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## Introduction

Promotion of sulfated zirconia (SZ) with manganese and/or iron results in an enhancement of its maximum alkane isomerization activity by 1-2 orders of magnitude [1, 2]. The role of the promoters was first seen in an increase of acidity [3], but this assumption was soon questioned [4]. Further ideas concerned a redox function of the promoters with oxidative dehydrogenation as an initial reaction step [4]. Here, we present measurements on the oxidation state of Mn during *n*-butane isomerization that shine new light on the question of a redox function of this promoter. Furthermore, characterization of the promoters, the zirconia, and the sulfate reveal a complex interplay between all three components.

## Experimental

Catalysts were produced from a sulfated precursor (MEL Chemicals XZO 682/01). Solutions of Mn(II) or Fe(III) nitrates were added according to the incipient wetness method in amounts corresponding to 0.5–5 wt% promoter in the final catalyst. Calcination was conducted in 20 g batches in air flow at 823 K or 923 K, with a heating rate of 3 K/min and a 3-h holding time. *n*-Butane isomerization was performed at 323, 333, or 378 K in either a tubular flow reactor or an in situ flow cell [5], using a fixed bed of 500 mg catalyst activated at 723 K in various atmospheres, 1 kPa *n*-butane in inert gas, and a total flow of 80 ml/min. X-ray absorption spectra at the Mn-K edge, whose position is correlated to the Mn valence [6], were obtained at HASYLAB beamline E4 in fluorescence mode. X-ray diffractograms were recorded in transmission geometry with a STOE STADI-P diffractometer using Cu K $\alpha$  radiation. Electron paramagnetic resonance (EPR) was performed with a JEOL JES-RE2X system at X-band frequency, and ion scattering spectroscopy (ISS) with a Leybold LHS 12 MCD instrument with a hemispherical analyzer, using 2 keV He<sup>+</sup> ions. For thermogravimetry (TG, Netzsch STA 449) samples were heated in Ar to 1373 K at 10 K/min, held at 1373 K for 30 minutes, and then cooled at 10 K/min to 473 K. Gas phase products were analyzed by MS.

## Results and Discussion

X-ray absorption spectra taken in situ after activation at 723 K in inert gas show the initial oxidation state of a 2 wt% Mn-promoted SZ catalyst to be about 2.5. The method gives an average oxidation state, suggesting the presence of Mn(II) as well as of higher oxidation states. In the subsequent isomerization reaction at 333 K, a typical reaction profile was observed: the rate first increased for 20 min, then reached a maximum and then rapidly declined within 60 min to a relatively stable conversion. The Mn valence, however, remained unchanged. Variation of the activation or regeneration atmosphere allowed tuning of the Mn valence prior to reaction. Seemingly, an interesting correlation emerged showing an increasing maximum rate with increasing initial Mn valence. As there was no correlation between isomerization rate and the Mn valence during reaction, the initial Mn valence may just reflect a certain state of the catalyst and Mn itself may not be directly involved in the reaction.

The catalysts were characterized using X-ray diffraction, ISS and EPR. Stabilization of the tetragonal phase in the presence of Fe or Mn and an increasing contraction of the lattice given by a shrinkage of the lattice parameter  $c$  with increasing Mn content suggest incorporation of the promoters into the zirconia lattice. The formation of such solid solutions has been reported and is often the result of a preparation by co-precipitation. Further evidence for the incorporation of Mn or Fe was given by EPR data, which showed the presence of isolated  $\text{Mn}^{2+}$  or  $\text{Fe}^{3+}$  ions in a highly symmetric environment as expected only inside a crystal. The highly surface sensitive ISS measurements did not detect Mn but did detect Fe on the surface of samples with 2 wt% promoter content. All data consistently showed that both promoters are incorporated into the lattice and are stabilizing the – catalytically more favorable [7] – tetragonal phase. While there were clearly Fe surface species at typical promoter content of 2 wt%, Mn appeared more or less completely incorporated, raising doubts about a direct involvement in isomerization. As the promoted SZ catalysts are more active than purely tetragonal SZ, there should be an additional effect beyond mere phase stabilization. An explanation that would encompass many promoter cations is the formation of oxygen vacancies in the zirconia lattice as compensation of the lower valence of the promoter with respect to zirconium. Near the surface, such vacancies can create highly unsaturated sites. The above XAS results also imply that the bulk of zirconia is not inert during activation, because a large fraction of the (incorporated) Mn can change its oxidation state.

TG profiles were characterized by 3 events: (i) water loss at about 365 K, endothermic and typically amounting to 3.4–4.6 %, (ii) nearly heat-neutral 3.3–3.8 % weight loss at about 1080 K corresponding to decomposition of sulfate to give  $\text{SO}_2$  and  $\text{O}_2$ , and (iii) a very small weight loss of only about 0.1–0.2%, which occurred either towards the end of the heating phase (promoted SZ) or in the cooling phase (unpromoted SZ). This last weight loss coincided with the detection of  $\text{SO}_2$  in the off-gas and a sharp exothermic peak in the DTA curve. A minority of the total sulfate is obviously thermally very stable: the decomposition temperatures reached 1200 K or more for the promoted SZ samples; for SZ the event occurred at 980 K but after holding the sample for 30 min at 1373 K. All samples were monoclinic after the TG experiment, the exotherm was thus ascribed to the transition of tetragonal to monoclinic zirconia. Obviously, the minority sulfate species is less stable in presence of the promoters.

## Conclusions

Depending on the method of preparation and the content, the promoters Fe and Mn are present as a species incorporated into the lattice of zirconia and as a surface species. Mn is more easily incorporated than Fe, and can be predominantly incorporated at a content of 2 wt%. Nevertheless it can change its oxidation state, showing participation of the zirconia bulk. Although the Mn valence after activation seems to predetermine the maximum isomerization rate, no correlation of valence and actual performance exists. An additional effect of both promoters is to render a minority of the sulfate less stable. As main function of the promoters emerges thus not direct involvement in the isomerization reaction but modification of the base components of the catalyst.

## References

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