



## Effect of Mn and Fe on the reactivity of sulfated zirconia towards H<sub>2</sub> and *n*-butane: A diffuse reflectance IR spectroscopic investigation

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### Abstract

Sulfated zirconia (SZ) and sulfated zirconia promoted with 2 wt% manganese (MnSZ) or iron (FeSZ), all active in *n*-butane isomerization, were investigated using diffuse reflectance Fourier transform IR spectroscopy (DRIFTS). By adsorption of H<sub>2</sub> at 77 K or of *n*-butane at room temperature it was found that the promoters neither enhance the Lewis nor the Brønsted acidity. The acid strength of both samples is not higher than that of zeolites.

In a batch experiment using 70 hPa of H<sub>2</sub>, SZ did not react at 473 K. Reaction of H<sub>2</sub> with MnSZ produced water (band at 5242 cm<sup>-1</sup>) and a decrease in the sulfate groups (multiple bands). Heating of SZ in 10 hPa *n*-butane to 573 K caused total reduction of sulfate to H<sub>2</sub>S (2583, 2570 cm<sup>-1</sup>) and partial and total oxidation of butane to olefinic species (3062 cm<sup>-1</sup>), CO<sub>2</sub>, and water. MnSZ and FeSZ reacted with *n*-butane already at 373 K; products of skeletal isomerization (methyne CH vibration at 2910 cm<sup>-1</sup>) were detected and sulfate groups were consumed. Rather than increasing the acidity, the promoters enhance the oxidation potential of sulfate and facilitate alkane activation via oxidative dehydrogenation.

**Keywords:** DRIFTS, *n*-butane, hydrogen, adsorption, alkane isomerization, sulfated zirconia, manganese, iron, promoter, oxidation potential

### Introduction

Sulfated zirconia (SZ) is known to catalyze low temperature (< 373 K) isomerization of light alkanes.<sup>1</sup> The activity was first explained by superacidic sites that are able to ionize bases as weak as alkanes. Even though many groups could not detect superacidic sites in sulfated zirconia,<sup>2-4</sup> part of the community is not convinced and the term is still used for this type of materials in the recent literature.<sup>5-7</sup> Transition metals in cationic form act as promoters of sulfated zirconia in skeletal isomerization reactions.<sup>8-10</sup> The increase of isomerization activity was first explained by an enhanced acidity of the catalyst according to the idea of an acid-catalyzed reaction.<sup>8,11</sup> As an increase of acidity through promoters could not be substantiated, it was later speculated that these catalysts are bifunctional and that isomerization occurs through cooperative action of redox and acid sites.<sup>12-14</sup>

The catalytic cycle is believed to proceed via adsorbed carbenium ions, which, in the case of butane, are isomerized following a monomolecular or bimolecular mechanism.<sup>15</sup> Incoming reactant molecules transfer hydrides to the carbenium ions, isobutane is formed and can desorb, while new carbenium ions are created. In the last 25 years no universally acknowledged picture of the initial step for the reaction mechanism and the nature of the active sites has evolved. Three possibilities for forming the first carbenium ions have been proposed: (i) protonation of the alkane by very strong Brønsted acid sites via an alkanium (carbonium) ion-like transition state,<sup>16</sup> (ii) hydride abstraction by strong Lewis acid sites,<sup>17</sup> or (iii) oxidative or non-oxidative dehydrogenation of the alkane and protonation of the resulting alkene by moderately strong Brønsted acid sites.<sup>18,19</sup> Because Fe<sup>2+</sup> was present in deactivated catalysts<sup>20</sup> and the activity after activation in air was higher than after activation in He,<sup>21</sup> it has been proposed that promoters act as redox partners in an

oxidative dehydrogenation mechanism. However, these different mechanisms and the involved sites are still controversially discussed.

Characterization of the surface of SZ catalysts has focused on acidic sites using probe molecules with free electron pairs such as ammonia, pyridine or carbon monoxide. These investigations did not deliver an unambiguous picture. H<sub>2</sub> is a more weakly interacting probe and can serve as a model for the reactant butane since both molecules exhibit only sigma-bond basicity. H<sub>2</sub> has been used to probe Brønsted as well as Lewis acid centers of zeolites or metal oxides at low temperatures, using IR spectroscopy for analysis.<sup>22,23</sup> Lewis acid sites can be probed with high sensitivity because shifts of the H-H stretching frequency tend to be large due to polarization of the corresponding bond.<sup>24,25</sup> At higher temperature hydrogen can be employed to test the reducibility (= oxidation potential) of the catalyst, so that the plausibility of an initiation by oxidative dehydrogenation (ODH) can be evaluated. Furthermore, useful reference spectra for hydrides may be generated, because frequencies given in the literature for zirconium hydrides span a wide range and overlap with species such as water.

Essential for the catalysis is the interaction with the reactant, viz. *n*-butane, which can also be followed by IR spectroscopy. According to the three possible mechanisms listed above, reaction with butane should result in (i) a shift or decrease of bands of OH groups, (ii) formation of a hydride, or (iii) oxidation to e.g. an alkene with hydrogen or water as a side product.

The goal of this paper is to identify the relevant sites on SZ catalysts, to elucidate the mechanism(s) of *n*-butane activation, and to investigate the role of sulfate and hydroxyl groups therein. We probe Brønsted and Lewis acid sites on the surface of SZ and iron- or manganese-promoted SZ using hydrogen at 77 K or butane at room temperature. The products of reaction with hydrogen or butane at increasing temperatures deliver information on the reaction initiation; and the oxidation potential of unpromoted and promoted catalysts is compared. Diffuse reflectance Fourier transform IR spectroscopy (DRIFTS) is used as analytical technique.

## Experimental

The following samples were investigated: sulfated zirconia (SZ) and sulfated zirconia promoted either with 2 wt% Mn (MnSZ) or with 2 wt% Fe (FeSZ). SZ was prepared from hydrous sulfated zirconia (MEL Chemicals, XZO 682/01) by drying it for 21 hours at 383 K followed by calcination in a 20 g batch in flowing air at 823 K for 3 hours. Promoted samples were obtained using the *incipient wetness* method. Dried hydrous sulfated zirconia was impregnated with an aqueous solution of either Mn(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O or Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (both Merck, p.a.), dried at room temperature and then calcined in 20 g batches in air at 923 K for 3 hours.<sup>26</sup> For comparison purposes, one Mn-promoted sample was calcined at 823 K.

Catalytic tests were performed in a tubular fixed bed reactor. Samples were activated in 48 ml·min<sup>-1</sup> nitrogen at 723 K for 30 min. *n*-Butane isomerization was carried out at 378 K (SZ) or 323 K (promoted SZ) using 80 ml·min<sup>-1</sup> 1 vol% *n*-butane in nitrogen at atmospheric pressure.

Diffuse reflectance IR spectra were recorded with a Nicolet Impact 410 FTIR spectrophotometer equipped with a further developed version of the setup described by Kazansky et al.<sup>27</sup> Low temperature spectra were recorded in an all-quartz cell. For room temperature measurements, a section equipped with a CaF<sub>2</sub> window was used. The powders were pressed at 10 MPa for 2 s and sieved into fractions of 0.2–0.5 or 0.5–1.0 mm. Pressing can cause partial transition of tetragonal to monoclinic zirconia,<sup>28</sup> analysis of selected samples after pressing revealed a minor fraction of monoclinic phase (10–20 %). Samples were placed directly at the window, hence the beam path through the gas phase was limited to the void space within the catalyst bed, and gas phase contributions were minimized. CaF<sub>2</sub> powder was used to generate the background spectra. A typical activation procedure was: heating under vacuum (10<sup>-3</sup>–10<sup>-4</sup> hPa, diffusion pump with liquid N<sub>2</sub> trap) from ambient temperature to 383 K in 15 min, keeping at this temperature for 1 h to remove water, heating further up to 723 K for 1 h, evacuation at this temperature for 1 h, heating in 67 hPa of oxygen for 1 h to remove grease contaminations, evacuation for 20 min at 723 K. All presented spectra were recorded at room temperature except for the hydrogen adsorption experiments at 77 K. The samples were exposed to hydrogen at 77 K, room temperature, and 473 K, to *n*-butane at room temperature and in steps up to a maximum of 573 K. These batch-type experiments were performed using one sample in a series of experiments with increasing temperature and intermittent cooling for the measurement; fresh samples were used when the gas type was changed.

For all spectra the reflectance  $\rho$  with respect to CaF<sub>2</sub> was converted into Kubelka-Munk units (KM) by the Kubelka-Munk equation, setting the reflectance  $\rho$  at 5000 cm<sup>-1</sup> to a value of 0.9:

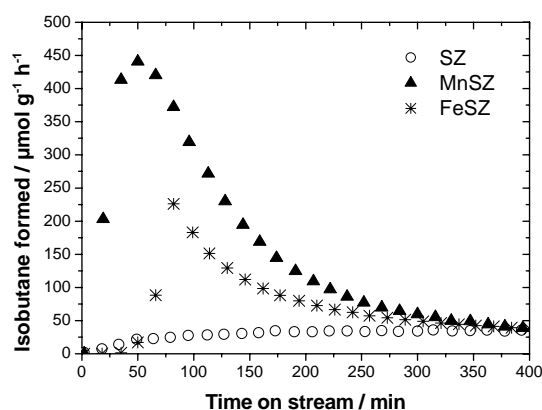
$$KM = \frac{(1 - \rho)^2}{2 \cdot \rho} \quad (1)$$

## Results

### Catalyst characterization

In X-ray diffractograms all investigated samples showed reflections typical of the tetragonal phase of ZrO<sub>2</sub>, no monoclinic phase could be detected. By N<sub>2</sub> adsorption the following BET surface areas were obtained: 119 m<sup>2</sup>·g<sup>-1</sup> (SZ), 108 m<sup>2</sup>·g<sup>-1</sup> (MnSZ), and 134 m<sup>2</sup>·g<sup>-1</sup> (FeSZ). The rate of *n*-butane isomerization in a flow reactor is shown in Figure 1. The promoted catalyst samples deactivate under the applied conditions. The measured maximum rate for FeSZ is 225 μmol·g<sup>-1</sup>·h<sup>-1</sup> and that of MnSZ is 440 μmol·g<sup>-1</sup>·h<sup>-1</sup>. The long term activity (800 min) of FeSZ amounts to ca. 20 μmol·g<sup>-1</sup>·h<sup>-1</sup> and exceeds that of MnSZ (≈ 5 μmol·g<sup>-1</sup>·h<sup>-1</sup>). SZ has a lower maximum rate (35 μmol·g<sup>-1</sup>·h<sup>-1</sup>) than the promoted catalysts, even though isomerization was carried out

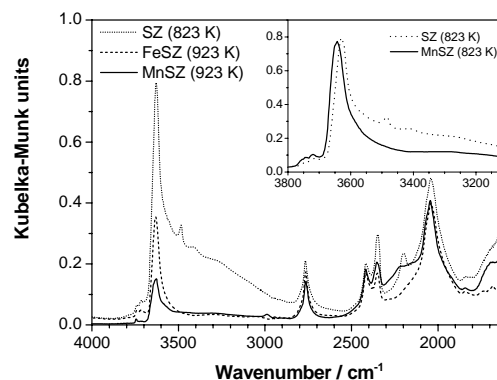
at a temperature that was 55 K higher. In contrast to the promoted samples it shows nearly no deactivation: the rate after 1000 min is still 30  $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ .



**Figure 1:** Rate of isobutane formation of SZ calcined at 823 K (open circle), MnSZ (solid triangle) and FeSZ (asterisk) calcined at 923 K; reaction after activation in nitrogen at 723 K, 1 vol% *n*-butane in nitrogen at 378 K (SZ) / 323 K (promoted SZ).

### DRIFT spectra after activation

Prior to DRIFT measurements the samples were activated by heating in vacuum to remove adsorbed water. In Figure 2 the spectra of SZ, MnSZ, and FeSZ are compared. Band positions are listed in Table 1. The spectra are similar but show the following differences: The spectrum of SZ exhibits a band at 3485  $\text{cm}^{-1}$ , which is not visible for the



**Figure 2:** DRIFT spectra of SZ and promoted SZ (calcined at indicated temperature) recorded at room temperature after activation at 723 K. Inset: comparison of SZ and MnSZ calcined at 823 K.

**Table 1:** Band positions from DRIFT spectra of SZ, MnSZ, and FeSZ calcined at indicated temperature (Figure 2) after activation at 723 K.

Catalyst	$\nu(\text{OH})$	$\delta(\text{OH})$	overtone of vibration of $\nu(\text{S}=\text{O})$	combination of vibrations of $\nu(\text{S}=\text{O})$ and $\nu(\text{S}-\text{O})$	overtone of vibration of $\nu(\text{S}-\text{O})$
SZ (823 K)	3740 (vw) 3714 (vw) 3629 (vs) 3485 (w)	1627 (w)	2767 (s)	2417 (w)	2352 (w) 2340 (w) 2198 (w) 2042 (vs)
MnSZ(823 K)	3745 (vw) 3720 (vw) 3643 (vs)	1629 (w)	2755 (s)	2410 (w)	2350 (w) 2341 (sh) ca. 2200 (sh) 2043 (vs)
MnSZ(923 K)	3744 (vw) 3719 (vw) 3631 (vs)	1629 (w)	2765 (s)	2418 (w)	2353 (w) 2343 (sh) 2218 (sh) 2044 (vs)
FeSZ (923 K)	3742 (vw) 3718 (vw) 3631 (vs)	1630 (w)	2766 (s)	2417 (w)	2352 (w) 2346 (sh) 2190 (sh) 2040 (vs)

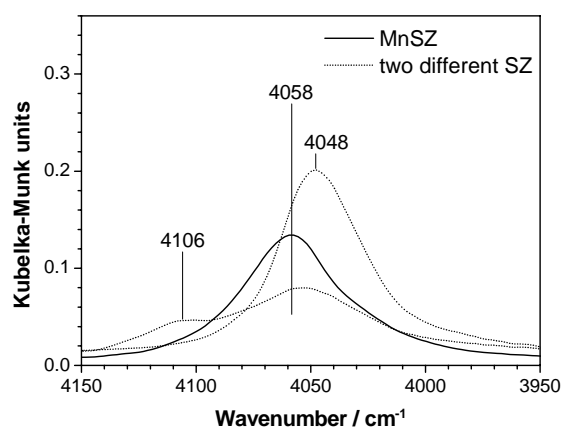
vw very weak  
w weak  
s strong  
vs very strong

sh shoulder  
v stretching vibration mode  
 $\delta$  deformation vibration mode

promoted catalysts. The relative intensity of the OH stretching vibrations centered at 3720 and 3630 cm<sup>-1</sup> and in the range of hydrogen bonded OH groups between 3500 and 3000 cm<sup>-1</sup> is higher for SZ (calcined at 823 K) than for MnSZ (923 K). Spectra of a MnSZ sample calcined at the same temperature as SZ, namely, 823 K (Figure 2, inset), reveal an OH band intensity close to that of SZ, but without the band at 3485 cm<sup>-1</sup>. The spectrum of FeSZ is similar to that of MnSZ calcined at the same temperature (923 K).

### Low temperature adsorption of hydrogen

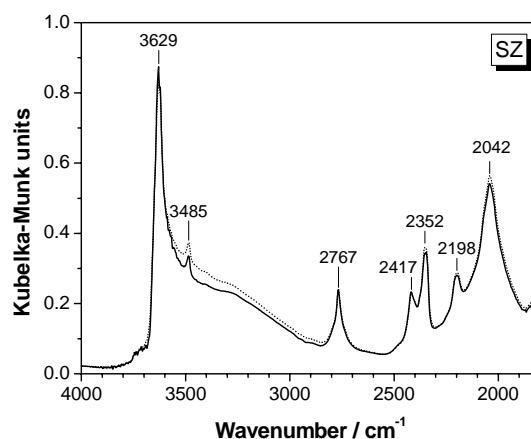
After adsorption of H<sub>2</sub> (70 hPa) on SZ or MnSZ at 77 K bands of the perturbed H–H stretching frequency appear in the DRIFT spectra (Figure 3). One band, located between 4058 and 4048 cm<sup>-1</sup>, is always observed. An additional band at 4106 cm<sup>-1</sup> is sometimes detected. Formation of the band at 4048 cm<sup>-1</sup> is not connected with a shift of the OH groups; for the band at 4106 cm<sup>-1</sup>, such a correlation could not be excluded.



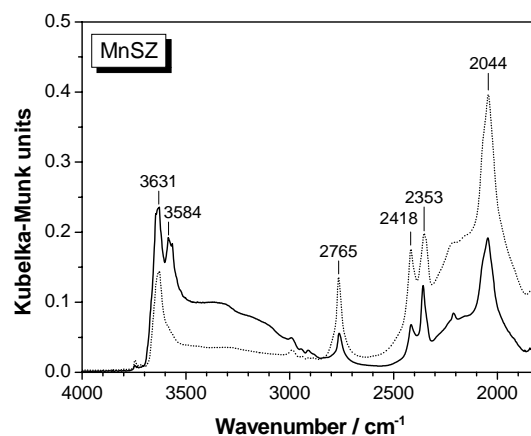
**Figure 3:** DRIFT spectra of two different batches of SZ (dotted lines) and MnSZ (solid line) recorded at 77 K after adsorption of 70 hPa hydrogen.

### Reaction with hydrogen at elevated temperatures

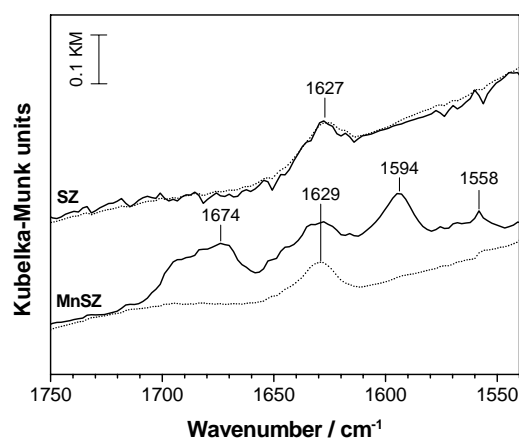
The spectrum of SZ did not change significantly after heating in hydrogen to 473 K (Figure 4). This is different for MnSZ (Figure 5): after heating in hydrogen to 473 K the band at 3631 cm<sup>-1</sup> shows a shoulder at 3645 cm<sup>-1</sup>, an additional band with a maximum at ≈3584 cm<sup>-1</sup> appears, and the intensity in the region of H-bonded OH stretching vibrations between 3000 and 3500 cm<sup>-1</sup> increases. Furthermore, the intensity of the overtone and combination modes of sulfate vibrations decreases. Shifts of sulfate bands were less than 5 cm<sup>-1</sup>. A band at 5242 cm<sup>-1</sup> appears (not shown). Several new bands are also observed between 1558 and 1710 cm<sup>-1</sup> (Figure 6), including a well-defined band at 1594 cm<sup>-1</sup> and a broad feature between 1660 and 1700 cm<sup>-1</sup>.



**Figure 4:** DRIFT spectra of SZ recorded at room temperature after activation at 723 K (dotted line) and after hydrogen adsorption and 20 min heating in hydrogen at 473 K (solid line).



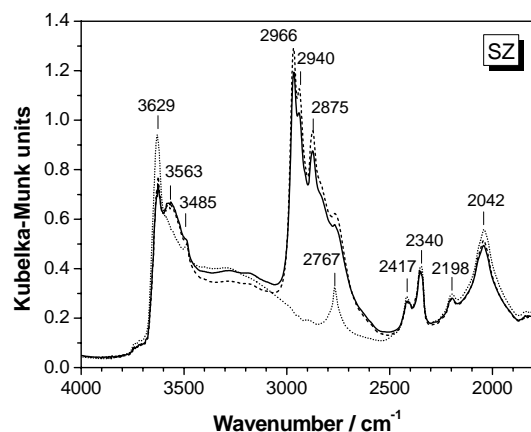
**Figure 5:** DRIFT spectra of MnSZ recorded at room temperature after activation at 723 K (dotted line) and after hydrogen adsorption and 20 min heating in hydrogen at 473 K (solid line).



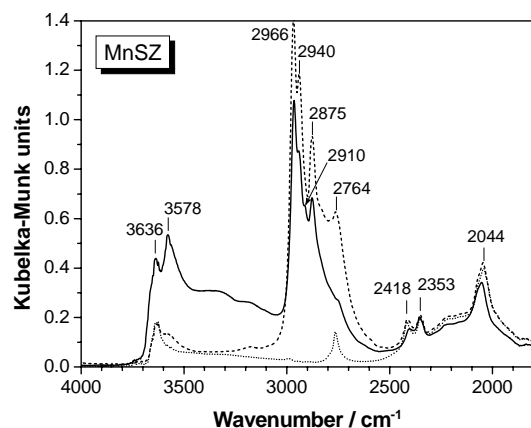
**Figure 6:** DRIFT spectra of SZ and MnSZ recorded at room temperature after activation at 723 K (dotted line) and after H<sub>2</sub> adsorption and 20 min heating in H<sub>2</sub> at 473 K (solid line).

### Adsorption of *n*-butane at room temperature

After addition of 10 hPa *n*-butane at room temperature to SZ, MnSZ or FeSZ, bands of CH vibrations are visible in the spectra. For all catalysts, there are five bands in the CH stretching region, three with distinct maxima at 2966, 2940, and 2875 cm<sup>-1</sup> and two shoulders at 2830 and 2747 cm<sup>-1</sup> (SZ, Figure 7 and MnSZ, Figure 8). Two bands in the CH deformation region are centered at 1465 (shoulder at 1455 cm<sup>-1</sup>) and at 1387 cm<sup>-1</sup> (not shown). A comparison of the spectrum of *n*-butane adsorbed on SZ with the gas phase spectrum is given in Figure 9.



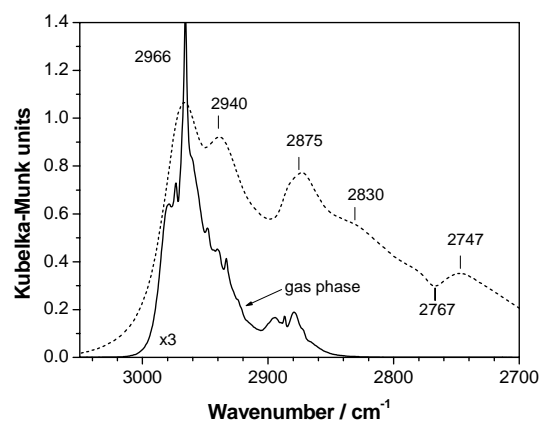
**Figure 7:** DRIFT spectra of SZ recorded at room temperature: before *n*-butane adsorption (dotted line), after adsorption of *n*-butane at room temperature (dashed line), and after 30 min heating in *n*-butane at 373 K (solid line).



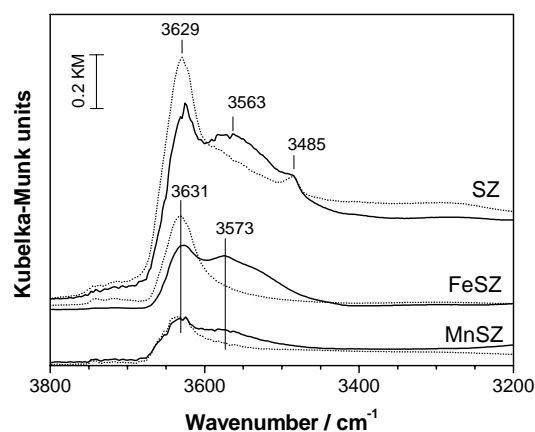
**Figure 8:** DRIFT spectra of MnSZ recorded at room temperature: before *n*-butane adsorption (dotted line), after adsorption of *n*-butane at room temperature (dashed line), and after 30 min heating in *n*-butane at 373 K (solid line).

After adsorption of 10 hPa *n*-butane on SZ at room temperature a band appears in the OH stretching region at  $\approx 3563$  cm<sup>-1</sup> while the band at 3629 cm<sup>-1</sup> decreases in intensity (Figure 10). Addition of *n*-butane to the promoted catalysts at room temperature leads to appearance of a small broad band in the OH stretching region with a maximum near 3573 cm<sup>-1</sup>; concomitantly, the band at 3631 cm<sup>-1</sup> shrinks. Two very weak bands at about 3742 and 3720 cm<sup>-1</sup> are also diminished in intensity by adsorption of *n*-butane

for all three catalysts; this effect is more pronounced at higher pressure (100 hPa). All shifts of OH bands were reversed upon evacuation.



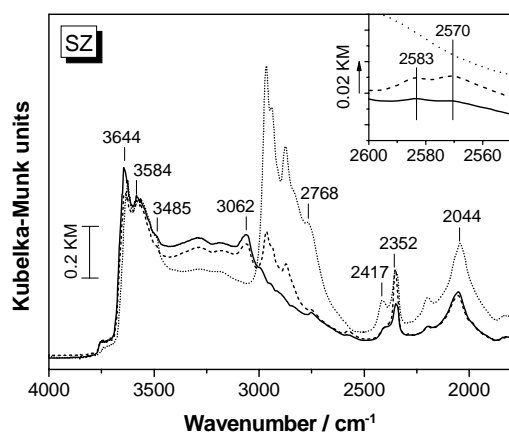
**Figure 9:** DRIFT difference spectrum of *n*-butane adsorbed on SZ recorded at room temperature (spectrum of activated SZ subtracted, dashed line) and spectrum of gas phase *n*-butane (solid line).



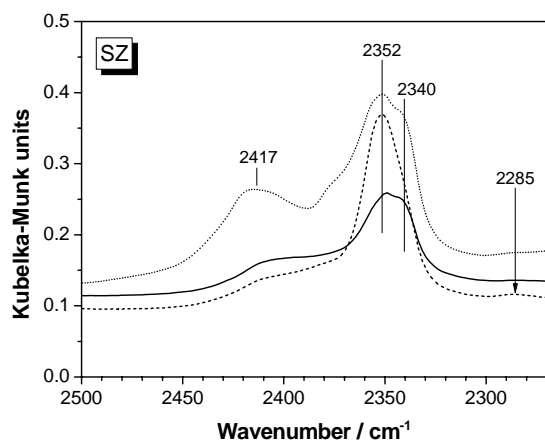
**Figure 10:** DRIFT spectra of SZ, MnSZ and FeSZ recorded at room temperature: before *n*-butane adsorption (dotted lines) and after adsorption of 10 hPa *n*-butane at room temperature (solid lines).

### Interaction with *n*-butane at elevated temperatures

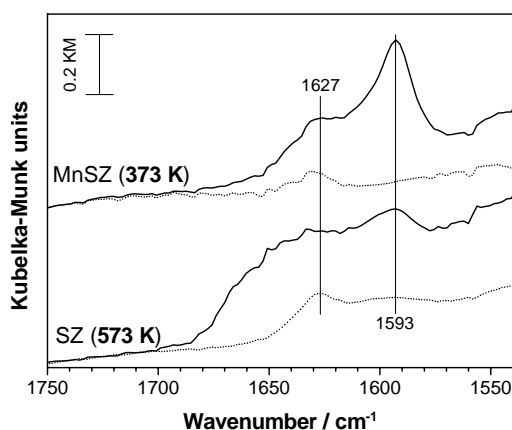
After heating SZ for 30 minutes at 373 K in 10 hPa *n*-butane (pressure at room temperature), no changes are visible except a small decrease in the intensity of the CH vibration bands and a small increase in the region of H-bridging (Figure 7). Longer heating at 373 K (one hour) as well as an increase of the temperature up to 473 K cause no further changes. The spectra change significantly only after heating the sample to 573 K (Figure 11). The intensity of the CH bands decreases dramatically. A pronounced band in the region of CH stretching vibrations is recognized at 3062 cm<sup>-1</sup>. The band at 3629 cm<sup>-1</sup> is shifted to 3644 cm<sup>-1</sup>. The overall intensity in the range 3000–3500 cm<sup>-1</sup> increases. The broad features around 3290 and 3185 cm<sup>-1</sup> indicate H-bridging. The sulfate bands at 2417, 2198, and



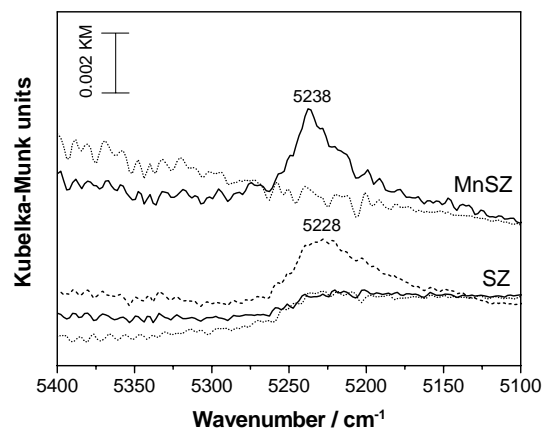
**Figure 11:** DRIFT spectra of SZ recorded at room temperature: after 60 min heating in *n*-butane at 373 K (dotted line), after 40 min heating in *n*-butane at 573 K (dashed line), and after evacuation of *n*-butane (solid line).



**Figure 12:** DRIFT spectra of SZ recorded at room temperature: after *n*-butane adsorption at room temperature (dotted line), after 40 min heating in *n*-butane at 573 K (dashed line), and after evacuation of *n*-butane (solid line).



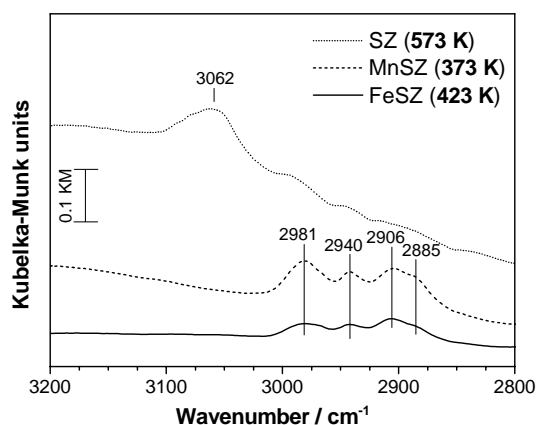
**Figure 13:** DRIFT spectra of SZ and MnSZ recorded at room temperature after activation at 723 K (dotted line) and after heating in butane at indicated temperature (solid line).



**Figure 14:** DRIFT spectra of SZ and MnSZ recorded at room temperature after activation at 723 K (dotted line) and after heating in *n*-butane at 373 K (solid line) or at 573 K (dashed line).

2042 cm<sup>-1</sup> decrease in intensity and in part experience shifts (2042→2053 cm<sup>-1</sup>; 2417→2406 cm<sup>-1</sup>). Two weak bands appear at 2583 and 2570 cm<sup>-1</sup> (Figure 11, inset). The band at 2352 cm<sup>-1</sup> loses its shoulder at 2340 cm<sup>-1</sup> without decreasing in intensity at all, i.e. most likely this band is actually increasing (Figure 12). A band at 2285 cm<sup>-1</sup> becomes discernable. The band at about 1627 cm<sup>-1</sup> gains in intensity and shoulders form towards higher and lower wavenumbers with a distinct maximum at 1593 cm<sup>-1</sup> (Figure 13). A new band appears at 5228 cm<sup>-1</sup> (Figure 14). After evacuation all bands of CH vibrations have almost, but not entirely disappeared (Figure 15) except for the bands at 3062 and at 1455 cm<sup>-1</sup>. The band at 2352 cm<sup>-1</sup> is reduced (Figure 12). The other features remain unchanged.

In contrast to SZ, MnSZ and FeSZ react with *n*-butane already at 373 K. The intensity of the CH bands is decreased after 30 min (example MnSZ, Figure 8). The OH stretching band at 3631 cm<sup>-1</sup> increases and is shifted to 3636 cm<sup>-1</sup> while the OH stretching band centered at about 3580 cm<sup>-1</sup> that is present after adsorption of *n*-butane also grows and becomes more distinct. At the same time a general increase in intensity in the region 3000–3500 cm<sup>-1</sup> is observed. The bands at 2764, 2417 and 2046 cm<sup>-1</sup> lose in intensity. A shift can be recognized for the two low frequency bands, after the treatment they are located at 2406 cm<sup>-1</sup> and 2052 cm<sup>-1</sup>. The band at 2353 cm<sup>-1</sup> and its shoulder at 2343 cm<sup>-1</sup> decrease slightly in intensity but the area ratio remains unchanged. The band at 1629 cm<sup>-1</sup> grows and an even larger, well-defined band develops at 1593 cm<sup>-1</sup> (Figure 13). Furthermore, a band is detected at 5238 cm<sup>-1</sup> (Figure 14). After evacuation of the sample, the intensity in the CH region is strongly diminished and four bands with maxima at 2981, 2942, 2906, and 2885 cm<sup>-1</sup> become visible (Figure 15). Otherwise the spectra are unaffected. The results for FeSZ are largely comparable to those obtained for MnSZ, except that there is no distinct band at 5238 cm<sup>-1</sup> and a less intense band at 1593 cm<sup>-1</sup>. The CH stretching bands that are discernable after evacuation are located at similar positions for MnSZ and FeSZ (Figure 15).



**Figure 15:** DRIFT spectra of SZ, MnSZ and FeSZ recorded at room temperature after heating in *n*-butane at indicated temperature and evacuation.

## Discussion

### Spectra of the activated samples

A complete interpretation of spectra of activated sulfated zirconia and promoted sulfated zirconia with the help of DFT theory has been presented recently.<sup>29</sup> Briefly, all OH bands could be assigned to Zr-OH groups, and the positions of SO vibrations are consistent with S<sub>2</sub>O<sub>7</sub><sup>2-</sup> as the predominant species. The setup used here allowed further dehydration of the samples in comparison to the previously reported data and hence, OH bands are better resolved. The band at 3485 cm<sup>-1</sup>, which is only detected in absence of promoters, is attributed to a triply bridged ν(OH) on dehydrated ZrO<sub>2</sub>. It is not understood why on the SZ sample more sulfate-free surface should be exposed because the sulfate density is not lower than on the promoted samples (estimation on the basis of sulfate content and surface area).

The relative intensity of the OH bands is lower in the spectra of promoted SZ than in the spectrum of SZ. However, in order to achieve optimum isomerization performance, SZ was calcined at 823 K while the promoted SZ catalysts were calcined at 923 K. A decrease in the OH pattern with increasing calcination temperature has been reported for unpromoted SZ.<sup>30</sup> The spectrum of a MnSZ sample calcined at a lower temperature, namely 823 K, shows OH band intensities comparable to those in the spectrum of SZ. Hence, the reduced number of OH groups on MnSZ or FeSZ after calcination at 923 K is due to the calcination temperature and not to the promoters.

### Lewis and Brønsted acid strength

At the chosen adsorption temperatures, 77 K for H<sub>2</sub> and room temperature for *n*-butane, both molecules can be desorbed through evacuation. The facile desorption of *n*-butane is consistent with calorimetric results, which, on SZ, yield differential heats of adsorption of 45–60 kJ·mol<sup>-1</sup>.<sup>31</sup>

The surface is reverted to its pre-adsorption state, i.e. the molecules fulfill the requirements for probes.

The bands resulting after low-temperature adsorption of 70 hPa hydrogen on SZ or MnSZ are red-shifted in comparison with the gas phase frequency (IR inactive, from Raman spectroscopy: 4160.2 cm<sup>-1</sup>)<sup>32</sup> indicating a weakening of the H–H bond through electron donation towards acid sites.

The band at 4048 cm<sup>-1</sup> observed for SZ can be assigned to H<sub>2</sub> adsorbed on Lewis acid sites because it is not associated with a shift of OH bands. The position is also very close to that of a band at 4054 cm<sup>-1</sup>, which was previously reported by Kondo et al. for H<sub>2</sub> adsorbed on pure and thus not Brønsted-acidic ZrO<sub>2</sub>.<sup>33</sup> A slightly higher frequency of 4059 cm<sup>-1</sup> is observed for MnSZ. We also believe this band originates from H<sub>2</sub> adsorbed on Lewis sites, because of its position and because its intensity decreases with increasing degree of hydration (after heating the sample in hydrogen). The largest shift compared to the gas phase vibration of hydrogen is observed for adsorption on SZ (band at 4048 cm<sup>-1</sup>), i.e. the presence of Mn does not enhance the Lewis acid strength. The shifts are ≈110 cm<sup>-1</sup> (SZ) and ≈100 cm<sup>-1</sup> (MnSZ) and are slightly smaller than that observed for H<sub>2</sub> adsorption on Si electron-acceptor centers in dehydroxylated ZSM-5, which is 130 cm<sup>-1</sup>.<sup>22</sup> Larger shifts are observed for adsorption on group 11 and 12 cations, e.g. 1035 cm<sup>-1</sup> (Cu<sup>+</sup>)<sup>24</sup> or 222 cm<sup>-1</sup> (Zn<sup>2+</sup>).<sup>34</sup>

The band at 4106 cm<sup>-1</sup> cannot be unambiguously assigned to H<sub>2</sub> adsorbed on Brønsted or Lewis sites, but its position corresponds to that of H<sub>2</sub> coordinated to the bridging OH groups of [Al]-HZSM-5.<sup>23</sup> If this band arose from adsorption on OH groups, then the Brønsted acidity of SZ materials would approximately correspond to that of H-ZSM-5. Earlier, it was reported that the Brønsted acid sites of SZ catalysts are “weaker, at any rate not stronger than those of H-ZSM-5 and HY”.<sup>34</sup> For zeolites, the bands for H<sub>2</sub> adsorbed on Lewis acid sites are much less intense than those for H<sub>2</sub> on the Brønsted acid sites. In our case the bands arising from H<sub>2</sub> adsorbed on Lewis acid sites were always stronger than the band at 4106 cm<sup>-1</sup>. This intensity distribution reflects the different nature of the zirconia surfaces in comparison to the zeolites, whose acidic properties are dominated by the Brønsted functionality of the OH groups.

Admission of *n*-butane results in a pattern of CH stretching vibrations that differs from the gas phase spectrum. The intense narrow bands of the rotation-vibration spectrum of gas phase *n*-butane are not detectable in the spectra (e.g. SZ, Figure 9), which thus represent adsorbed species. The band at 2966 cm<sup>-1</sup> is less sharp and less pronounced; accordingly, the band at 2940 cm<sup>-1</sup>, which is only a shoulder in the gas phase spectrum, becomes distinct. The band at 2875 cm<sup>-1</sup> is more intense and shifted by about -12 cm<sup>-1</sup> with respect to the gas phase feature. The largest intensity increase is observed for the bands at 2830 and 2747 cm<sup>-1</sup>, which are barely discernable in the gas phase spectrum. Butane adsorption results in a measurable shift of the OH bands to lower wavenumbers, indicating interaction

between *n*-butane and Brønsted acid sites. An H-bridge from butane to the oxygen of an OH group could be responsible for the observed low frequency CH vibrations.

For the intense OH band at ca. 3630 cm<sup>-1</sup>, the red-shift can be determined. At 10 hPa butane, the shift is ca. 66 cm<sup>-1</sup> for SZ and ca. 58 cm<sup>-1</sup> for MnSZ and FeSZ. Again the values are similar and there is certainly no increased interaction due to addition of the promoters. Paukshtis et al. obtained a shift of ca. 92 cm<sup>-1</sup> after adsorption of *n*-pentane on unpromoted SZ; however, the initial position of the OH band was higher. For comparison, the shift of the OH groups in H-mordenite after *n*-butane adsorption is ≈110 cm<sup>-1</sup>.<sup>36</sup> The interaction of the zirconia catalysts with *n*-butane, i.e. with the reactant, via OH groups is obviously weaker than in the case of a typical acidic zeolite. From the OH-band shifts it seems unlikely that the activation of the alkane is achieved through interaction with OH groups on the zirconia catalysts. In any case, the OH groups serve as anchoring points for the reactant molecules at the surface.

### *Interaction of sulfated zirconia and Mn-promoted sulfated zirconia with hydrogen*

As far as detectable with IR spectroscopy, SZ shows no interaction with hydrogen at room temperature or at 473 K. In contrast to our observations, Paukshtis et al. found oxidation of hydrogen on promoter-free SZ at 473 K;<sup>17</sup> the different behavior may be due to deviations in sample preparation or experimental procedure. At a hydrogen partial pressure of 100 hPa, a positive effect on the stability of the *n*-butane isomerization rate on SZ at 523 K has been observed by Garin et al. while a lower partial pressure of 80 hPa had no obvious influence.<sup>37</sup> These reaction kinetic results confirm that for interaction between SZ and molecular hydrogen a minimum partial pressure and a minimum temperature are required.

At room temperature the spectra of MnSZ also remain unchanged, but during heating at 473 K for 20 min the sample reacts with the hydrogen. The band at 1594 cm<sup>-1</sup> is attributed to the deformation mode of water because it matches nearly exactly the gas phase vibration at 1595.0 cm<sup>-1</sup>.<sup>32</sup> The corresponding stretching vibration is seen as a shoulder of the band at 3631 cm<sup>-1</sup> appearing at about 3645 cm<sup>-1</sup>. The band at 5242 cm<sup>-1</sup> is a combination mode of these two, the deformation and stretching vibration of the water molecule (3645 + 1594 = 5239). At 3584 cm<sup>-1</sup> a new OH band becomes visible. The formation of OH groups and water together with the increasing intensity in the hydrogen bonding region 3000–3500 cm<sup>-1</sup> are evidence for the oxidation of hydrogen.

Several species could give rise to the absorption bands at 1660–1700 cm<sup>-1</sup>. Reported frequencies for Zr-H are lower; they range from 1555 in ZrO<sub>2</sub> to 1660 cm<sup>-1</sup> in Zr(BH<sub>4</sub>)/SiO<sub>2</sub>.<sup>17,33</sup> Molecular MnH or MnH<sub>2</sub> are also observed at lower wavenumbers (1493.3 cm<sup>-1</sup> or 1600.8 cm<sup>-1</sup> in solid neon).<sup>38</sup> Vibrations of Mn-H in complexes occur at higher frequencies, which range from 1782 cm<sup>-1</sup> in

HMn(CO)<sub>5</sub> to 1900 cm<sup>-1</sup> in HMn(CO)<sub>2</sub>(π-Cp)SiPh<sub>3</sub>.<sup>39,40</sup> Thus, zirconium or manganese hydrides are unlikely to cause the vibrations. SH groups can be excluded as well since they vibrate at a different position, ca. 2600 cm<sup>-1</sup>.<sup>41</sup> A possible explanation for the bands at 1660–1700 cm<sup>-1</sup> are water clusters. The bending vibration of water is known to shift to higher frequencies as the degree of association increases, e.g. bands at 1600 and 1618 cm<sup>-1</sup> are reported for (H<sub>2</sub>O)<sub>2</sub> clusters and at 1640 cm<sup>-1</sup> for liquid water.<sup>41,42</sup> In addition to the blue shift, DFT calculations for small water clusters show an increase in the range of deformation vibrations from the dimer (1615–1636 cm<sup>-1</sup>) to different octamer structures (1614–1701 cm<sup>-1</sup>).<sup>43</sup> Further support for this theory comes from spectra of unactivated SZ catalysts,<sup>29</sup> which show a broad band centered at 1630 cm<sup>-1</sup> that extends up to 1700 cm<sup>-1</sup>. As the sample is heated and partially dehydrated the high frequency species disappear, suggesting that they are aggregated water species. The fact that defined bands are observed here indicates the formation of water clusters of a distinct size.

On MnSZ, H<sub>2</sub> is, at least in part, oxidized and converted to OH groups and water. The position of the OH vibration is ambiguous; the band at 3584 cm<sup>-1</sup> can be assigned to S-OH of e.g. sulfuric acid,<sup>44</sup> to Zr-OH, or to water.<sup>45</sup> For proton formation, electrons must be accepted by another species. There are three possible scenarios: (i) disproportionation of H<sub>2</sub> into H<sup>+</sup> and H<sup>-</sup>, (ii) reduction of zirconium or manganese, and (iii) reduction of sulfur. According to Paukshtis et al.<sup>17</sup> and Kondo et al.,<sup>46</sup> species absorbing at 1555 or 1562 cm<sup>-1</sup> could be Zr-H. However, the band at 1558 cm<sup>-1</sup> in our spectra is extremely weak, so H<sub>2</sub> disproportionation should not be the main reaction path. Changes to the valence of manganese or zirconium cannot be directly detected by IR spectroscopy; there is only the possibility that functional groups attached to these ions change their vibrational frequency. We do not observe any dramatic band shifts. Furthermore, these components should be reduced only at higher temperatures, specifically ZrO<sub>2</sub> above 473 K<sup>47</sup> and Mn in MnSZ above 500 K.<sup>48</sup> SO vibrations of sulfate are strongly reduced in intensity and no new types of SO vibrations appear. Hence, oxygen from sulfate is at least in part being transferred to give new OH groups and water. Reduced species such as e.g. adsorbed SO<sub>2</sub> would most likely absorb below 1200 cm<sup>-1</sup> and would not be detectable with our setup. Reduction of sulfate is thus the most likely scenario.

### *Interaction of sulfated zirconia with n-butane*

For unpromoted SZ, differences in the spectra become apparent only after heating to 573 K (Figure 11). The CH bands are weakened in intensity. The formation of water is evidenced by the OH deformation band at 1593 cm<sup>-1</sup>, the OH stretching band at 3644 cm<sup>-1</sup> and their combination band at 5228 cm<sup>-1</sup>. At the same time the amount of hydrogen bonding increases. All SO bands of sulfate decrease. These results are similar to those obtained with MnSZ at



373 K and can be explained by an ODH reaction involving sulfate as oxidant. A fraction of the sulfate is completely reduced to H<sub>2</sub>S, as evidenced by the according antisymmetric and symmetric stretching vibrations at 2583 and 2570 cm<sup>-1</sup> (gas phase: 2628 and 2614 cm<sup>-1</sup> <sup>41</sup>). Similarly, Ng and Horvát<sup>49</sup> reported the formation of H<sub>2</sub>S during *n*-butane isomerization at 523 K in a flow experiment.

No bands of methyne groups appear in the spectra of SZ after reaction at 573 K, i.e. there is no significant fraction of isobutane. *n*-Butane is activated and converted, but not to its isomerization product. A new band in the CH stretching region at 3062 cm<sup>-1</sup> indicates a species with an sp<sup>2</sup>-hybridized carbon atom as product. The band is not affected by evacuation; hence it must represent stable surface species. Corresponding C=C stretching vibrations are expected between 1600 and 1700 cm<sup>-1</sup>, which is also a possible range for water deformation vibrations. The bands at around 5230 cm<sup>-1</sup> in the spectra in Figure 14 suggest that about equal amounts of water are present on SZ and MnSZ. Hence, the pronounced shoulder at ≥1640 cm<sup>-1</sup> in the spectrum of SZ in comparison to that of MnSZ (Figure 13) is more likely due to C=C vibrations than to water clusters. The position at roughly 1650–1660 cm<sup>-1</sup> is too high for the vibrations of aromatics, and bands of aryl CH stretching vibrations are expected at somewhat lower frequency (3040–3010 cm<sup>-1</sup>) than the observed band and should be weak. The spectrum shows no intense aliphatic CH stretching vibrations and only a sharp but weak band at 1455 cm<sup>-1</sup> in the CH deformation region. A temperature of 573 K is sufficient for SZ to crack *n*-butane, e.g. into ethane and ethene,<sup>50</sup> and a strongly attached surface species could be formed from ethene upon cooling to room temperature. It follows that the adsorbate characterized by the band at 3062 cm<sup>-1</sup> could be a short-chain alkene-type species.

An additional feature in the spectra of SZ is the band at 2352 cm<sup>-1</sup>. The position is very close to the gas phase vibration of CO<sub>2</sub> at 2349 cm<sup>-1</sup>.<sup>41</sup> A weak band at 2285 cm<sup>-1</sup> for <sup>13</sup>CO<sub>2</sub> confirms the presence of CO<sub>2</sub> (Figure 12), which desorbs upon evacuation.

### *Interaction of promoted sulfated zirconia with n-butane*

For MnSZ and FeSZ, changes are seen in the spectra already after heating to 373 K. The intensity distribution in the CH stretching region is altered; specifically a band at 2906 cm<sup>-1</sup> becomes visible. The position is typical for methyne groups, indicating that *n*-butane has been isomerized and a fraction of isobutane is present. For MnSZ, OH vibrations grow significantly as CH stretching vibrations decrease in intensity (Figure 8), indicating a transfer of H from hydrocarbon to catalyst. Specifically, the intensity in the hydrogen bonding region 3000–3500 cm<sup>-1</sup> increases and two bands at 1593 and 5238 cm<sup>-1</sup> appear, which are stable during evacuation at room temperature. These two bands have been previously assigned to vibrations of water (vide supra). The simultaneous disappearance of *n*-butane and

appearance of water can be explained by oxidative dehydrogenation of *n*-butane. ODH is considered as one of the possible initiation reactions to form an alkene, which can be easily protonated to give a carbenium ion as active intermediate for the isomerization of *n*-butane.<sup>21,29,51</sup> In analogy to the oxidation of hydrogen by MnSZ, the intensity of the SO bands of sulfate decreases also after heating in *n*-butane, indicating that these groups are involved in the reaction with *n*-butane and possibly serve as oxidizing agent.

For FeSZ a decrease in CH vibrations is discernable and the methyne species are unambiguously present, but there are no obvious bands around 1600 cm<sup>-1</sup> and 5200 cm<sup>-1</sup> (water) and only a slight increase in the hydrogen bonding region 3000–3500 cm<sup>-1</sup> is observed. This behavior does not fit the picture of *n*-butane activation by ODH. An alternative activation could be simple dehydrogenation, which has been postulated for unpromoted sulfated zirconia.<sup>19</sup> However, non-oxidative dehydrogenation does not explain a decrease of the sulfate vibrations.

After evacuation, the CH intensity decreases, indicating that a large fraction of hydrocarbons is removed. Four individual bands become discernable in the region of CH stretching vibrations. The positions and the intensity distribution are almost the same for MnSZ or FeSZ. The bands at 2981 and 2942 cm<sup>-1</sup> are typical of asymmetric CH stretching vibrations of methyl and methylene groups, respectively, while the band at 2885 cm<sup>-1</sup> arises from symmetric CH vibrations. The additional band at 2906 cm<sup>-1</sup> again can be assigned to methyne groups. Hence, alkyl species must be attached to the surface. The methylene groups indicate non-isomerized (*n*-butyl) species or, in general, chains containing a secondary carbon atom; the methyne groups indicate isobutyl species or chains containing a tertiary carbon atom.

### *Effect of promoters*

Through promotion, sulfate becomes more reactive towards hydrogen and *n*-butane, and, as can be extracted from early TPD results, also towards benzene.<sup>52</sup> It is not clear whether sulfate is directly associated with the promoters. Yamamoto et al. proposed that Mn is present as MnSO<sub>4</sub> on the surface,<sup>53</sup> Scheithauer et al.<sup>54</sup> and Tábora and Davis<sup>55</sup> reported small Fe<sub>2</sub>O<sub>3</sub> rafts on the surface. However, our preparation method produces materials with the majority of Mn and a significant fraction of Fe incorporated into the zirconia lattice.<sup>10</sup> As a consequence of the foreign ions in the lattice, the unit cell size shrinks and due to the lower valence of Mn or Fe in comparison with Zr, oxygen defects are generated in the bulk. The sulfate may become more reactive because of the change in support structure, or near-surface vacancies may act as a catalyst in the reduction process because they can accept negative charges. Electrons may also intermittently be localized at the more easily reducible promoter ions. Definitely, the promoters enhance the oxidation potential of sulfate.

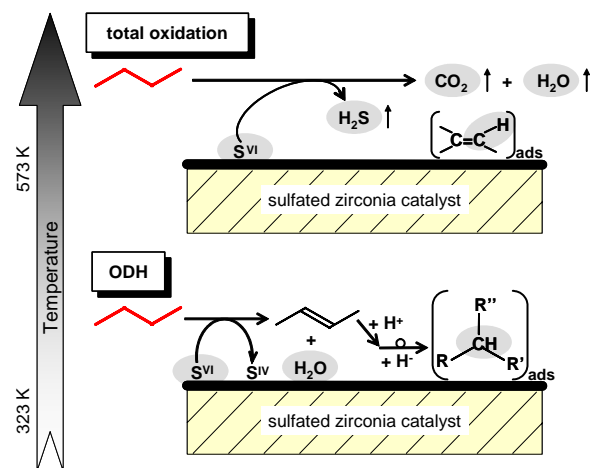
**Table 2:** Reactivity of un-promoted and promoted SZ catalysts towards molecular hydrogen or *n*-butane at different temperatures observed by DRIFT spectroscopy.

Catalyst	Temperature	Reactant	Observations made by DRIFT spectroscopy
SZ	473 K	H <sub>2</sub>	no change
MnSZ	473 K	H <sub>2</sub>	formation of H <sub>2</sub> O, Zr-hydride; decrease of sulfate
SZ	573 K	<i>n</i> -C <sub>4</sub> H <sub>10</sub>	formation of H <sub>2</sub> O, H <sub>2</sub> S, CO <sub>2</sub> , alkene; decrease of sulfate
MnSZ	373 K	<i>n</i> -C <sub>4</sub> H <sub>10</sub>	formation of H <sub>2</sub> O, isoalkane; decrease of sulfate
FeSZ	373 K	<i>n</i> -C <sub>4</sub> H <sub>10</sub>	formation of isoalkane; decrease of sulfate

## Conclusions

The Lewis acid sites of SZ, as probed with H<sub>2</sub>, are comparable to those of other oxidic compounds. Manganese effects a slight decrease in Lewis acid strength rather than an increase. The Brønsted acidity of the OH groups of SZ, as probed with *n*-butane, is lower than that of strongly acidic zeolites. Manganese or iron do not enhance the Brønsted acidity of SZ. Promoters thus do not improve the hydride abstraction or protonation ability of the catalyst, and their effect on the reaction rate must be related to a different functionality.

**Scheme 1:** Reaction pathways of *n*-butane on sulphated zirconia catalysts depending on temperature. Detected species underlaid in gray.



The reactions of *n*-butane with sulfated zirconia catalysts are depicted in Scheme 1. At high temperatures (573 K), partial (unsaturated hydrocarbons) and complete (CO<sub>2</sub>, H<sub>2</sub>O) oxidation was observed, with concomitant total reduction of S(+VI) to H<sub>2</sub>S. At low temperatures, water and species with methyne groups were detected on the surface. Previously, we have found that the rate of butane isomerization during the period of increasing conversion is proportional to the area increase of a number of overlapping bands in the region 1540–1760 cm<sup>-1</sup>.<sup>29</sup> Here, we could partially

resolve these bands and assign them to water clusters. Besides the formation of water, a decrease in the sulfate vibrations is observed. Mn had already been excluded as a stoichiometric redox partner,<sup>48</sup> and also for unpromoted sulfated zirconia, alkane activation paths must exist. It is concluded that at the low temperatures, which are suitable for isomerization, S(VI) also acts as oxidizing agent. One initiation pathway for the initiation of alkane isomerization is, thus, oxidative dehydrogenation. Because the catalysts can usually be reactivated several times, the corresponding reduced sulfur species remains on the surface and can be reoxidized.<sup>29</sup>

The results of interaction between H<sub>2</sub> or *n*-butane and SZ or promoted SZ at elevated temperatures are summarized in Table 2. The easier reducibility of the promoted materials observed in the reaction with *n*-butane is confirmed using hydrogen as a reducing agent. It can only be speculated on exactly how the promoters alter the structural and electronic properties of the zirconia, which in turn affect the reactivity of the sulfate. Previously, we had found a positive effect of manganese on the isomerization step (after initiation had already occurred);<sup>29</sup> from the new investigations presented here, we conclude that the promoters enhance the oxidation potential of the sulfate and thus facilitate initiation via oxidative dehydrogenation and accordingly isomerization at lower temperature.

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