

# Effects of *n*-Butane on Iron and Manganese in Promoted Sulfated Zirconia; Effect of Iron and Manganese on Zirconia

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Sulfated zirconia was promoted with 0.5-5.0 wt% Fe and/or Mn. These materials were tested for *n*-butane isomerization at 338K in a fixed bed flow reactor. The typical reaction profile of induction period, maximum, and deactivation was used to obtain samples at various states of activity. Mn K edge absorption spectra showed a decrease in the average oxidation state from 2.4 to 2.2 through the states "calcined", "activated", "maximum conversion", and "deactivated", suggesting redox reactions involving the Mn. Similar observations could not be made at the Fe K edge. X-ray diffraction revealed mixtures of tetragonal and monoclinic zirconia; or, at 5% promoter content, predominantly cubic zirconia. The stabilization of the cubic phase indicates [1] that Fe and Mn are partly incorporated in the zirconia bulk.

## 1. INTRODUCTION

The activity of sulfated zirconia (SZ) for the conversion of light hydrocarbons can be increased by the addition of transition metal promoters such as manganese, iron, nickel, or cobalt [2]. Promotion with iron *and* manganese (FMSZ) was found to be particularly successful, leading to an increase in *n*-butane conversion of two orders of magnitude [3]. Because it had already been claimed that SZ was a solid superacid [4], and because the FMSZ was more active and showed greater affinity for substituted benzenes in thermodesorption experiments [5] it was believed that these promoted materials were strongly acidic if not superacidic [3,5]. However, it has been found that probe molecules the size of benzene or pyridine do not desorb without decomposition [6,7], and probe molecule experiments with IR or NMR spectroscopy [8] have also failed to confirm the presence of strongly acidic sites. Alternatively, it was proposed that redox sites initiate the hydrocarbon isomerization through a dehydrogenation step [7]. An argument in favor of acidity as a key function of these materials is the observation that in the presence of FMSZ C<sub>2</sub>-C<sub>6</sub> alkanes undergo reactions typical of acid catalysis, i.e. isomerization, oligomerization (alkylation), and cracking reactions [9,10,11].

While the identification of active sites of sulfated zirconia remains in debate, it appears more likely that iron and manganese contribute to the hydrocarbon activation with a redox rather than an acid function. Although the Fe and Mn species in promoted sulfated zirconia have been characterized [e.g. 12] no correlation of their nature with the catalytic activity has yet evolved. The goal of this work was to use X-ray absorption spectroscopy (XAS) to identify the structural and electronic properties of Fe, Mn, and S in promoted sulfated zirconia and to follow changes occurring upon reaction with *n*-butane.

## 2. EXPERIMENTAL SECTION

*Sample Preparation:* Samples were prepared from hydrous zirconia (MEL XZO 632) and sulfated hydrous zirconia (MEL XZO 682), both kindly provided by Magnesium Elektron. After pre-drying for at least 20h at 383K, the powders were impregnated with solutions of Fe(III) nitrate and/or Mn(II) nitrate according to the incipient wetness method. Fe-promoted and Mn-promoted zirconias with and without sulfate (named FeZ, FeSZ, MnZ, MnSZ) were prepared with promoter concentrations of 0.1 - 5.0 wt% metal. For combined promotion, 1.5 wt% Fe and 0.5 wt% Mn were added (FMZ, FMSZ). For calcination, the samples were heated with 3K/min to 823 K (unpromoted) or to 923K (promoted) in 200ml/min flowing air; and these temperatures were held for 3h.

*Catalytic tests:* Activity for *n*-butane conversion was tested at 338K in a fixed bed once-through plug flow reactor made of glass with an inner diameter of 12 mm. Before reaction the samples were activated for 1.5 h at 723 K in a flow of N<sub>2</sub>. The *n*-butane partial pressure was 0.01 bar in N<sub>2</sub> and the total flow was 80 ml/min (NTP). Analysis of gas phase products was performed with on-line gas chromatography using flame ionization detection.

*X-ray absorption:* Mn and Fe K edge data were collected at HASYLAB, Hamburg, in the fluorescence detection mode; with the samples pressed into pellets. S K edge data were collected at SSRL, Stanford, in the electron yield mode; with the powders dusted on adhesive tape. Samples were removed from the reactor at different times on stream, corresponding to different states of activity of the materials. These samples were handled under inert conditions and mixed with polyethylene for pelletization before Fe and Mn XAS measurements, but were exposed to air before S XAS.

*Surface Area and X-ray diffraction:* Surface areas were determined with the BET method. X-ray diffraction measurements were conducted using a *STOE* transmission diffractometer *STADI-P* (Ge primary monochromator, Cu K<sub>α1</sub> radiation) equipped with a position sensitive detector. Crystalline phase identification based on XRD patterns was aided by the ICDD-PDF-2 database.

## 3. RESULTS

### 3.1. Appearance, surface area, X-ray diffraction

Mn-promoted samples were pink in the uncalcined and bluish-gray in the calcined state. Fe-promoted samples were ochre (uncalcined) or reddish (calcined). The color deepened with increasing promoter content. Fe- and Mn-promoted samples were grayish-brown. Typical surface areas were 75-95 m<sup>2</sup>/g.

Sulfated zirconias with a promoter content from 0–2 wt% (Fe or Mn) were mixtures of monoclinic and tetragonal zirconia; with the tetragonal fraction increasing with increasing promoter content and being >75 % at 2 wt%. The lattice constants of the tetragonal phase were found to vary up to 0.2 % with varying promoter content. At a promoter content of 5 wt% (Fe or Mn), the zirconia was cubic, and Fe<sub>2</sub>O<sub>3</sub> was detected in some cases but no crystalline Mn-phase. In situ XRD experiments with the 5 wt% promoter samples showed a transformation from cubic zirconia into the tetragonal phase above ~ 973K. Fe- and Mn-promoted samples were also mixtures of tetragonal and monoclinic zirconia, containing typically 60 to 90 % tetragonal phase. In most cases, sulfate-containing samples had a higher fraction of tetragonal zirconia than their sulfate-free counterparts.

### 3.2. Catalytic tests

All FeSZ, MnSZ, and FMSZ samples were significantly more active for *n*-butane isomerization than unpromoted SZ. These promoted samples were characterized by the reaction profile shown in Figure 1, consisting of a period of increasing conversion, a maximum in conversion, and a decline in activity. Mn-promoted sulfated zirconias reached the maximum conversion faster, i.e. within 20-50 min, than Fe-promoted samples (40-140 min). The selectivity towards isobutane was always >90%. Samples with 0.5 or 5 wt% promoter were less active than samples with 2 wt% promoter. A synergistic effect between Fe and Mn was not found.

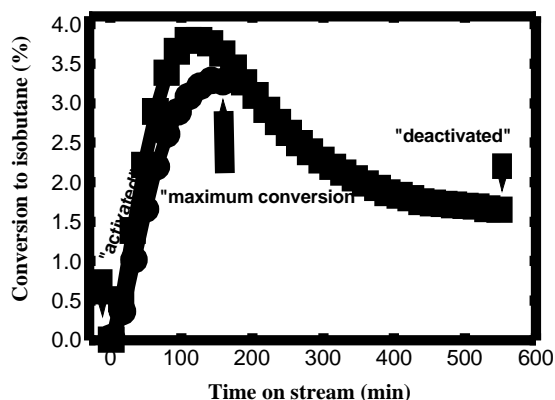


Figure 1. Conversion of *n*-butane to isobutane in the presence of FMSZ. 2 different runs with 1 sample. Arrows indicate sampling for XAS.

### 3.3. X-ray absorption

Mn K edge spectra of FMZ after calcination and of FMSZ after calcination, activation, and after reaction are presented in Figure 2. The edge energy of calcined FMZ and 2 wt% MnZ is about 3 eV lower than that of calcined FMSZ. Upon activation of the sample the Mn K edge of 2 wt% MnSZ and FMSZ is shifted to lower photon energies and still further after participation in the *n*-butane isomerization reaction. The Mn K edge energy is a linear function of the Mn valence [13], and the edge energy shifts of our samples are presented with a Mn valence calibration line, Figure 3, and show a reduction of the Mn valence from about 2.4 to 2.2 as FMSZ is activated and reacted. Fe K edge spectra for both FeZ, FeSZ, FMZ, and FMSZ are very similar, and FeSZ and FMSZ show no significant changes with the treatments.

Principal component analysis (PCA) of normalized XANES spectra of the Mn K edge in 2 wt% MnSZ and FMSZ indicates that there are 2 components in the spectra, and that one species is converted into the other during reaction. PCA of spectra of the Fe K edge in 2 wt% FeSZ and FMSZ suggests that, should several species be present, their ratio remains almost constant throughout the treatments. S K edge spectra bore the greatest similarity to a  $Zr(SO_4)_2$  reference.

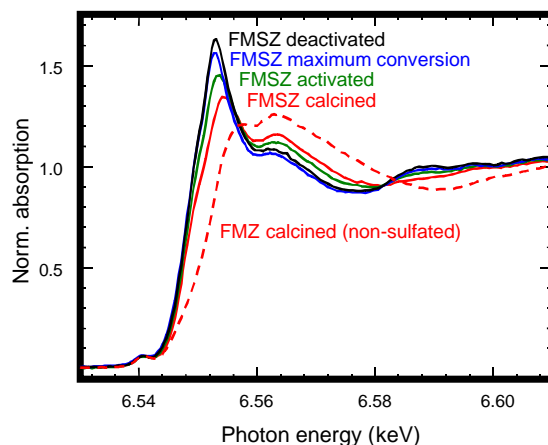


Figure 2: Mn K edge spectra of FMSZ at different states of activity, and of FMZ.

## 4. Discussion

Stabilization of the cubic phase of zirconia at 5 wt% promoter content is consistent with the incorporation of a fraction of the promoter ions in the zirconia bulk. Stabilization of the tetragonal phase at 2 wt% promoter content may also be attributed to incorporation of promoter ions in zirconia. The same

behavior, i.e. stabilization of the tetragonal phase at low, and of the cubic phase at high dopant concentration, is observed for  $\text{Y}_2\text{O}_3$ -doped  $\text{ZrO}_2$  [14].

Consistent with the presence of 2 components, one of which is in the zirconia bulk, Mn K edge XANES and EXAFS could not be assigned simply to Mn sulfates or oxides. The incorporation of Mn also offers an explanation as to why Mn in FMSZ is difficult to detect with XPS [12]. Fe K edge EXAFS analysis of FeZ, FeSZ, FMZ, and FMSZ suggests the presence of  $\text{Fe}_2\text{O}_3$  and of a second phase, possibly the incorporated ions. The presence of 2 species is supported by the shape of the XANES. This picture is more complicated than what Yamamoto et al. [15] have proposed, i.e. incorporation of Fe ions (FMSZ, FeSZ) and the presence of Mn as  $\text{MnSO}_4$  (FMSZ, MnSZ).

The shift of the Mn valence demonstrates that there are oxidation/reduction reactions occurring on the catalyst which reduce Mn during activation and *n*-butane isomerization. A lack of change in the Fe K edge under the reaction conditions applied here does not support previously suggested oxidation/reduction reactions involving an Fe species.

The incorporation of Fe and Mn into the zirconia bulk suggests a second possibility for understanding the promotional effect: Besides the possibility of direct interaction with the alkane, the promoters alter the properties of the zirconia bulk, and this modified zirconia (surface) may play a key role in activity.

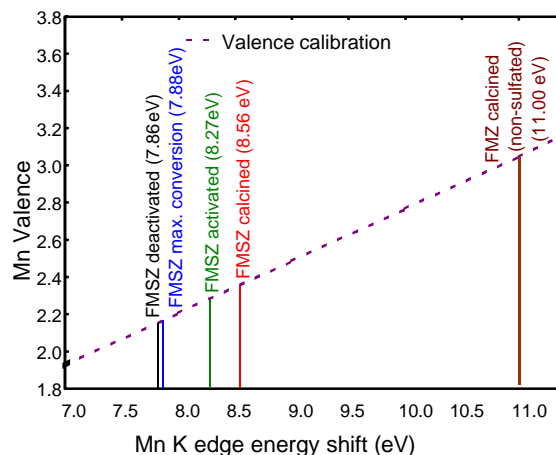


Figure 3: Mn K edge energy shift of FMSZ at different states of activity, and of FMZ.

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