

X-ray absorption studies of iron- and manganese-promoted sulfated zirconia: evidence of redox reactions

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Branched hydrocarbons are more valuable than straight chain hydrocarbons as both feed stocks for the chemicals industry, and for replacement of carcinogenic, or potentially carcinogenic automobile fuel constituents. The increasing demand for branched light hydrocarbons has driven interest in improving light hydrocarbon isomerization catalysts, which are typically acid catalysts. Branched isomerization products are thermodynamically favored at low temperatures and so extremely strong acid catalysts are favored for their high activity at low temperatures. The current industrial technology uses solid acid catalysts that are corrosive and pose disposal problems. Sulfated zirconia based materials have been identified as possible alternatives, being extremely active for light hydrocarbon isomerization, and promoting sulfated zirconia with iron and manganese increases the rate of isomerization over that of unpromoted sulfated zirconia by several orders of magnitude allowing for the room temperature isomerization of *n*-butane [1].

Product distributions for light hydrocarbon isomerization with iron- and manganese-promoted sulfated zirconia (FMSZ) suggest acid catalyzed reactions; however, despite extensive study, no measure of the acidity can be found that correlates with the high activity. More recently it has been proposed that the high activity may be due to oxidation/reduction reactions involving the promoter oxides [2]. It may in fact be the case that the high activity observed with FMSZ is not catalytic, but instead the activity may be due to stoichiometric reactions with the FMSZ surface. Our goal is to investigate the nature of the Mn and Fe species in the promoted sulfated zirconia catalyst.

FMSZ is prepared by impregnation of sulfated zirconium hydroxide with iron and manganese nitrate solutions. The impregnated hydroxide is then heated in flowing air at 650°C, 2h, (calcined). The calcined sample, after storage in air, is activated by heating in dry nitrogen to 450°C just prior to reaction. For low temperature light hydrocarbon isomerization on FMSZ the reaction profile typically shows a period of increasing conversion (induction period), followed by a maximum in conversion, and then decreasing conversion or deactivation, Figure 1. The increase in activity suggests that there are changes at the catalyst surface; either the production of active sites in the catalyst or the formation of an active species adsorbed on the catalyst surface. We have analyzed samples from all stages of preparation and reaction: calcined, activated but not reacted, and after use for the isomerization of *n*-butane at maximum conversion, and after

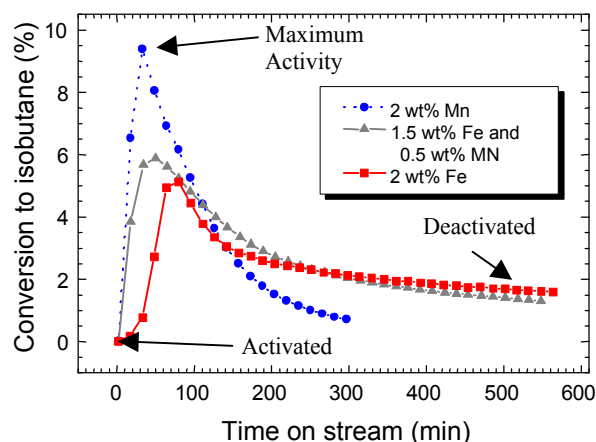


Figure 1. Reaction profile for conversion of *n*-butane to isobutane at 65°C with promoted sulfated zirconia catalysts. Arrows indicate stage of reaction at which samples were removed for pelletization with PE and later analysis.

deactivation. Activated or reacted samples were mixed with polyethylene and pressed (10 tons, 2 cm

diameter) into wafers, without exposure to air or water, for transport to beamline E4 where both the Fe K edge (7.1 keV) and the Mn K edge (6.5 keV) absorption spectra were measured in fluorescence mode using a 5 element Ge detector at a 90° angle to the beam.

XANES spectra of iron- and manganese-promoted zirconia (FMZ) after calcination and of FMSZ after calcination, activation, and after reaction are presented in Figure 2. The Mn K edge energy is about 3 eV lower for FMSZ than for the FMZ sample. The Mn K edge of the FMSZ sample is shifted to even lower energy by activation of the sample and still further after participation in the *n*-butane isomerization reaction. The Mn K edge energy is a linear function of the Mn valence [3], 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 the FMSZ sample is activated and reacted. XANES spectra of the Fe K edge for both sulfated and non-sulfated samples (not shown) have no discernable pattern to correlate with sample treatments.

Principal component (PC) analysis of normalized XANES spectra of the Mn K edge indicates that there are 2 components in the spectra when all promoted sulfated samples were included in the analysis, and indicates that there are 3 components when non-sulfated promoted zirconia samples were included in the analysis. No reference oxides or sulfates of Mn have yet been identified which match the components in these spectra. PC analysis of the Fe K edge XANES spectra indicate the presence of 3 components in the spectra with or without the sulfated samples.

We can conclude from these results that there are oxidation/reduction reactions occurring on the catalyst which reduce the Mn valence after activation and after use for *n*-butane isomerization. PC analysis indicates that the Mn reduction does not form a new phase, but instead it seems that one of the existing phases is converted to another. The strong effect of the addition of sulfate on the oxidation state of Mn in the calcined samples indicates a close association between sulfate and Mn. The Fe K edge was not greatly affected by the addition of sulfate, and did not show much change during reaction, giving no evidence to support previously suggested [2] oxidation/reduction reactions involving an Fe species. The EXAFS spectra for both the Mn and Fe edges are currently being fit using WinXAS software [4].

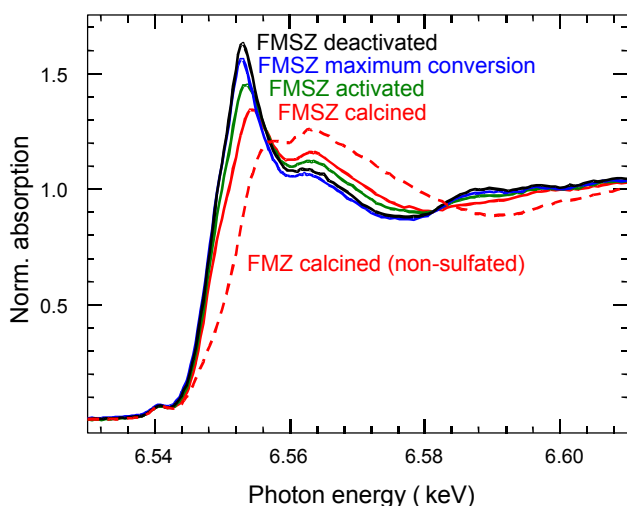


Figure 2. XANES spectra of FMSZ sample taken at different stages of activation and reaction (*n*-butane isomerization at 65°C) as indicated, solid lines. Non-sulfated sample, dashed line.

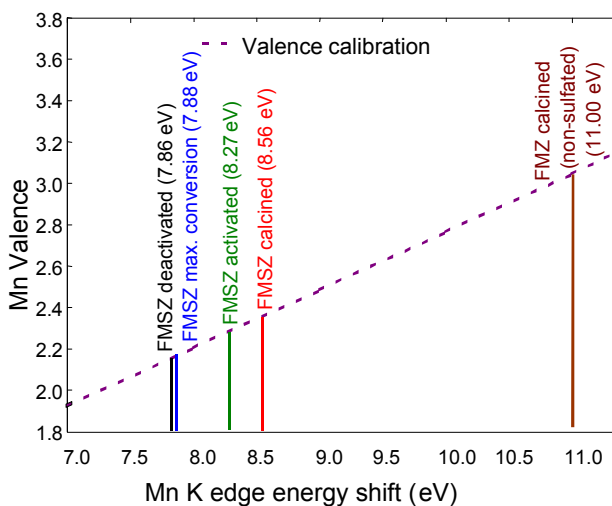


Figure 3. Mn K edge energy shift for samples presented in Figure 2 plotted with Mn valence calibration relationship, dashed line [4].

We would like to thank Robert Nietubyc for his assistance at beamline E4 and Gisela Lorenz for her assistance with sample preparation.



References

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