

B.S. Klose, R.E. Jentoft, T. Ressler, P. Joshi, A. Trunschke, R. Schlögl, F.C. Jentoft;  
Department of Inorganic Chemistry; Fritz Haber Institute of the Max Planck Society,  
Faradayweg 4-6, 14195 Berlin; Germany; email: jentoft@fhi-berlin.mpg.de

## Deactivation and Regeneration of Mn-Promoted Sulfated Zirconia Alkane Isomerization Catalysts: An In-Situ Spectroscopic Study

### Abstract

Mn-promoted sulfated zirconia (0.5 or 2 wt% Mn) was investigated during activation (in inert or oxidizing atmosphere at 703–773 K), during *n*-butane isomerization (323–333 K, 1 kPa *n*-butane) and during regeneration (see activation conditions) using in situ UV–vis–NIR, diffuse reflectance IR, and X-ray absorption spectroscopies. While the activation atmosphere did not influence the degree of hydration and the state of the sulfate, manganese—which was always present as a mixture of  $\text{Mn}^{2+}$  and higher oxidation states—was slightly reduced in the absence of oxygen. Catalytic data did not give a clear picture as to whether activation in oxygen-containing atmosphere is advantageous or not. The catalysts deactivated within hours, but complete recovery in  $\text{O}_2$  was possible. Heating of a deactivated catalyst in  $\text{N}_2$  produced an inactive material and unsaturated compounds on the surface.

**Keywords:** low temperature alkane isomerization, deactivation, sulfated zirconia, manganese, in situ, diffuse reflectance, IR, UV–vis–NIR spectroscopy, XAFS, *n*-butane

### Introduction

Sulfated zirconia (SZ) is a highly active catalyst for the skeletal isomerization of light alkanes, e.g. *n*-butane can be converted to isobutane at room temperature [1]. The activity can be further enhanced through addition of transition metal cations; particularly effective promoters are ions of iron and manganese [2,3]. When SZ was discovered, its activity was believed to arise from superacidic properties. Probe molecule experiments, however, revealed only strongly acidic sites on SZ [4]; and, moreover, promoters were found not to increase the acidity [4,5]. Later, it was proposed that with the promoters, a redox function is introduced [6,7]. The first reaction step was then suggested to be oxidative dehydrogenation (ODH) resulting in a butene [6], which is easily protonated to a carbenium ion, which in turn serves as a reaction chain carrier. If such an ODH mechanism occurred, water would have to be formed and a catalyst component—such as the promoter [8], zirconium [9], or sulfate

[9]—would have to be reduced. If no pathway for reoxidation exists, the reduction would be a non-catalytic step and would contribute to deactivation, which can be severe with SZ catalysts. Understanding of the reaction mechanism and identification of suitable activation and regeneration procedures require application of several in situ methods, i.e. the oxidation state of the promoter, the nature of the surface sulfur species, and the potential formation of water have to be monitored during the catalytic reaction. Here, we selected a system promoted with manganese ("MnSZ") and applied in situ diffuse reflectance IR spectroscopy (DRIFTS) to analyze for water and sulfate vibrations, in situ UV–vis–NIR spectroscopy to identify individual manganese species and monitor water content, and in situ X-ray-absorption fine structure spectroscopy (XAFS) to determine the average manganese valence. For evaluation of the role of the catalyst oxidation state, oxidizing as well as inert conditions were employed in activation and regeneration procedures. Isomerization of *n*-butane at 323–333 K was used as a test reaction.

## Experimental

Mn-promoted SZ catalysts with 0.5 or 2 wt% Mn were produced from dried sulfated zirconium hydroxide (MEL Chemicals XZO 682/01) via incipient wetness impregnation with a solution of  $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (Merck, p.a.). After drying at room temperature, the raw materials were calcined in 20 g batches in a stream of 200 ml/min synthetic air with a 3 K/min heating rate and a 3 h holding time at 923 K [10]. In situ DRIFTS was conducted using a Graseby-Specac "Selector" attachment with "Environmental Chamber" placed in a Bruker ifs 66 spectrometer. About 150–185 mg of catalyst were loaded into a gold cup. In situ UV–vis–NIR spectra were acquired with a PerkinElmer Lambda 9 spectrophotometer and a Harrick Praying Mantis™ diffuse reflectance attachment type DRA-4-PE7 with a HVC-DR3 reaction chamber. About 160–200 mg of catalyst were supported on a stainless steel grid. Reflectance reference materials were KBr (IR) and Spectralon® (UV–vis–NIR). Product analysis for IR and UV–vis experiments was performed by on-line gas chromatography (Varian 3800, flame ionization detection). XAFS spectra were taken in fluorescence mode at the Hamburg Synchrotron Radiation Laboratory beamline E4 using a fixed-bed flow-through reactor of in-house design [11] charged with 500 mg of catalyst. Product analysis was performed using on-line mass spectrometry (Pfeiffer

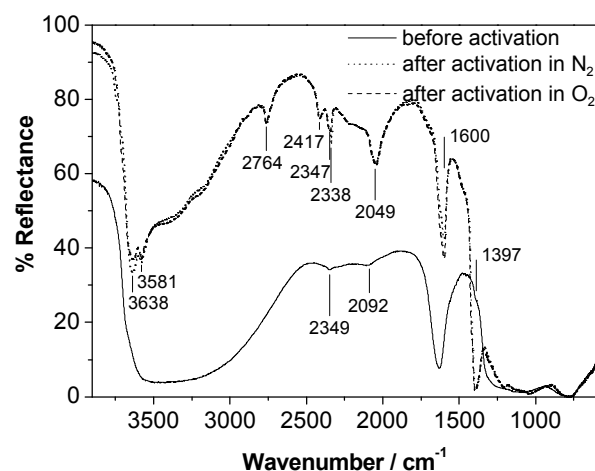
Omnistar®). All experiments were done in flow at atmospheric pressure. Activation and regeneration were performed at 703 K (XAFS) or nominal 773 K (DRIFTS; UV-vis–NIR) in inert (N<sub>2</sub> or He) or oxidizing atmosphere, and reactions were conducted at 323–333 K at 1 kPa *n*-butane and flows between 20 and 80 ml/min.

## Results and discussion

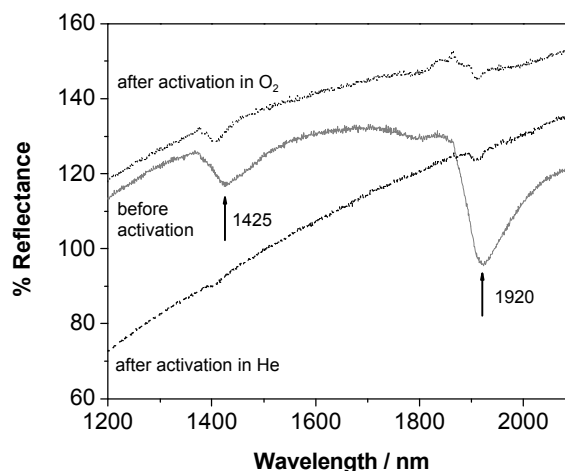
### *Catalyst activation*

Fig. 1 shows DRIFT spectra of MnSZ before and after activation in N<sub>2</sub> or O<sub>2</sub>. The spectrum of the calcined hydrated catalyst is dominated by bands of adsorbed water (stretching vibrations with hydrogen bonding contributions in the range 3700–3000 cm<sup>-1</sup> and bending vibration at 1630 cm<sup>-1</sup>). After activation, the catalyst is largely dehydrated and the spectrum shows defined bands of the surface sulfate groups (overtone and combination modes at 2764, 2417, 2347 and 2049 cm<sup>-1</sup>, fundamentals at 1397 and 1045 cm<sup>-1</sup>). Comparison of the spectra obtained after activation in inert gas or O<sub>2</sub> reveals slight differences in the OH vibrations but otherwise identical spectra; i.e. the state of the functional groups appears to depend mainly on the degree of hydration. This is essentially confirmed by the NIR spectra after activation in inert gas or O<sub>2</sub> in Fig. 2, which show an overtone of the OH stretching band (1425 nm ≈ 7020 cm<sup>-1</sup>) and a combination mode of OH stretching and bending mode (1920 nm ≈ 5210 cm<sup>-1</sup>). These bands of adsorbed water are diminished during the activation, independent of the atmosphere. After activation in He, a broad absorption due to Mn species extends into the NIR range. The UV-vis spectra of MnSZ, shown in Figs. 3 and 4 show one strong absorption located at 320 nm and at least two overlapping bands with maxima at about 555 and 690 nm. The band at 320 nm can be assigned to a charge transfer from O<sup>2-</sup> to Mn<sup>3+</sup> [12], the band around 555 nm to a d-d transition of Mn<sup>2+</sup> or Mn<sup>3+</sup> [13] and the band at the highest wavelength to a d-d transition of Mn<sup>3+</sup> [14]. Mn<sup>2+</sup> d-d transitions are spin-forbidden [13] and should be weak; however, such transitions should contribute to the spectra because the average Mn valence in these catalysts according to XAFS is around 2.65 [15]. The intensity of the d-d bands decreases with increasing temperature and broadening lets them appear to be one band. Inert or oxidizing activation atmospheres exert different effects on the Mn species (Figs. 3 and 4). In O<sub>2</sub> (Fig. 4), the spectral features remain essentially the same as those of the calcined catalyst with some weakening of the

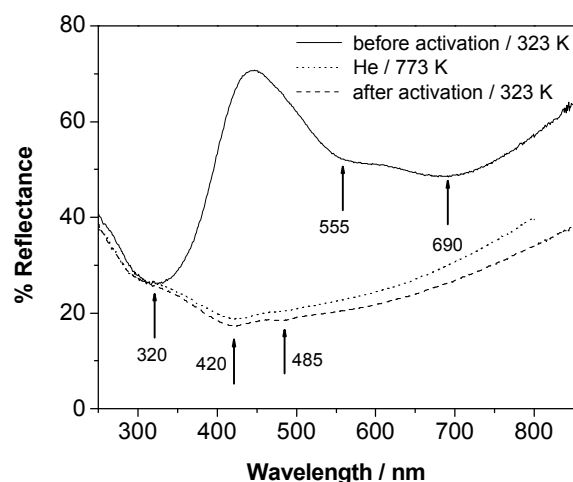
band at 690 nm. However, in He (Fig. 3), a very broad absorption over the entire UV–vis range evolves with two weakly pronounced maxima at 420 and 485 nm. The band at 420 nm is characteristic of  $\text{Mn}^{2+}$  in octahedral environment [16], the band at 485 nm has been reported for  $\text{Mn}^{2+}$  ( $\text{MnO}$ , [16]) and for  $\text{Mn}^{3+}$  ( $\text{Mn}_2\text{O}_3$  [12]).



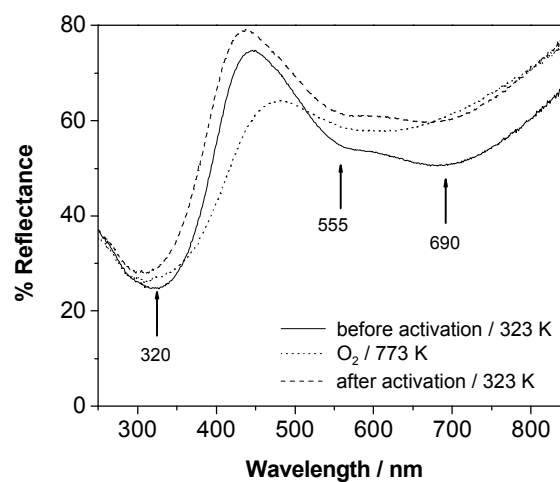
**Figure 1:** DRIFT spectra of MnSZ (2 wt% Mn) before and after activation at 773 K in flowing  $\text{O}_2$  or  $\text{N}_2$ .



**Figure 2:** NIR spectra of MnSZ (0.5 wt% Mn) before and after activation at 773 K in flowing  $\text{O}_2$  or He, all recorded at 323 K.



**Figure 3:** UV–vis spectra of MnSZ (0.5 wt% Mn) before activation, at 773 K, and after cooling to 323 K, all in flowing He.



**Figure 4:** UV–vis spectra of MnSZ (0.5 wt% Mn) before activation, at 773 K, and after cooling to 323 K, all in flowing  $\text{O}_2$ .

Given the treatments and additional information from XAFS [11,15], which indicates a change of the average valence from 2.65 to 2.48 through treatment at 703 K in He, the following consistent picture can be derived from all three methods: In its initial state, i.e. after calcination and exposure to ambient conditions, the catalyst contains  $\text{Mn}^{2+}$  and (more)  $\text{Mn}^{3+}$  and adsorbed water. Activation in  $\text{O}_2$  only dehydrates the catalyst, while activation in He additionally leads to partial reduction of manganese (formation of new species  $\text{Mn}^{2+}$ ). The state of the functional groups (hydroxyls,

sulfate) is identical for both activation gases and thus not affected by the change in the Mn oxidation state, suggesting that these functional groups are not in any way associated with the Mn. This observation is perfectly consistent with the idea of predominant incorporation of Mn in the zirconia lattice in form of a solid solution [17].

#### *Influence of activation conditions on catalytic performance*

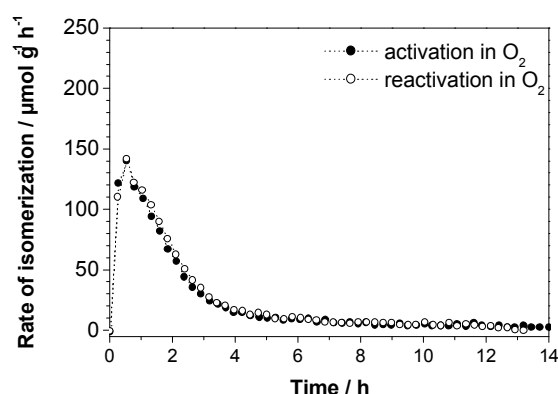
Wan [6] and Song and Kydd [18] have reported that promoted catalysts are more active after activation in oxidizing conditions, which was seen as evidence for an ODH initiation reaction. Our data point towards a more complex relationship between performance and activation. With time on stream, the catalysts first pass through a phase of rapidly increasing conversion (induction period), then through a conversion maximum followed by partial deactivation to a steady state (Figs. 5 and 7). MnSZ (2 wt% Mn) activated in inert gas exhibits a maximum isomerization rate of 185  $\mu\text{mol}/(\text{g}\cdot\text{h})$ ; activation in 100%  $\text{O}_2$  only yields a maximum rate of 140  $\mu\text{mol}/(\text{g}\cdot\text{h})$ . These different rates were obtained with the samples whose DRIFT spectra were almost identical after activation (Fig. 1). However, in situ UV–vis spectra indicate reduction of Mn in inert gas (Fig. 3), and the combination of these results suggests that reduction of  $\text{Mn}^{3+}$  to  $\text{Mn}^{2+}$  should be advantageous. On the other hand, according to a series of in situ XAFS data, a higher maximum rate is achieved with higher average Mn valence at the start of the reaction within the range 2.36 to 2.69. This correlation was obtained with a maximum  $\text{O}_2$  content of 50%. It appears that an oxidizing atmosphere may exert positive and negative effects, and the oxygen partial pressure and the exact heating conditions determine the resulting state and thus the activity of the catalyst.

#### *Spectral changes during *n*-butane isomerization*

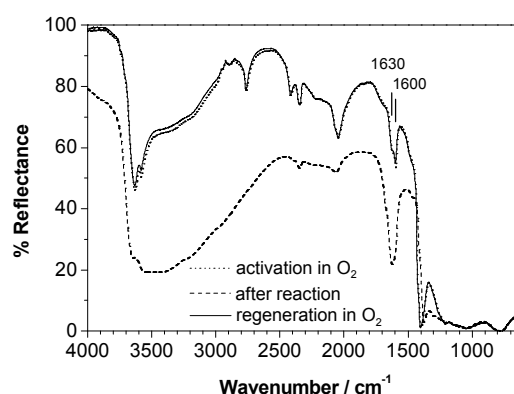
Large sections of the DRIFT spectra recorded during *n*-butane isomerization are dominated by the intense bands of gaseous butane. An overall decrease in the reflectivity of the material is observed, which makes it difficult to create meaningful difference spectra. With increasing time on stream, bands at ca. 1630 and 1600  $\text{cm}^{-1}$  increase in intensity (Figs. 6 and 8). These bands, which grow fastest during the induction period, could represent the bending mode of water or C=C stretching vibrations. As no further evidence for unsaturated compounds (corresponding CH

vibrations) could be found, water, so far, seems the more likely explanation. Water has been proposed to have a poisoning effect on the catalyst [9,19] but we found that minor changes in the degree of hydration do not affect the catalytic performance. The S=O vibration initially at ca.  $1400\text{ cm}^{-1}$  is shifted to lower wavenumbers during the isomerization. The total area of the bands at  $1600\text{--}1630\text{ cm}^{-1}$  and the downward shift of the S=O band are linearly correlated, indicating interaction between sulfate and the newly forming surface species (presumably water). A further, not yet identified, band evolves at  $1307\text{ cm}^{-1}$ . The general development of the spectra during reaction appears to be independent of the pretreatment of the catalyst. This is different for the evolution of XAFS spectra with time on stream. During isomerization, the average Mn valence does not change when the catalyst has been activated in inert gas, but there is an almost linear and thus non-performance related decrease of the valence after the catalyst has been activated in 50%  $\text{O}_2$ . In summary, neither the results of the in situ XAFS spectroscopy nor the effect of activation in various atmospheres support the idea of an ODH initiation reaction with the promoter manganese as oxidizing agent.

### Catalyst regeneration



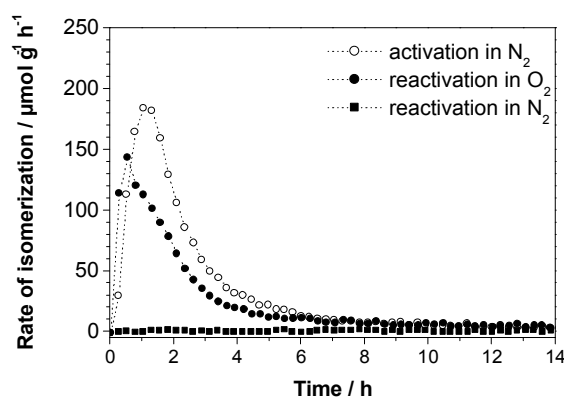
**Figure 5:** Rate of isomerization of *n*-butane vs. time on stream. MnSZ (2 wt% Mn), 323 K, 1 kPa *n*-butane, 30 ml/min flow at atmospheric pressure. Activation and regeneration at 773 K for 30 min in  $\text{O}_2$  flow.



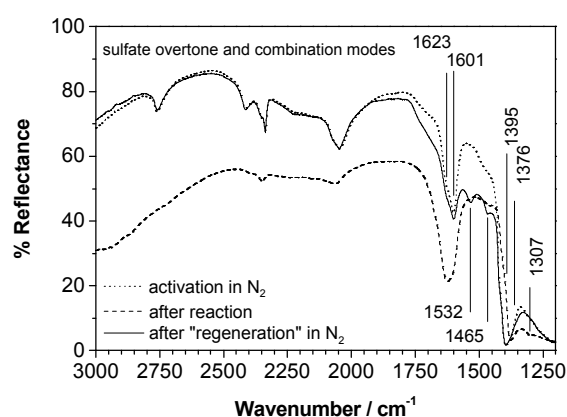
**Figure 6:** DRIFT spectra of MnSZ (2 wt% Mn) recorded at 323 K. Activation and regeneration at 773 K for 30 min in  $\text{O}_2$  flow. “After reaction” corresponds to 16.5 h on stream at 323 K and 1 kPa *n*-butane followed by 1 h purging in  $\text{N}_2$ .

Complete recovery of the catalyst's activity is possible by treatment in  $\text{O}_2$  at 773 K as can be seen from Fig. 5. Also, the spectrum of the catalyst is equivalent to that of the activated catalyst (Fig. 6). After “regeneration” in  $\text{N}_2$ , the catalyst is totally inactive (Fig. 7). This behavior can be understood with the help of the DRIFT spectra in Fig.

8. Treatment of the deactivated Mn-promoted sulfated zirconia catalyst at 773 K in N<sub>2</sub> causes the appearance of two new bands at 1532 and 1465 cm<sup>-1</sup>. The band at 1532 cm<sup>-1</sup> can be assigned to C=C double vibrations conjugated with other double bonds, e.g. in an aromatic ring. The band at 1465 cm<sup>-1</sup> is relatively unspecific and can arise from the C-H bending modes of methyl or methylene groups, which may be attached to carbon or oxygen atoms. Assignment to an aromatic ring is also possible.



**Figure 7:** Rate of isomerization of *n*-butane vs. time on stream. Conditions: MnSZ (2 wt% Mn), 323 K, 1 kPa *n*-butane, 30 ml/min flow at atmospheric pressure. Activation and regeneration at 773 K in N<sub>2</sub> or O<sub>2</sub> flow.



**Figure 8:** DRIFT spectra of MnSZ (2 wt% Mn) recorded at 323 K. Activation and regeneration at 773 K for 30 min in N<sub>2</sub> flow. “After reaction” corresponds to 16 h on stream at 323 K and 1 kPa *n*-butane followed by purging in N<sub>2</sub>.

Species with C=C bonds on the surface of the catalyst after reaction and heating in N<sub>2</sub> can only be explained by the presence of adsorbed hydrocarbon species at the end of the catalytic reaction. On sulfated zirconia, such species have been detected with in situ UV–vis spectroscopy [20]. On our MnSZ catalyst, surface hydrocarbon species, although so far not detectable, must be present at the end of the reaction, and they are dehydrogenated during heating in N<sub>2</sub>. Information from the literature [9,21] suggests that during regeneration in inert gas, sulfur should be lost. However, all overtones and combination modes of the sulfate are recovered within the accuracy of the experiment (Fig. 8). Reestablishment of the initial state of the majority of hydroxyl and sulfate groups is insufficient to recover the catalytic activity; either a minority of these groups or another type of site must be freed from deposits with the help of an oxidizing agent such as e.g. O<sub>2</sub>.

## Conclusions

The activation step, usually a treatment at 703–773 K, for promoted sulfated zirconia catalysts adjusts the degree of hydration and thus the structure of the sulfate and the

accessibility of hydroxyl groups; however, these functionalities do not fully determine the resulting activity. Variations in activity resulting from different atmospheres during activation suggest an additional functionality whose formation depends on the oxygen partial pressure. Excessive oxidation or reduction evoke poor catalytic performance, not supporting the idea of reaction initiation through oxidative dehydrogenation by manganese or other species.

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