

XANES Evidence on Active Species over MCM-48 Doped with Chromium

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1 Introduction

Although isobutene is a key compound for the production of various chemicals, it is mainly supplied from ethylene and FCC plants via a supply route that is undoubtedly insufficient. Under these circumstances, oxidative dehydrogenation (ODH) of isobutane to isobutene have been investigated in our laboratory. In the present study, the ODH of isobutane to isobutene was examined using MCM-48 introduced with chromium via the template ion exchange method. It was found out that the catalytic performance of MCM-48 was greatly improved by the introduction of a small amount of chromium. Although various characterization procedures were used to clarify the role that chromium played in the improvement, only XAFS returned the most valuable information. In the present report, XAFS results were described comparing to those obtained via XPS.

2 Experiment

Testing of catalytic performances was carried out with a fixed-bed continuous flow reactor under atmospheric pressure at 723 K, using 0.25 g of pelletized and sieved catalyst (0.85-1.07 mm). The partial pressures of the reactant gases were adjusted to $P(\text{He}) = 74.6$ kPa, $P(\text{O}_2) = 12.3$ kPa and $P(\text{iso-C}_4\text{H}_{10}) = 14.4$ kPa. No homogeneous reaction was detected under these conditions. The preparation method of MCM-48 introduced with chromium was described elsewhere [1]. The surface property of the catalysts was analyzed using XPS (PHI-5000VersaProbe II, ULVAC-PHI Inc.). The fine-structure changes around the chromium species were estimated using XAFS measurement carried out via synchrotron radiation using the BL9C station at the Photon Factory of the High Energy Accelerator Research Organization. The storage ring energy and current were 2.5 GeV and 450 mA, respectively. The X-rays were monochromatized using a Si(111) water-cooled double crystal.

3 Results and Discussion

On MCM-48, isobutane was barely converted. The yields of isobutene were 1.9% for MCM-48. However, the conversion of isobutane and the selectivity to isobutene were greatly improved by introducing only a small amount of chromium into MCM-48 (Cr-MCM-48). The maximum catalytic performance up to 50% or greater of the yield of isobutene was detected when using Cr-MCM-48 (Si/Cr ratio = 1,000). When Cr-MCM-48 (Si/Cr ratio = 100 or 1,000) were analyzed using XPS, any evident XPS peaks due to Cr^{3+} and Cr^{6+} were not detected

even though the integration number was extensively increased. However, chromium species from Cr-MCM-48 (Si/Cr ratio = 100 or 1,000) were detected using XANES as shown in Fig. 1. The XANES spectra of both Cr-MCM-48 before the reaction showed a pre-edge absorption at ca. 5,990 eV, indicating that the chromium species possesses a tetrahedral coordination structure consisting the Cr^{6+} . After the reaction, the absorption peak was shifted by ca. 3.6 eV to a lower energy level, followed by the disappearance of the pre-edge absorption peak. The XANES spectra of the catalysts after the reaction were similar to that of Cr_2O_3 , indicating that the chromium species had an octahedrally coordinated structure. These XANES information revealed that the structure of chromium species changed from tetrahedral to octahedral coordination, while the chromium species was reduced from Cr^{6+} to Cr^{3+} during the reaction.

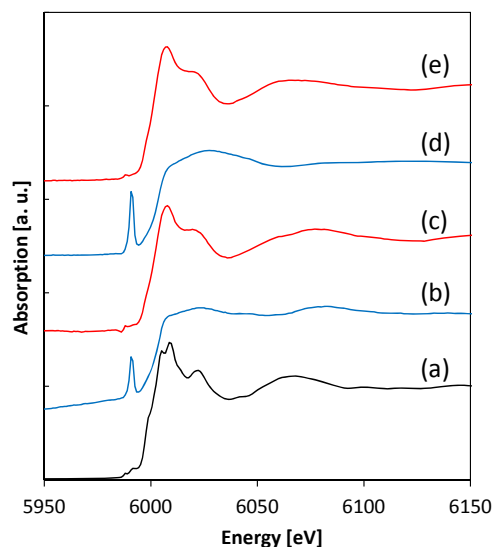


Fig. 1: Cr K-edge XAFS spectra of (a) Cr_2O_3 , (b) Cr-MCM-48 with a Si/Cr ratio = 1,000 before the reaction, (c) Cr-MCM-48 with a Si/Cr ratio = 1,000 after the reaction, (d) Cr-MCM-48 with a Si/Cr ratio = 100 before the reaction, and (e) Cr-MCM-48 with a Si/Cr ratio = 100 after the reaction.

References

- [1] Y. Kato, S. Nitta, S. Shimazu, M. Kurashina, M. Katoh, W. Ninomiya and S. Sugiyama, Submitted to *J. Chem. Eng. Japan* (2018).

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