Incorporation of transition metal ion promoters in sulfated zirconia catalysts

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Sulfated zirconia can catalyze the skeletal isomerization of n-butane at 373 K [1]. The promotion of sulfated zirconia by the addition of transition metal (Fe, Mn, Co, Ni) cations increases the maximum n-butane isomerization rate by up to two orders of magnitude [2, 3]. At first these materials were considered to be active due to extremely strong acidity; more recent literature has suggested a multifunctional nature in which the stoichiometric reduction of a promoter (Fe) is responsible for the high isomerization activity at low temperature (< 373 K) [4, 5]. Ex-situ measurements of the Mn K-edge have indicated stoichiometric reduction of Mn during the isomerization reaction [6]. In order to confirm these ex-situ results with in-situ measurements, we have constructed an in-situ cell to measure the fluorescence mode X-ray absorption spectra of catalyst powder samples during their use for the isomerization of n-butane. Additional characterization with XRD and Zr K-edge XAS helps us to gain an understanding of the reactivity and role of promoter metal ions in sulfated zirconia.

Manganese promoted sulfated zirconia (x%MnSZ, x% gives promoter content as weight% metal) and iron promoted sulfated zirconia (x%FeSZ) were prepared from a commercial sulfated zirconium hydroxide (MEL Chemicals) which was impregnated with Mn(II) or Fe(III) nitrates in aqueous solution using the incipient wetness technique. Non-sulfated Mn doped zirconia (MnZ) was prepared by co-precipitation from a Mn (II) nitrate zirconyl nitrate solution. Samples were calcined in flowing 20% oxygen at 923 K for 3 hours (3 K/min ramp). The samples were calcined in batches of either 3, 12, or 25 g [7]. The catalyst was activated in flowing He at 703 K for 30 minutes (10 K/min ramp). The isomerization reaction conditions were 0.5 grams of catalyst, 80 ml/min flow of 1% n-butane in He at 1 bar and 333 K. The reactor design includes a bypass for a fraction of the beam which is then used for simultaneous transmission mode measurement of a reference foil. Mn and Fe K-edge spectra were measured at Hasylab beamline E4 with a scan time of 10 minutes per spectrum. Zr K-edge spectra were measured at Hasylab beamline X1 in transmission mode.

Figure 1  In-situ activation of a 2% MnSZ catalyst in flowing He. A) Normalized fluorescence yield spectra of Mn K-edge. B) Average Mn valence in 2% Mn SZ during activation.
Figure 1A shows Mn K-edge spectra of a 2% MnSZ during activation in He. Figure 1B shows the average Mn valence in the 2% MnSZ catalyst which is calculated using the linear relationship between the Mn K-edge energy and the Mn valence [8]. The average Mn valence is about 2.5 in the fresh catalyst. Part of the Mn is reduced during activation, decreasing the average Mn valence to about 2.25. The Mn valence of the catalyst does not change, on average, during reaction of the catalyst with n-butane at 333 K, demonstrating that for the MnSZ catalyst the role of Mn is not to activate hydrocarbons through a stoichiometric redox mechanism. After reaction the catalyst was reactivated in 50% oxygen at 703 K for 30 min. The activity for n-butane isomerization was higher after reactivation in oxygen than after activation in He; however, the majority of the Mn which was reduced during activation, was not oxidizable in 50% oxygen at 703 K. The Mn in the catalyst was reducible to an average valence of about 2 during heating in 50% hydrogen at 703 K for 30 min. The XANES of a series of Fe K-edge absorption spectra of a similarly treated 2% FeSZ catalyst did not show any significant changes during the treatments.

Principal component (PC) analysis of all spectra of the 2% MnSZ catalyst during the treatments described above gave 3 major components which were sufficient to describe the changes in the spectra. Figure 2 shows the mixing coefficients for the three most significant components. From these results it appears that the third PC is associated with changes in the spectra during heating, and that the second PC is associated with the transition of a Mn\(^{3+}\) or Mn\(^{4+}\) species into Mn\(^{2+}\), both during the initial activation in He, as well as during the reduction in Hydrogen.

Figure 3 shows the radial distribution function from the Zr K-edge spectra of a series of non-sulfated zirconia samples containing 0.2 to 3.5 wt% Mn. The series shows that the addition of Mn decreases the shells at 3.2, 4.7, and 6.8 Å, consistent with incorporation of Mn into the zirconia.

In situ XAS measurements give evidence that the main role of transition metal ions in sulfated zirconia is not to directly participate in hydrocarbon activation through a stoichiometric redox reaction. Rather we see that the ions are altering the bulk structure of the zirconia, presenting the possibility that these bulk structural changes may alter the surface, and thus the activity of the promoted sulfated zirconia catalyst.
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References