

## Manganese, iron and sulfur K edge XAFS of promoted sulfated zirconia catalysts

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Promoted sulfated zirconia samples were prepared by the incipient wetness technique to produce isomerization catalysts which were active for the conversion of *n*-butane to isobutane at 338K (up to 10% conversion of 1% *n*-butane, 1atm., 0.25 h<sup>-1</sup> WHSV). The local structure of Fe and Mn in promoted sulfated zirconia was investigated using fluorescence yield XAS. Spectra were taken of calcined samples, activated samples, and samples after reaction with *n*-butane (maximum activity and deactivated). Factor analysis reveals that the Mn K edge XANES can be described by a linear combination of the spectra of two separate components, and that the ratio of these components changes with activation of the catalyst, and during use in the *n*-butane isomerization reaction. The change in ratio of the Mn species during activation and reaction results in a reduction of the average Mn valence from 2.4 to 2.2. The Fe K edge XANES was not similarly affected by activation and reaction with *n*-butane.

**Keywords:** sulfated zirconia, promoted, manganese, iron, XANES, principle component analysis, *n*-butane isomerization, catalysis.

### 1. Introduction

Sulfated zirconia (SZ) has been identified as being active for the isomerization of light alkanes, and iron- and manganese-promoted sulfated zirconia (FMSZ) is two orders of magnitude more active (Hsu et al., 1992). The isomerization activity of FMSZ is consistent with the presence of extremely strong acid sites and since the initial discovery of these materials there has been a great effort to identify these sites. Despite these efforts, no very-strongly-acidic sites have been identified (Umansky & Hall (1990), Adeeva et al. (1995), Spielbauer et al. (1996)). The inability to correlate activity to acid strength in promoted SZ has led to the search for an additional functionality in these catalysts. Ghenciu & Farcasiu (1996) have proposed a mechanism in which an oxidation function participates in the formation of a radical cation through a one-electron oxidation. The radical can then form surface esters or alkenes which could participate in chain reaction isomerization mechanisms. Wan et al. (1996) have proposed that iron oxide sites, some formed only through activation in air at temperatures above 735K, are responsible for oxidative dehydrogenation of *n*-butane to form butene which can then participate in chain reaction mechanisms on the acid sites formed by the sulfate. Some of these mechanisms may not be catalytic and it has been proposed that the high initial activity of promoted SZ may be due to non-catalytic reactions (Lange et al., 1996).

Recently Yamamoto et al. (1999) used in-situ XAS, Raman, and XRD in an investigation of Fe and/or Mn promoted sulfated and non-sulfated zirconia. They concluded that Fe oxide and Zr oxide always formed interstitial-type solid solutions, but that Mn was present as MnSO<sub>4</sub> on sulfated samples and as Mn<sub>2</sub>O<sub>3</sub> on unsulfated zirconia.

## 2. Experimental

### 2.1 Sample preparation

All samples were prepared from zirconium hydroxide, sulfated or non-sulfated, supplied by MEL (Manchester, UK). The hydroxide was first dried at 383K in static air for 21 hours. Promoters were added using the incipient wetness technique with aqueous solutions Mn II and/or Fe III nitrates. The impregnated hydroxides were dried at room temperature and then calcined in flowing 20% O<sub>2</sub> in N<sub>2</sub> (293-923K at 3K/min, holding at 923K for 3h, cooling at 3K/min). The calcined samples were stored under ambient conditions. The samples considered in this work are listed in Table 1.

Sample name	Nominal composition			Surface area, m <sup>2</sup> /g	Crystallite size, Å
	wt % Mn	wt % Fe	wt % S		
MnSZ	2	0	1.8	89	111
FeSZ	0	2	1.8	83	111
FMSZ	0.5	1.5	1.8	89	102
MnZ	2	0	0	-	84
FeZ	0	2	0	-	80
FMZ	0.5	1.5	0	-	75

Table 1: Nominal sample compositions, surface areas (BET) and zirconia crystallite sizes (XRD) for zirconia catalysts.

### 2.2 XRD

X-ray diffraction measurements were performed using a Stoe transmission diffractometer STADIP-P (Ge Primary monochromator, Cu-K<sub>α1</sub> radiation) with a curved position sensitive detector.

### 2.3 Catalyst testing

Samples were tested for activity in a once through plug-flow fixed-bed reactor with a sample loading of 500 mg. The samples were first activated in dry nitrogen (7K ramp to 723K, and held at 723K for 1.5h) and then cooled to the reaction temperature of 338K. The reactor feed was 1% *n*-butane in N<sub>2</sub> with a total flow rate of 80 ml/min at 1 atm (WHSV = 0.25 h<sup>-1</sup>).

### 2.4 X-ray absorption spectroscopy

The Mn K edge X-ray absorption measurements were performed in fluorescence mode at beamline E4, Hasylab, Hamburg, Germany (Si(111) double crystal monochromator). The fluorescence signal was measured with a five element Ge detector which was at 90° to the incident beam. The sample surface was at a 45° angle to the incident beam. In order to measure changes that occur in the samples when they were activated and reacted with *n*-butane, the powdered samples were used in a plug flow reactor as described in section 2.3 and removed at different stages of the catalyst's life: after activation, after the catalyst had reached maximum conversion and after 9h, when the catalyst was deactivated. The used samples were transferred from the reactor in an inert atmosphere to an oxygen-free dry box (< 1ppm H<sub>2</sub>O, < 1 ppm O<sub>2</sub>). All samples were mixed with powdered polyethylene and pressed into wafers (3.8 tons/cm<sup>2</sup>), for activated or reacted samples this was done in an inert atmosphere.

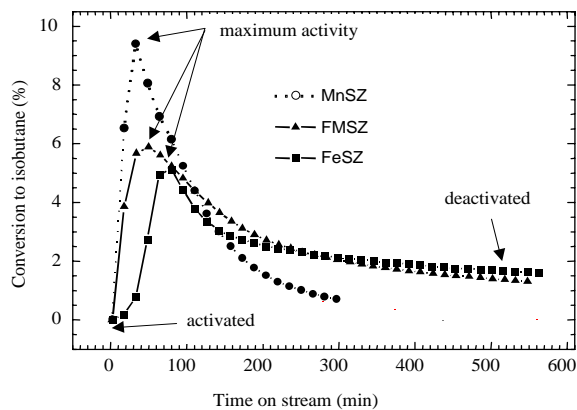
The XAS spectra were processed with the software package WinXAS v2.0. The fluorescence data of the Fe and Mn K edges were calibrated to the first root of the second derivative of the K edge of a Mn or Fe foil which was measured simultaneously in transmission mode. XAS spectra were normalized and principal component analysis (PCA) was performed on the XANES. Normalized spectra were converted to k-space with E<sub>0</sub> set at the

foil edge energy. The  $\mu_0(E)$  fit was performed using a cubic spline function (4 splines) between 1.8 and 8.5  $\text{\AA}^{-1}$ . The  $\chi(k)$  was windowed with a Bessel function from 2.2 - 8.4  $\text{\AA}^{-1}$  prior to Fourier transformation.

### 3. Results

#### 3.1 Catalysis Results

The reaction profiles for isomerization of *n*-butane to isobutane in the presence of the promoted SZ samples listed in Table 1 are presented in Figure 1. The non-sulfated samples were not active for the isomerization of *n*-butane under the conditions applied. The reaction profile for all 3 samples is similar. The conversion of *n*-butane to isobutane initially increases during an "induction" period to a maximum in conversion followed by deactivation. Of the three sulfated catalysts presented here MnSZ has the highest maximum conversion followed by the most rapid deactivation. FeSZ has the lowest maximum conversion and the least rapid deactivation, and the FMSZ catalysts is characterized by a reaction profile that is consistent with a simple weighted average of the profiles of the singly promoted catalysts.



**Figure 1.** Reaction profiles for the isomerization of *n*-butane to form isobutane. Arrows indicate time when samples were removed for XAS measurement. Conditions: 338K, 1% *n*-butane in nitrogen, 1 atm., 0.5 g catalyst, 0.25 WHSV.

#### 3.2 XRD

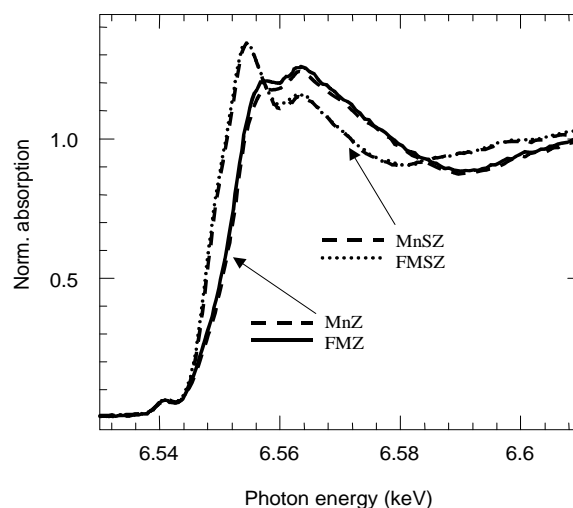
X-ray diffraction measurements (not shown) on the samples presented in Table 1 show that both the Mn and Fe stabilize the tetragonal phase of zirconia. The samples presented here are a mixture of tetragonal and monoclinic with the majority being tetragonal.

#### 3.3 Mn and Fe K edge XANES

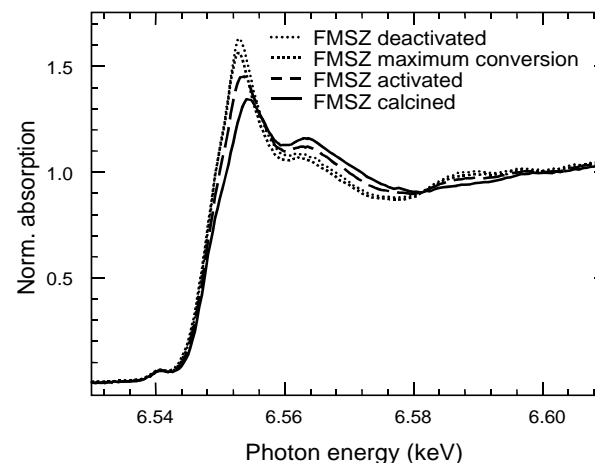
The Mn K edge XANES for the calcined manganese promoted samples with and without sulfate are presented in Figure 2. The XANES spectra for the sulfur containing samples are nearly identical for both MnSZ and for FMSZ, and are distinctly different from those of the samples which do not contain sulfate. The Mn K edge XANES for the activated, maximum activity, and deactivated FMSZ samples are presented in Figure 3. The spectra are characterized by a shift in the edge to lower energy and an increase in the intensity of the first maximum above the edge. Principle component analysis (PCA) of these spectra and XANES spectra of a set of 4 similarly treated MnSZ catalyst samples (not shown) indicate that there are two main components in the Mn K edge XANES for these samples. The PCA results

are corroborated by the isosbestic points at 6.556 and 6.582 keV in Figure 3.

The Fe K edge XANES (not shown) were the same for sulfated and non-sulfated samples and did not change after activation or reaction.



**Figure 2.** Mn K edge XANES comparing samples containing sulfate and samples without sulfate.



**Figure 3.** Mn K edge XANES comparing calcined FMSZ with FMSZ that was removed from the reactor after activation, after reaching maximum activity, and after 9h (deactivated). The circles indicate the positions of isosbestic points.

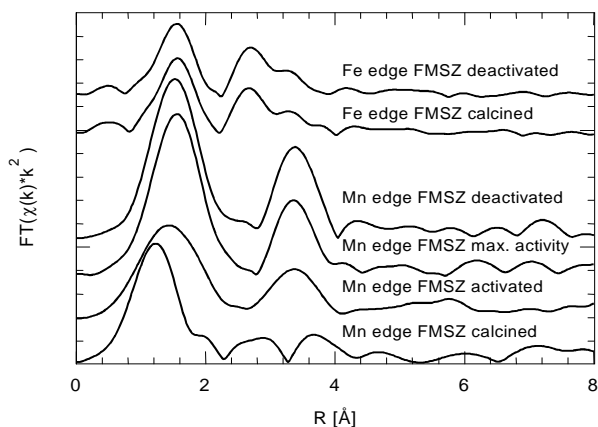
#### 3.4 Mn and Fe K edge EXAFS

The radial distribution function (RDF) for the Mn K edge for calcined, activated, maximum activity and deactivated FMSZ samples are presented in Figure 4. The initial maximum in the RDF of the calcined sample increases and becomes broader after activation, and increases further with some narrowing for the maximum activity sample. A second distinct maximum emerges after activation, and reaction. The RDF for the Fe K edge does not change during activation or reaction.

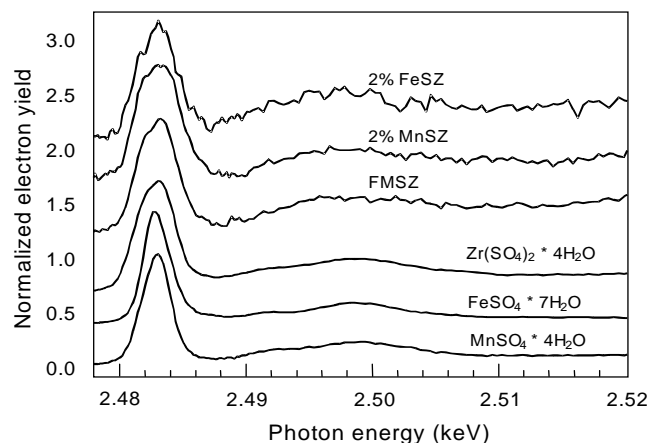
#### 3.5 S K edge XANES

The sulfur K edge XANES for MnSZ, FMSZ, and FeSZ are presented in Figure 5 along with several reference compounds. The spectra of all of the samples are similar, consisting of one broad doublet. The  $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  reference spectrum is similar

to that of the samples, the spectra of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$  both have much narrower edge features.



**Figure 4.** Radial distribution function for the Mn K edge of the calcined, activated, maximum conversion and deactivated FMSZ samples, and the Fe K edge RDF for calcined and deactivated FMSZ samples.

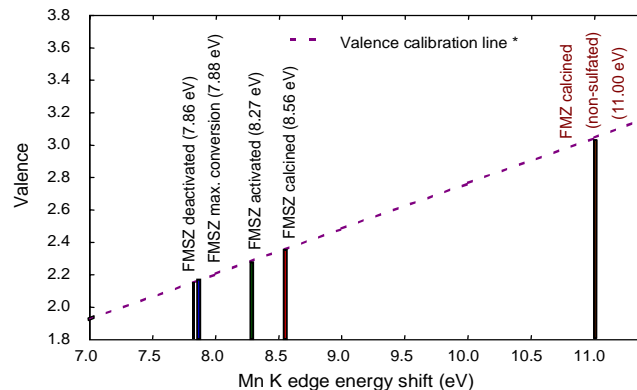


**Figure 5.** Sulfur XANES spectra of calcined sulfated samples and reference compounds. Spectra normalized to maximum of edge feature.

#### 4. Discussion

The reaction results indicate that all promoted SZ catalysts including FeSZ, MnSZ, and FMSZ are active for *n*-butane isomerization. The Mn K edge XANES of sulfated and unsulfated samples indicates that the presence of sulfate in the catalyst precursor effects the final state of the Mn in the calcined samples (Figure 2). Figure 3 shows that the Mn K edge shifts to lower energy when the calcined FMSZ sample is activated in dry  $\text{N}_2$ , and shifts further when the sample is exposed to *n*-butane until the catalyst reaches maximum activity. The Mn edge energy correlates with the Mn valence (Ressler et al. 1999), and Figure 6 shows this relationship as well as the values of the edge energy and corresponding average Mn valence for the samples presented in Figure 3. The effect of the addition of sulfate to the sample precursor is a change of the average valence of Mn in the calcined samples from 3 to about 2.4. Activation results in reduction the average Mn valence to about 2.3. The average valence of Mn in the samples that were reacted with *n*-butane and removed at the point of maximum activity or after deactivation was reduced even further to about 2.2. The two components revealed by PCA to be sufficient to describe the spectra of the FMSZ samples shown in Figure 3 as well as the spectra of

similarly treated MnSZ samples indicate that there are two different Mn species in the calcined samples. The changes in Mn valence as well as the isosbestic points visible in Figure 3 indicate that one of the Mn containing species is being converted into the other as FMSZ is being activated, and is being further converted as the catalyst reacts with *n*-butane.



**Figure 6.** Calibration line for Mn edge shift vs. valence

Finally, the sulfur K edge XANES seems to indicate that the majority of the sulfate is associated with zirconium, and not with either Fe or Mn. This is contrary to the findings of Yamamoto et al. (1999) who concluded that Mn in 0.5% MnSZ was present as  $\text{MnSO}_4$  on the zirconia surface. However, it is in agreement with the XPS results presented by Milburn et al. (1998) who found no evidence for Fe or Mn sulfates in an iron and manganese promoted sample.

#### 5. Conclusion

We have promoted SZ with Fe, Mn, and both Fe and Mn to produce catalysts active for *n*-butane isomerization. Mn K edge XANES indicates that there are two species of Mn in the calcined sulfated catalysts, and that one of these species is converted into the other during activation of the catalyst, and is converted further during reaction with *n*-butane. The change in the ratio of the Mn species results in a reduction of Mn valence from 2.4 to 2.2. The radial distribution function of the Mn edge also shows that during this reduction the local structure of the Mn changes. No changes were observed during activation or reaction in the Fe K edge XANES or in the Fe K edge radial distribution function.

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