

X-ray Absorption Spectroscopy of Promoter Metal Ions Promoted Sulfated Zirconia Catalysts

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Introduction

Sulfated zirconia, when exposed to *n*-butane, can form active sites which are able to catalytically isomerize *n*-butane at room temperature [1]. The promotion of sulfated zirconia with transition metals ions increases the maximum *n*-butane isomerization rate by two orders of magnitude [2, 3]. However, the promotion effects observed have not yet been understood. It has been suggested that promotion with Fe is due to the creation of surface Fe^{3+} species which are active for the low temperature ($< \sim 100^\circ\text{C}$) isomerization of *n*-butane [4, 5]. Ex-situ measurements of the Mn edge have indicated that Mn is also reduced during the isomerization reaction [6]. We have constructed an in-situ cell to measure the fluorescence mode X-ray absorption spectra of powdered catalyst samples. Additional characterization with XRD and Zr K-edge X-ray absorption spectroscopy helps us to gain an understanding of the effects of promoter metal ions on sulfated zirconia.

Experimental

Promoted sulfated zirconia samples were prepared by the impregnation of a commercial sulfated zirconium hydroxide (MEL chemicals) with aqueous solutions of iron (III) or manganese(II) nitrates by the incipient wetness technique. Non-sulfated zirconia was produced by co-precipitation of zirconyl nitrate and Fe (III) or manganese(II) nitrates. Both non-sulfated and sulfated promoted zirconia samples were calcined at 650°C for 3 hours in flowing synthetic air, and in batches of at least 20 grams [7].

XAS of the Zr K-edge was performed ex-situ, in transmission mode. XAS of the Mn and Fe K-edges was performed in-situ, in fluorescence mode. The newly designed in-situ cell consisted of a powder bed reactor with a flat Kapton® window. For temperature control of the measured sample volume, near the window, the reactor and window are enclosed in a He filled, temperature controlled chamber with 3

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Kapton windows for incident radiation, fluorescence signal, and for a fraction of the incident radiation which bypasses the reactor. The incident X-rays which bypass the catalyst bed are used to measure a Mn foil in transmission. The reactant product stream was monitored with an on-line mass spectrometer.

Results

X-ray absorption near edge spectra of the Mn K-edge of a 2% Mn sulfated zirconia catalyst taken in-situ during activation in He are presented in Fig. 1. The Mn edge energy shift can be used to measure the average Mn valence which shows no change during reaction with *n*-butane at 60 °C. Zr K-edge XAS and XRD measurements are consistent with the incorporation of Fe or Mn in the zirconia bulk, and to changes in the bulk structure resulting from incorporation.

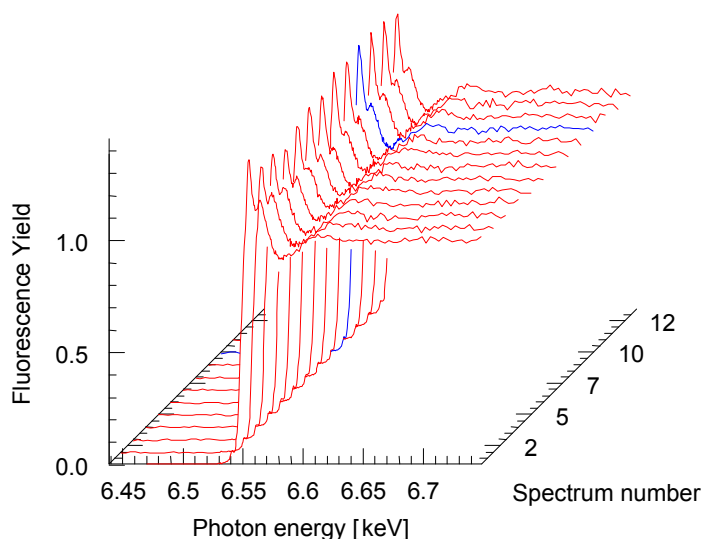


Figure 1, Mn K-edge X-ray absorption near edge spectra taken in-situ during the activation of 2% MnSZ catalyst in flowing He. Temperature: RT to 630 °C at 10 K/min, 30 min at 630 °C.

Conclusions

Mn does not participate in stoichiometric redox reactions during the low temperature isomerization of *n*-butane on promoted sulfated zirconia. Promoter ions are incorporated into the zirconia bulk. Incorporation of metal ions of valence lower than 4 into the zirconia lattice will form oxygen vacancies, reducing the coordination of zirconium ions and increasing ion conductivity. The function of promoter ions the zirconia bulk may be to tune the zirconia structural and electronic properties resulting in a more active sulfated zirconia.



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