

Mn and Zr K edge in situ XAS measurements of promoted sulfated zirconia catalysts

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The high activity of sulfated zirconia based catalysts for the isomerization of *n*-butane has led to intensive study of these materials. Their skeletal isomerization ability is thought to arise from acidic sites on the catalyst, and attempts have been made to relate the acidity of sulfated zirconia to its activity, as has been successfully done for homogeneous catalysts and some classes of heterogeneous catalysts. However, the activity of sulfated zirconia is exceptional for its measured acidity. Promotion of sulfated zirconia through the addition of ~2 wt% of transition metal cations (manganese, iron) increases the low temperature isomerization activity by two orders of magnitude [1,2]. Despite the increased activity, the acidity of the promoted catalysts is no higher than that of sulfated zirconia [3]. The failure to explain activity through acidity has led to the search for a second functionality in the catalyst, and suggestions for this additional functionality include oxidation/reduction reactions involving the promoter oxides [4]. We have reported a trend in the Mn oxidation state that was observed during activation and reaction of Mn-promoted sulfated zirconia ("MnSZ") with *n*-butane, and was obtained from ex situ measurements [5]. Here we report results from in situ measurements of the Mn K edge during catalyst activation. In addition we present in situ and ex situ Zr K edge measurements which investigate the calcination step of the catalyst preparation. Data were reduced using the WinXAS software package [6].

Ex situ measurements have shown that Mn in MnSZ is reduced from a valence of about 2.4 to 2.3 during activation (in flowing N₂ at 450 °C for 1.5 hours), and is further reduced to an average valence of 2.2 after reaction with *n*-butane at 65 °C [5]. To obtain more detailed information on the reduction of Mn during activation we constructed an in situ cell that is potentially suitable for both transmission and fluorescence measurements. The cell models as a well mixed semi-batch reactor with a volume of about 750 ml. The sample is pressed into a 13 mm pellet which is suspended on a heating block at 45° to the incident X-ray beam. The cell is sealed with Kapton windows. A stainless steel bellows pump is used to recirculate the gas phase the composition of which is monitored with a mass spectrometer. Measurements were taken at beamline E4 in transmission mode in order to follow changes during catalyst activation with a high time resolution (3.5 minutes/scan). The XANES of the Mn K-edge of a MnSZ sample measured during activation in He are given in Figure 1. The average Mn valence was calculated using the linear relationship between the Mn K-edge energy shift and the Mn valence [7], and is presented as a function of temperature in Figure 2. Here it appears that the Mn is reduced to an average valence of about 2.1 already with heating to 350 °C. These results indicate that reduction happens much faster than indicated by the ex situ experiment. In addition the oxidation state increases on cooling, perhaps due to some re-adsorption and reaction of gas phase impurities, or structural change during cooling. A temperature dependence of our edge energy measurements must also be investigated and ruled out. The Mn valence measured after cooling is still much lower than that measured ex situ after treatment in N₂ at 450 °C, and possible reasons for this discrepancy may include reoxidation of the ex situ samples (sealed in polyethylene) during transfer, or may lie in the configuration of the in situ cell, and the use of a pellet instead of a powder bed. The pelletization of sulfated zirconia appeared to subdue the activity for the isomerization of *n*-butane, probably due to transport limitations indicated by visible coking of the outside of the pellet at higher reaction temperatures, and suggesting the need for modification of the in situ cell to accommodate powdered samples.

In situ measurements of the Zr K edge were taken at beamline X1 in transmission mode with a time resolution of about 2 minutes. The evolution of the radial distribution function (RDF) of the Zr K edge of zirconium hydroxide during calcination (heating to 530 °C in air) is presented in Figure 3. The data show a

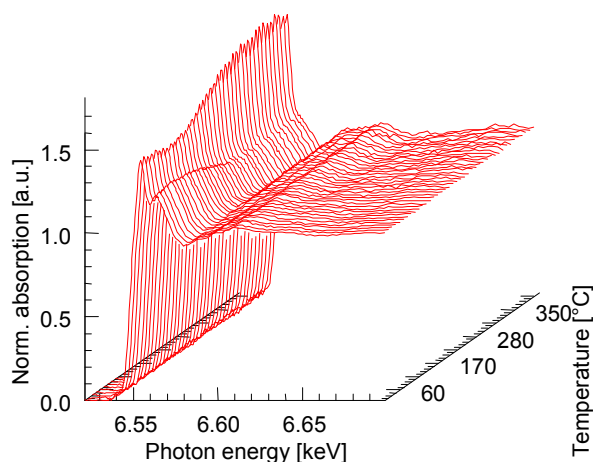


Figure 1: Mn K edge XANES of MnSZ (2 wt% Mn) during activation in He. Temperature ramp was 26 °C - 350 °C at 3 °C/min.

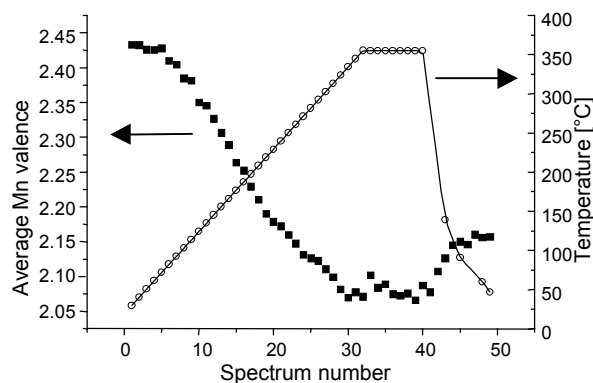


Figure 2: Apparent changes in the Mn valence during in situ measurement of the activation of MnSZ in He (calculated from data in Figure 1).

rapid change in structure at temperatures between 438 and 462 °C which coincide with an exothermic reaction (crystallization and/or decrease in surface energy) which has been observed during differential scanning calorimetry measurements. Figure 4 presents the RDF of three calcination batches of the same MnSZ (0.5%) precursor taken ex situ at beamline X1. The only difference between these samples is the calcination batch size (3, 12, or 25 g) which has been found to be a critical parameter in the preparation of active catalysts [8]. The catalyst activity is greatest for the large batch, and correlates with the decrease observed here in the RDF maxima at about 3.3 Å. Further analysis of the data to determine structural details is ongoing. An additional implication of these results can be seen from the final RDF of the in situ calcination (<100 °C), which was by necessity obtained from an 8.7 mg batch, and which is clearly not comparable to the RDF of the most active catalyst which is obtained only through calcination of larger batches.

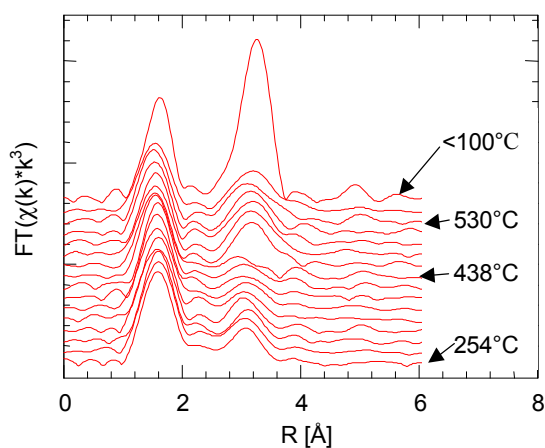


Figure 3: Zr K edge RDF of zirconium hydroxide precursor during calcination in flowing He. Temperature ramp was 254 °C – 530 °C at 10 °C/min. Data taken in transmission mode at beamline X1.

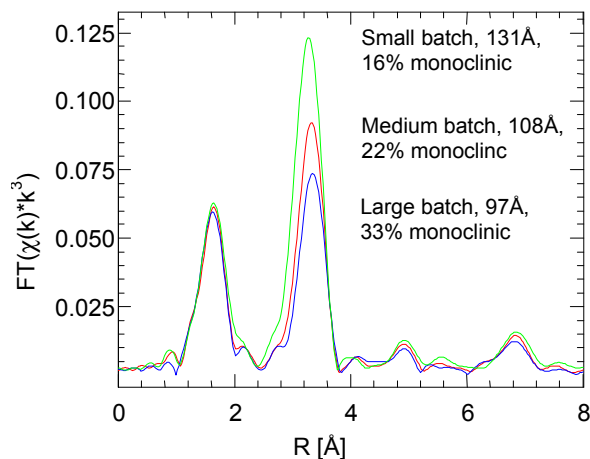


Figure 4: RDF of MnSZ (0.5%) samples calcined in different batch sizes. The samples are a mixture of monoclinic (% from XRD) and tetragonal (domain size from XRD) phases.



MAX-PLANCK-GESELLSCHAFT



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