

Fine Structure around Chromium Species Incorporated into MCM-41 Using Template Ion-exchange Procedure

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1 Introduction

Previously, we reported that Cr-doped FSM-16 (#16 folded sheets of mesoporous materials) showed the great catalytic activity for the oxidative dehydrogenation (ODH) of isobutane [1]. In the present study, template ion exchange (TIE) method [2] was applied to MCM-41 (#41 Mobil Composition of Matter) [3] to examine the relationship between the catalytic activity and fine structure around Cr specie in the catalysts.

2 Experiment

In the preparation of MCM-41, the hydrothermal synthesis method was applied [2]. After the hydrothermal synthesis at 413 K for 48 h without stirring, the obtained white wet solid was filtered, washed with distilled water, and dried at 333 K. Chromium-doping was carried out via the TIE method [3]. The catalytic activity tests were carried out in a fixed-bed continuous flow reactor at atmospheric pressure. Each catalyst (0.25 g, 0.85-1.70 mm) was pretreated with 12.5 mL/min of O₂ at 723 K. After the pretreatment, catalytic activity test was started by flowing 15 mL/min of He, i-C₄H₁₀ and O₂. The partial pressures were adjusted to P(He) = 74.6 kPa, P(i-C₄H₁₀) = 14.4 kPa, and P(O₂) = 12.3 kPa, respectively. Under these conditions, stable activity was observed for up to 6 h on-stream. The structural information on the Cr species were evaluated via X-ray absorption fine structure (XAFS) performed with Synchrotron radiation at the beam-line NW9A station of the Photon Factory in the High Energy Accelerator Research Organization (Tsukuba, Japan).

3 Results and Discussion

The catalytic activity of MCM-41 was quite low and the conversion of i-C₄H₁₀ and the yield of i-C₄H₈ were 8.8 and 0.9%, respectively. To improve this low catalytic activity, Cr-doping into MCM-41 was conducted via the TIE method, resulting in the conversion and the yield to 20.6 and 6.8%, respectively. Unfortunately, XRD did not afford any information on Cr species. Therefore 2.2 wt% Cr-MCM-41 was analyzed using XAFS. Figure 1 shows the effect of the reaction (Figs. 1 (a) and (c) for those before and after the reaction, respectively) and the pretreatment using 12.5 mL/min of O₂ gas flow at 723 K for 2 h (Fig. 1 (b)) on Cr K-edge XANES spectra of the Cr-

MCM-41. As shown in Figures 1 (a) and (b), the intensity of the pre-edge peak was increased by O₂ treatment. The pre-edge peak at ca. 5991 eV represents tetrahedrally coordinated Cr⁶⁺ species [4]. The coordination state around Cr species was similar to that around the Si in MCM-41. However, the pre-edge peak was disappeared after the ODH of i-C₄H₁₀ (Fig. 1 (c)). Although our Cr-MCM-41 was not deactivated during 6 h on-stream, it can be concluded that the reduction rate of active chromium species during the ODH of i-C₄H₁₀ might have been faster than that of their regeneration by oxygen, since the pre-edge peak disappeared.

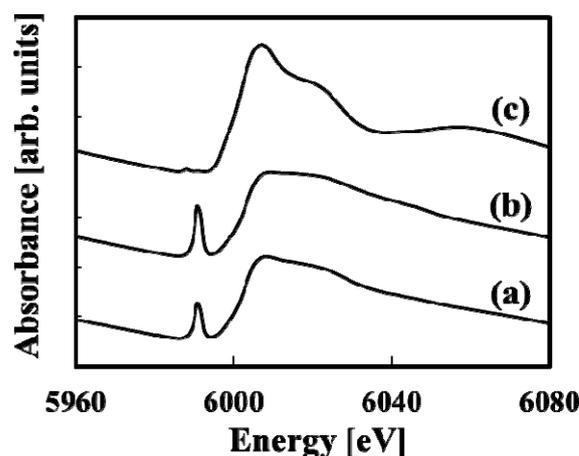


Fig. 1 Cr K-edge XANES spectra of (a) 2.2 wt% Cr MCM-41 (a) before ODH of isobutane, (b) after the pretreatment with O₂ flow and (c) after ODH of isobutane.

References

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