

Effects of incorporation of Fe³⁺ into magnesium *ortho*-vanadate on the catalytic activity and the redox of vanadium species

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Introduction

Although magnesium vanadates (MgV₂O₆, Mg₂V₂O₇ and Mg₃V₂O₈) are active catalysts for the oxidative dehydrogenation of propane, Mg₃V₂O₈ (magnesium *ortho*-vanadate) is known to show the lowest activities among three vanadates [1]. Since Mg₃V₂O₈ is more stable than Mg₂V₂O₇, that is a catalyst with the highest activity among these three vanadates, the activity on magnesium *ortho*-vanadate and the related catalysts should be improved. In the present study, Fe³⁺ was incorporated into Mg₃V₂O₈ in order to enhance the catalytic activity. Furthermore the redox nature of vanadium species in the Fe³⁺-incorporated catalyst was also analyzed with XAFS.

Experimental

Magnesium *ortho*-vanadates incorporated with Fe³⁺, Mg_{3(1-x)}Fe_{2x}V₂O₈ with x=0, 0.025, 0.05 and 0.10 (described as x%-Fe-*ortho*-MgVO), were prepared from Mg(OH)₂, Fe(NO₃)₃·9H₂O and NH₄VO₃. The preparation procedure was essentially identical to that reported by Sam *et al.* [1]. Fixed-bed continuous flow reactor operated at atmospheric pressure was employed for the catalyst activity test under the following conditions: T=723 K, W=0.5 g, P(C₃H₈)=14.4 kPa, P(O₂)=4.1 kPa and F=30 ml/min. X-ray absorption fine structure (XAFS) near V K-edge was measured (2.5 GeV) with a storage ring current of approximately 400 mA at the High Energy Research Organization. The X-rays were monochromatized with Si(111) at BL-7C station. The absorption spectra were observed using ionization chambers in a transmission mode.

Results and Discussion

With the incorporation of Fe³⁺ into Mg₃V₂O₈, the improvement of the conversion of propane from 4.8% on Mg₃V₂O₈ to 8.2% on 5%-Fe-*ortho*-MgVO together with the rather similar selectivity to propylene on un-doped and doped catalysts (62.3 and 61.0 %, respectively) were observed. It should be noted that the yield of propylene showed maximum on 5%-Fe-*ortho*-MgVO while 10%-Fe-*ortho*-MgVO was employed for various analyses due

to an excess presence of vanadium species in the catalyst. In order to evaluate the redox nature of 10%-Fe-*ortho*-MgVO, the catalyst was reduced for 6 h under the conditions of T=723 K, W=0.5 g, P(C₃H₈)=14.4 kPa, P(O₂)=0 kPa and F=30 ml/min. After the analyses of the reduced catalyst with XAFS and the related analytical procedures, the reduced catalyst was re-oxidized with O₂ (25 ml/min) for 1 h at T=723 K. An evident V K-pre-edge peak was detected from XAFS analyses with the fresh and the re-oxidized catalysts while the pre-edge peak became smaller after the reduction of the fresh catalyst. The decrease in intensity of the V K-pre-edge peak indicates a reduction of V⁵⁺ species in the fresh catalyst to V⁴⁺ species in the reduced catalyst, the latter of which could be re-oxidized to V⁵⁺ by the O₂ treatment. Fourier transformation of the XAFS oscillation around the V K-edge of fresh and the re-oxidized 10%-Fe-*ortho*-MgVO showed that the nearest-neighbor distance V-O in the catalysts was both 0.173 nm. This distance is comparable distance (0.172 nm) in VO₄³⁻ anion, which is stable, as a regular tetrahedron [2], indicating that the V-O distance in the catalysts is a typical distance between V⁵⁺ and O²⁻. The reduction of 10%-Fe-*ortho*-MgVO resulted in the enlargement of the V-O distance to 0.183 nm. Based on the discussion using V K-pre-edge peak and the nearest-neighbor distance V-O, it is confirmed that facile redox proceeds during the oxidative dehydrogenation propane on magnesium *ortho*-vanadate incorporated with Fe³⁺, resulted in the improvement of the catalytic activity. It should be noted that the redox nature of vanadium species confirmed by XAFS were also detected from the solid state ⁵¹V MAS NMR. Finally it is worthwhile to mention that such an improvement observed from the incorporation of Fe³⁺ into Mg₃V₂O₈ was not observed in incorporating reducible rare metal cations into Mg₃V₂O₈.

References

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