trans-2-butene on Cr-HMS (2.0 wt% as Cr) (A), imp-Cr/HMS (2.0 wt%) (B), Cr-HMS (0.2 wt%) (C), and CrS-1 (0.2 wt%) (D) catalysts.

#### 4. CONCLUSIONS

It has been found that Cr-HMS mesoporous molecular sieves contain tetrahedrally coordinated Cr-oxide species having terminal Cr=O groups in the framework and that the charge transfer excited state of Cr-oxide species are responsible for the efficient photoluminescence and photocatalytic reactivities.

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