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Template Ion Exchange Behaviors of Chromium into FSM-16 and Fine Structure around Chromium Species in the Exchanged Solid

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1 Introduction

We have reported that FSM-16 (#16 folded sheets of mesoporous materials) doped with chromium using template ion exchange (TIE) method showed the great catalytic activity for the oxidative dehydrogenation of isobutane to isobutene [1]. However the template ion exchange behaviors and the fine structure around chromium incorporated are not yet clear. In the present report, the results for these two factors will be described.

2 Experiment

According to the previous paper [1], FSM-16 was prepared. After the calcination of a hydrated sodium silicate powder at 973 K for 6 h, the resultant solid was ground, added to distilled water, and then stirred for 3 h at room temperature. The solid thus obtained was separated and was added to an aqueous solution consisting of cetyl trimethyl ammonium bromide. The solution was refluxed at 343 K for 3 h and then cooled to room temperature. The solution pH was adjusted to 8.5 using 2 M HCl and then stirred at 343 K for 18 h. The resultant solid was washed, filtered and dried at 333 K to obtain a white solid, which was denoted as “as-synthesized FSM-16”. Then FSM-16 was obtained by calcination of as-synthesized FSM-16 at 823 K for 8 h. To examine the TIE behaviors, the as-synthesized FSM-16 (5 g) was dispersed in 50 mL of distilled water. After 10 mL of 0.50 M $Cr(NO_3)_3 \cdot 9H_2O$ was added to the dispersed solution with vigorous stirring for 1 h, the temperature was adjusted to 353K. This segment was referred to as the start time of TIE (0 h TIE). The concentration of Cr cations incorporated into as-synthesized FSM-16 and that of Si cations released from as-synthesized FSM-16 during the TIE were monitored using ICP-AES. The resultant solid obtained after x h TIE was described as “x h Cr-FSM-16”. To detect the fine structure around the Cr species in Cr-FSM-16, XAFS measurement was performed at the BL9A station of the Photon Factory in the High Energy Accelerator Research Organization (Tsukuba, Japan).

3 Results and Discussion

As shown in Fig. 1, the releasing behavior of Si cations was similar to the incorporated behavior of Cr cations, indicating that the direct and stoichiometric ion exchange between Si^{4+} in as-synthesized FSM-16 and Cr^{3+} may proceed. In our previous studies [1], Cr cations could be incorporated into FSM-16 at only 0.3 wt%, while the loading was improved up to 2.89 wt% after 247 h of TIE.

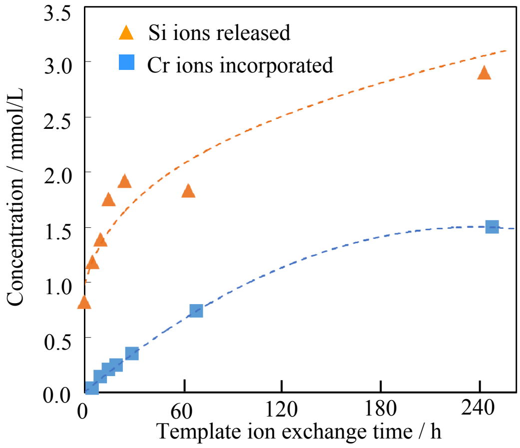

Fig. 1. Template Ion Exchange behaviors of as-synthesized FSM-16 and Cr ions at 353 K

As shown in Fig. 2, a pre-edge peak at ca. 5990 eV was detected along with a typical absorption spectrum. The pre-edge obtained from Cr-containing mesoporous silica was characteristic to tetrahedrally coordinated Cr^{6+} species [2]. Therefore the Cr K-edge XANES indicates the presence of Cr^{6+} together with Cr^{3+} species, although the starting Cr ion was Cr^{3+} only.

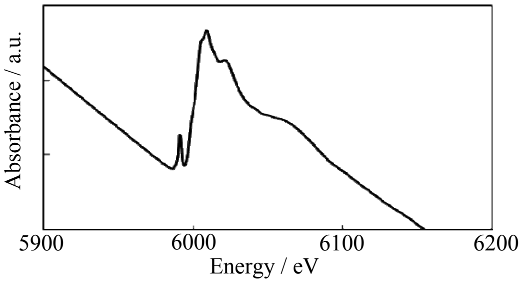

Fig. 2. Cr K-edge XANES spectra of 247 h Cr-FSM-16.

References

[1] S. Sugiyama *et al.*, *J. Chem. Chem. Eng.*, **7** (11), 1014 (2013).
[2] K. Takehira *et al.*, *J. Catal.*, **224**, 404 (2004).

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