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Activation and deactivation of Pt containing sulfated zirconia and sulfated zirconia studied by *in situ* IR spectroscopy

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In situ infrared spectroscopy (IR), thermogravimetric measurements (TG) and temperature-programmed evolution of gases (TPE) have been used to study activation and regeneration of sulfated zirconia with and without Pt (SZ, Pt/SZ). Isomerization and cracking of *n*-heptane was used as test reaction. The first activation of Pt/SZ is independent of the atmosphere, air or He and N_2, in each case the catalyst was active. But it was necessary to regenerate the catalyst in air to obtain the initial activity and selectivity. When regeneration was done in helium or nitrogen the catalyst lost its acid properties and only hydrogenolysis of *n*-heptane to propane and *n*-butane was observed. This can be explained by a loss of a part of sulfates between 400 and 500 °C measured by TG and TPE. In the IR spectrum the intensity of the SO band at 1400 cm^{-1} decreased and shifted to lower wavenumbers whereas the band of terminal Zr–OH groups at 3740 cm^{-1}, which was absent in the first spectrum after activation increased. The activation conditions of SZ are independent of the atmosphere, no loss of sulfate groups was observed. The reason for deactivation of SZ is coke formation during alkane conversion.

KEY WORDS: platinum; sulfated zirconia; activation; regeneration; sulfate loss.

1. Introduction

High-octane gasoline, which is free of aromatics and sulfur containing compounds can be produced either by isomerization of *n*-alkanes or by alkylation of isobutane with C3–C5 alkenes. For alkylation sulfuric and hydrofluoric acid, for isomerization Pt on chlorided alumina and Pt containing mordenite are commercially used. To find stable solid acid catalysts as compensation for liquid acids and for chlorided alumina is highly desirable.

Sulfated zirconia (SZ) is one of the benign alternatives for the substitution of liquid acids answering the demand for clean technologies [1]. Much work has been devoted to sulfated zirconia, which is compiled in several reviews [2–4]. SZ is able to catalyze the following reactions:alkane isomerization, alkane cracking, isoalkane alkylation and acylation of aromatics [2,5]. SZ has reached a lot of interest due to its high activity for the isomerization of light alkanes at low temperatures [6].

The industrial use of SZ is currently restricted to the isomerization of C5–C6 paraffinic cuts for enhancing the octane number of gasoline [7]. In contact with hydrocarbons SZ alone deactivated quickly. To set up a stable process addition of Pt and working under hydrogen is necessary to prevent SZ from deactivation [8,9].

The catalytic properties of SZ significantly depend upon the preparation method and the activating treatment [10]. It is reported that the calcination step, which selectively eliminates sulfates from some specific terminations of the zirconia crystallites belonging to the high symmetry crystal phases [11] is crucial for activity.

Until now a discussion exists about the nature of the active sites on Pt/SZ, as well as the mechanism through which the catalytic sites are formed [12]. Moreover, other factors than the strength of the acid sites are discussed to be the cause of the high activity. Liu *et al.* [13] proposed that an extremely active catalyst for an acid catalyzed reaction need not to be an extremely strong acid instead, the reaction can proceed via a less energy intensive bimolecular mechanism for small alkanes. Falco *et al.* [14] meant that the acidity of Pt/SZ and Pt/WZ is generated under reaction conditions by the simultaneous presence of Pt, hydrogen and SZ (WZ).

Besides the acid sites also the role of the Pt sites is discussed. Normally the Pt content is in the range of 0.1–0.5 wt%. Arata *et al.* [15] found the highest activity of SZ with 3 wt% Pt for the catalyst prepared by double calcination, while the highest activity was observed with 7.5 wt% Pt in the case of the single calcination.

According to Ebitani *et al.* [16] Pt on SZ remains mostly in an oxidized state, even after hydrogen reduction at 673 K. Ebitani [17] proposed that Brønsted acid sites were developed from dissociative adsorption of hydrogen on Pt, spillover of the H atoms onto the SZ and then electron transfer from the H atoms to Lewis acid sites left protons on the surface. Sachtler *et al.* [18] proposed $[Pt_nH]^+$ adducts, "collapsed bifunctional sites" which can act as active sites.

Dijs *et al.* [19] observed that water free SZ was not active; only after addition of water catalytic activity was exhibited. The main conclusion of this research was that

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the catalytic activity of SZ originates from supported sulfuric acid containing water.

A very fast deactivation was found when hydrocarbons react on sulfated zirconia. A deactivation process is observed over all SZ systems, cubic, tetragonal and monoclinic in the isomerization of *n*-butane at 423 K [20]. This process is not irreversible and the activity can be completely restored by reactivating the various catalysts in dry air at 673 K. The nature of this deactivation is still under discussion. Deactivation was attributed to carbon accumulation [21,22], to surface reduction of Zr^{4+} to Zr^{3+} during the reaction of hydrocarbons, to a loss of sulfur entities, to reduction of sulfate groups and H_2S formation or to change in the surface phase from tetragonal to monoclinic [23].

If sulfur is reduced to lower oxidation states irreversible deactivation could take place. García *et al.* [24] found that only 10% of the active sites in SZ probably SOHZr are the most active.

The aim of the present study is to investigate the catalytic activity of Pt/SZ and SZ in *n*-heptane isomerization by *in situ* IR measurements, to investigate the nature of active sites and to determine which factors influence the deactivation.

2. Experimental

2.1. Catalyst preparation

Sulfated zirconia (SZ) and Pt-promoted sulfated zirconia (Pt/SZ) were prepared from sulfated zirconium hydroxide, kindly provided by MEL. The hydroxide was impregnated with 2.5 wt% Pt using an aqueous solution of $PtCl_4$, and after impregnation it was calcined in static air at 600 °C for 3 h. SZ without Pt was calcined under the same conditions.

2.2. Catalyst characterization

After calcination the sample contained 5.7 wt% SO_3, as determined by thermogravimetric studies TG (Netzsch STA 409 PC/4/H Luxx). Furthermore a TG analysis was done after different activation procedures.

Temperature programmed evolution (TPE) of gases was measured after different pretreatments of SZ and Pt/SZ. As detector a quadrupol mass spectrometer (Balzers QMG) was used.

The characterization of the metallic and acidic sites is described in [25]. The infrared spectra were recorded on a Bruker IFS 28 FTIR spectrometer equipped with an MCT detector (resolution 4 cm^{-1}). The samples were prepared as self-supporting wafers (2 cm diameter and typically 7–8 mg/cm^2), placed inside a cell, which allowed heating the samples up to 600 °C.

2.3. Catalytic reaction

The *in situ* FTIR experiments were carried out in a flow cell approximating a continuously stirred tank reactor. The samples were pressed into self-supporting wafers and placed inside a ring shaped furnace. The partial pressure of *n*-heptane (15 mbar) was adjusted via a saturator kept at 0 °C. Since the activation procedure was very important, different activation gases and activation temperatures were used. Best results were obtained when the sample was activated in synthetic air at 500 °C for 1 h, cooled to 200 °C and then reduced at this temperature for (at least) 15 min. During the reaction (200 °C and the reagents flowing through the cell) IR spectra were recorded and the gas phase was analyzed by a gas chromatograph (HP 5980 II) equipped with an Al_2O_3/KCl column and a flame ionization detector. The reaction was carried out at atmospheric pressure in a H_2 flow of 40 mL/min.

3. Results and discussion

Hydroisomerization of *n*-heptane uses Pt, Pd or Ni supported on zeolites. With Beta as zeolite support the isomerization activity was always high, even when *n*-octane and *n*-nonane were used as reactants [26,27]. But when Pt is added to SZ a high selectivity to cracking products is observed. The isomerization selectivity of *n*-octane was found to be very low over Pt/SZ, cracking was the preferred reaction path [28]. That is a reason why industrial isomerization is limited in practice only to C4 and C6 alkanes [29].

The surface properties of sulfated zirconia change concomitantly with temperature, pressure and the presence of water vapor [30]. SZ is a very hygroscopic material and rehydration occurs easily after calcination at 600 °C and storage at room temperature. For this reason, reactivation prior to reaction is necessary. Since the catalytic activity of SZ and Pt/SZ is strongly dependent on the activation process different activation and regeneration procedures were followed by TG, TPE and IR measurements.

In figures 1–3 these different activation procedures followed by TG and TPE measurements are shown. Pt/SZ and SZ were activated in He or in air (or He/O_2 mixture, respectively) with a rate of 10 K/min up to 500 °C and kept at this temperature for 1 h, then the samples were cooled down to 200 °C and reduced in hydrogen for 15 min. Afterwards the sample was heated either in air (He/O_2) or in He until 900 °C. Only from Pt/SZ, which was reduced before heating in an inert gas stream a part of the sulfate groups was lost as SO_2 in the temperature interval between 350 and 550 °C and the other part between 750 and 850 °C. When the sample was heated in air after reduction, SO_2 was evolved only at the higher temperature. The same was found when heating the Pt/SZ sample twice in inert gas without carrying out a reduction in between. Kinetic measurements showed that Pt/SZ was inactive for isomerization when heated in He or N_2 to 500 °C after a reduction step, whereas it stays active when it is treated under oxidizing conditions after reduction.

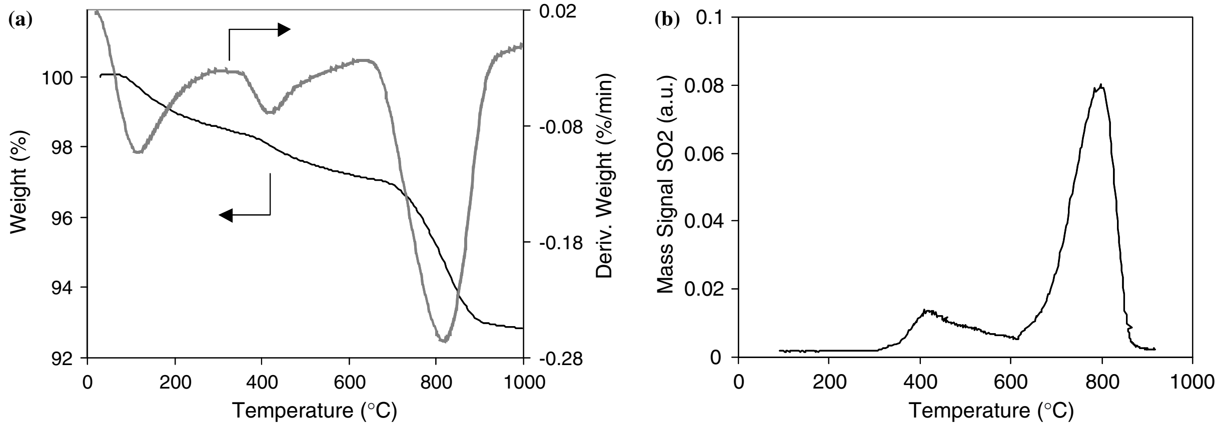

Figure 1. TG (a) and TPE (b) measurements of Pt/SZ in He flow after activation in synthetic air or He at 500 °C followed by reduction at 200 °C.

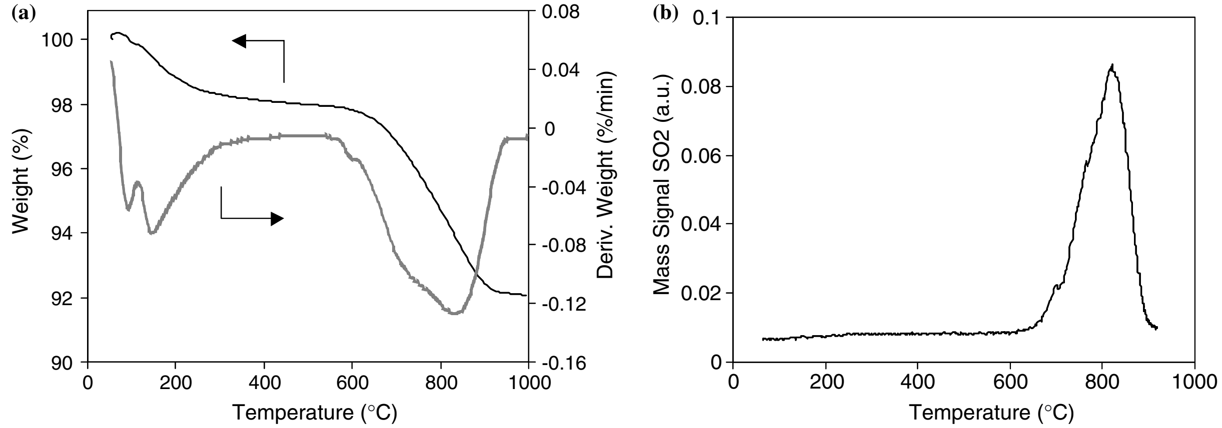

Figure 2. TG (a) and TPE (b) measurements of Pt/SZ in air after activation in He at 500 °C followed by reduction at 200 °C.

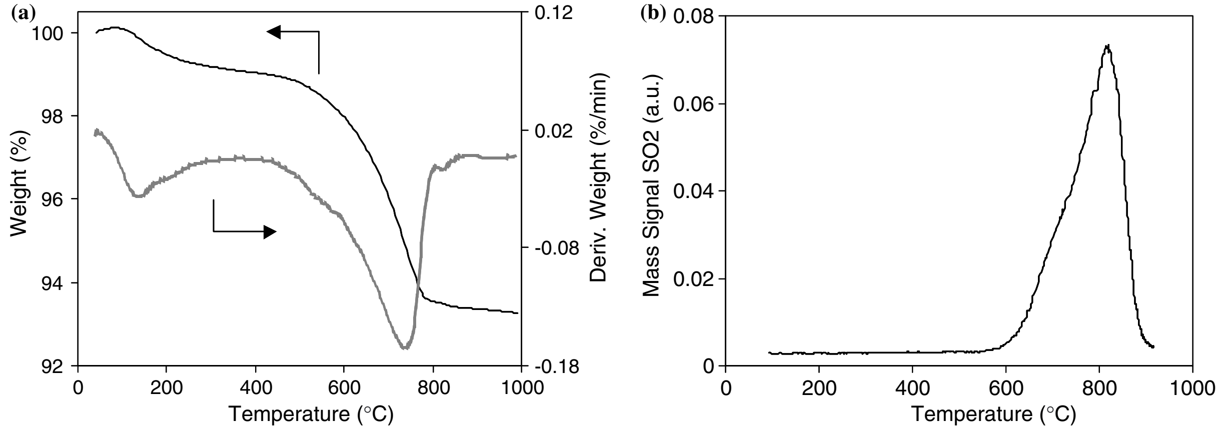

Figure 3. TG (a) and TPE (b) measurements of SZ in He flow after activation in synthetic air or He at 500 °C followed by reduction at 200 °C.

SZ showed the evolution of SO_2 always only between 750 and 850 °C whatever the activation procedure.

The amount of SO_2 evolved at lower temperatures depends on the reduction conditions. For the TPE and TG measurements described above the obtained values are shown in table 1.

Li and Gonzalez [31,32] found that regeneration of SZ in N_2 at 550 °C resulted in a complete loss of

Table 1
TG and TPE measurements of (Pt/)SZ after different pretreatment steps

	Activation procedure	TG/TPE in	SO_3^{LT} (wt%)*	SO_3^{HT} (wt%)*	$\sum SO_3$ (wt%)*	Ratio SO_3^{HT}/SO_3^{LT}*	Ratio of SO_2 peak areas calculated from TPE
Pt/SZ	He 500 °C, Red. 200 °C	He	0.74	4.16	4.90	5.7	3.9
Pt/SZ	Air 500 °C, Red. 200 °C	He	0.74	4.06	4.80	5.5	3.7
Pt/SZ	He 500 °C, Red. 200 °C	Air	–	5.87	5.87	–	–
SZ	He 500 °C, Red. 200 °C	He	–	5.15	5.15	–	–

LT: low temperature (< 600 °C).
HT: high temperature (> 600 °C).
*From TG measurements.

catalytic activity while regeneration in O_2 at 450 °C essentially restored the catalytic activity to that of a fresh catalyst. For the evolution of gases from the fresh catalyst only water and SO_2 at 800 °C were observed, whereas for a deactivated catalyst CO_2 and part of SO_2 are evolved around 600 °C. The authors concluded that two different types of sulfates are present on the surface–one, which evolved at low temperature, is the active one; the other evolved at higher temperature is inactive. In both cases sulfur was evolved as SO_2. The active part amounted 10–14% of the total sulfate content.

Also Vera *et al.* [8] found that calcination of SZ in N_2 at 600 °C produced sulfur losses, which were attributed to the reduction of surface sulfates to gaseous SO_2.

With Pt/SZ it is sufficient to carry out heating in an inert gas stream after a reduction step to lose a certain amount of SO_2 at lower temperature, i.e. 500 °C. With SZ, SO_2 is lost only at 800 °C even with a reduction step before a TPE measurement. It was shown that in the case of SZ a reaction with hydrocarbons is necessary to detect SO_2 at lower temperature [31]. Li and Gonzalez observed two SO_2 desorption maxima from deactivated SZ. The low temperature maximum corresponds to the release of SO_2 and CO_2 the other one to SO_2 alone. CO_2 can be burned off under air and the catalyst was active again, whereas under N_2 both components were released from the surface and the catalyst was irreversibly deactivated. The amount of coke deposited on SZ, which is capable of poisoning the active sites was found to be unusually small.

From HRTEM studies the presence of a small number of zirconia crystallites containing high Miller-index surfaces is revealed [33] and it was proposed that the presence of sulfate groups near or on these particles could give rise to the highly acidic sites of SZ. The number of such sites would therefore be small.

Hydrogen, which is activated on Pt and spilt over to the ZrO_2 surface, is able to reduce the bond between the sulfate groups or between the sulfates and the oxidic surface and SO_2 is evolved at lower temperature. If an oxidizing step is carried out after the reduction, the initial situation is reestablished and no SO_2 is lost at lower temperatures (below 600 °C).

Different activation procedures and the reaction of *n*-heptane were followed by *in situ* IR measurements using a flow cell. All measurements were done on the same Pt/SZ sample. Pt/SZ was first activated at 500 °C in a nitrogen flow for one hour and an IR spectrum was measured (figure 4). In the OH region several bands were observed, i.e. a very small band at around 3740 cm^{-1}, a bigger band at 3640, a small band at 3578 cm^{-1} and a very broad band with a maximum around 3200 cm^{-1}. In the literature [34,35], the first two bands are described as isolated Zr–OH groups and as hydroxyls groups bridging between 2 or 3 Zr atoms, respectively, the low frequency band at 3578 cm^{-1} was attributed to non-specified hydroxyl groups present on sulfated zirconia. The broad band around 3000 cm^{-1} has been attributed to terminal Zr–OH groups where the protons are substituted by HSO_4^- anions creating a new type of Brønsted acid sites, presumably protons forming multicenter bonds with sulfate anions, or to OH groups strongly interacting with each other or with the surface through hydrogen bonding [36]. The deformation vibration of adsorbed water was observed at 1605 cm^{-1}, even after activation at 500 °C.

In the SO region a very intense band at 1400 cm^{-1} was observed, other bands below 1200 cm^{-1} could not be detected due to our instrumental setup. The intense band at 1400–1380 cm^{-1} can be ascribed to the asymmetric stretching vibration of S=O [37,38]. Bands at lower wavenumbers are assigned to adsorbed forms of sulfuric acid. Li and Gonzalez [39] assigned bands at 1272, 1154, 1022 and 999 cm^{-1} to a bidentate sulfate ion coordinated to Zr^{4+}.

After the first activation step in nitrogen the catalyst was reduced at 200 °C for 15 min and then *n*-heptane reacted on the surface. Reduction in hydrogen led to a pronounced increase of the OH bands. A shift of the SO band to 1386 cm^{-1} and a shoulder at about 1300 cm^{-1} was observed after 11 min TOS in *n*-heptane. The

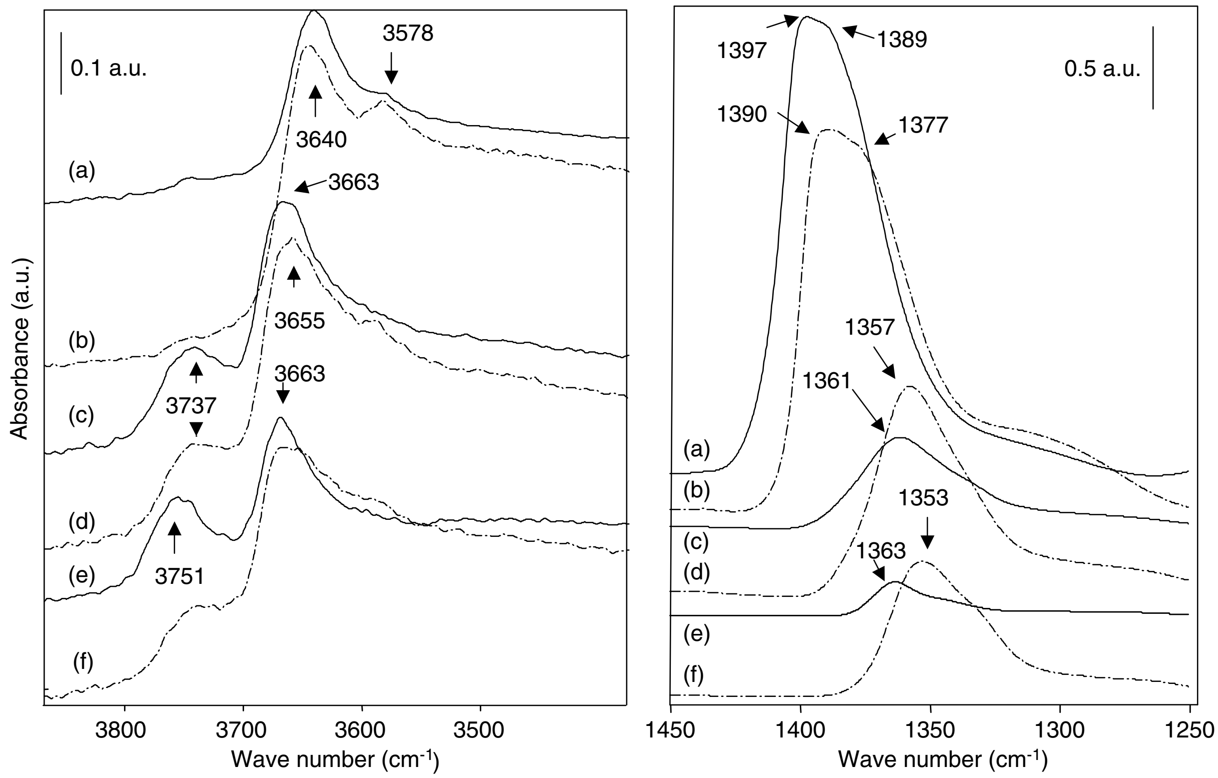

Figure 4. *In situ* IR spectra of Pt/SZ after different activation procedures carried out consecutively on the same sample; every activation step is followed by reduction at 200 °C and *n*-heptane isomerization at 200 °C in H_2 (spectra not shown here, only spectra directly after activation are displayed):(a) after activation in N_2, (b) in air, (c) in N_2, (d) in air, (e) in N_2 and (f) in air at 500 °C.

Table 2
Isomerization of *n*-heptane at 200 °C in H_2 over Pt/SZ after different activation procedures (carried out consecutively on the same sample)

Activation procedure	TOS (min)	Conversion (%)	Selectivity (%)				Area SO (%)[a]
			iC7	C3	iC4	nC4	
N_2 500 °C, Red. 200 °C	8	23.9	43.6	27.6	26.8	1.0	100
Air 500 °C, Red 200 °C	8	30.8	27.0	36.4	35.1	1.1	102
N_2 500 °C, Red. 200 °C	8	0.1	100	0.0	0.0	0.0	22
Air 500 °C, Red 200 °C	8	1.0	13.3	20.6	0.0	20.8	46
N_2 500 °C, Red. 200 °C	8	0.0	–	–	–	–	6
Air 500 °C, Red 200 °C	8	1.0	5.7	17.0	0.0	15.6	30

TOS = Time on stream. C7–sum of all branched heptane isomers; C3–propane; iC4–*iso*-butane; *n*C4–*n*-butane.
[a]Integrated area of SO-band between 1350 and 1400 cm^{-1} related to the area after the first pretreatment step.

catalyst was active with an isomerization selectivity of 44%, the cracked products were propane and *iso*-butane with only a small amount of *n*-butane (table 2).

The same sample was reactivated in air and then the same procedure as described above was applied. The intensity of the bands in the OH and SO region did not change during this treatment and the catalyst was active and the selectivity was approximately the same as before.

The next activation was done in nitrogen. The OH band at 3740 cm^{-1} increased strongly in intensity, the band at 3640 shifted to 3663 cm^{-1} and the band at 3578 cm^{-1} was absent. The SO band shifted to 1361 cm^{-1} and the intensity was drastically reduced to 22% of its initial value and the catalyst was practically inactive, only 0,1% conversion with 100% selectivity to monobranched isomers was found. These results together with results from TG and TPE measurements demonstrate that sulfate groups evolved as SO_2 were lost from the surface. Morterra *et al.* [40] found that the $\nu_{S=O}$ shifts from 1400 to 1360 cm^{-1} with decreasing concentration of sulfates on the surface. An additional hint is the formation of terminal Zr–OH groups at 3740 cm^{-1} and the shift from 3640 to 3663 cm^{-1}. The bands at 3640 and 3578 cm^{-1} are assigned to OH groups on SZ, whereas the bands at 3740 and 3663 cm^{-1} belong to OH groups on pure zirconia [38].

Reactivation in air at 500 °C, reduction at 200 °C led to *n*-heptane conversion of 1.0% with an isomerization selectivity of 13.3%. Note the cracking products were now propane and *n*-butane in approximately the same amounts. Bands belonging to Zr–OH at 3740 and 3655 cm^{-1} were observed, additionally a small band at 3578 cm^{-1}, which is characteristic for sulfated zirconia. The band in the SO region, 1357–1353 cm^{-1} increased in intensity to 46% of its initial value. Repeating this cycle in nitrogen the catalyst is totally inactive. Only bands for Zr–OH groups were detected and the intensity of the SO band at 1363 cm^{-1} decreased to 6%.

After reactivation in air the conversion was only 1.0% with a low selectivity of 5.7% to isomerization. The cracking products were as before propane and *n*-butane. The SO band at 1353 cm^{-1} increased in intensity to 30% of its initial value.

These changes of the area of the SO band between 1350 and 1400 cm^{-1} after the different activation steps are summarized in table 2, but since we cannot detect the sulfate species in the range below 1200 cm^{-1}, these values have to be treated with caution.

A loss of sulfate species from Pt/SZ was observed when the sample was activated in an inert gas stream, then reduced and a second treatment at 500 °C in He or N_2 followed, after these procedures Pt/SZ could not be reactivated. The catalyst lost its acid properties and the rest of activity comes rather from the metal sites on which isomerization and hydrogenolysis of *n*-heptane to propane and *n*-butane can take place.

During the reduction treatment, hydrogen can dissociate to form H-atoms on Pt followed by spillover to the zirconia support. Spillover hydrogen seems to be able to reduce sulfur species to a lower oxidation state. Heating in He or N_2 at temperatures above 400 °C, water and a part of sulfur species desorb as SO_2 and the catalyst loses its activity. Heating in air or oxygen restores the original oxidation state of sulfur and the sample stays active.

SZ was treated under the same conditions as Pt/SZ (figure 5). The intensity of the bands in the OH and SO region did not change during these treatments, and a small amount of coke after the reaction of *n*-heptane was formed (see band around 1500 cm^{-1} in [25]). When the same pretreatments are done on SZ no loss of sulfate species was observed.

SZ without Pt is hardly active for *n*-heptane conversion and deactivates very quickly. Only a very small amount of isomerized products was detected, the main part were cracked products, i.e. propane and mainly isobutane. It could be shown [25] that a plausible initiation

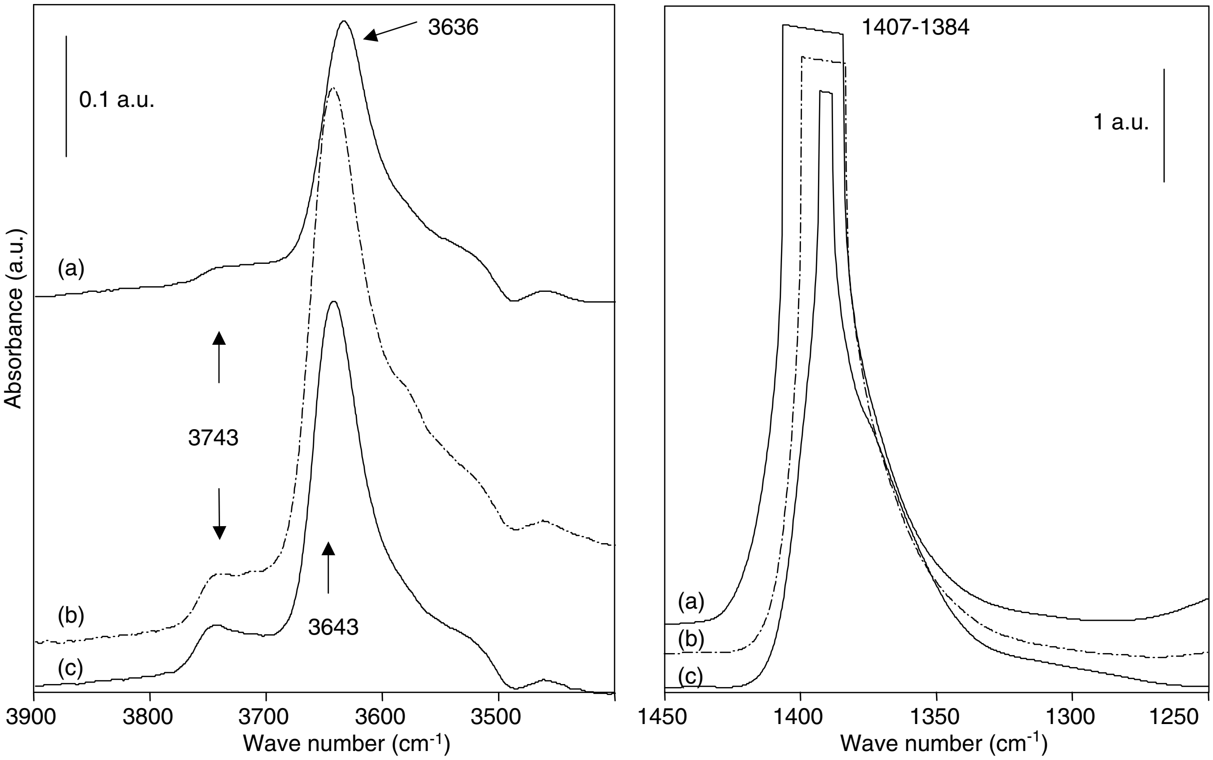

Figure 5. *In situ* IR spectra of SZ after different activation procedures carried out consecutively on the same sample; every activation step is followed by reduction at 200 °C and n-heptane isomerization at 200 °C in H_2 (spectra not shown here, only spectra directly after activation are displayed): (a) after activation in N_2, (b) in N_2 and (c) in air at 500 °C.

step of alkane activation over SZ is the oxidative dehydrogenation. In an inert atmosphere coke precursors or coke were built up.

Li and Gonzalez [39] using SZ for the isomerization of *n*-butane found that a deactivated catalyst could be completely restored by burning off the coke in the presence of oxygen or air. If, however, SZ is regenerated in nitrogen a loss of the surface sulfur species was observed and SZ was irreversibly deactivated. Also Resofszki *et al.* [22] observed that the activity of SZ can be fully regenerated by oxidation in air burning out carbon impurities.

Since the catalytic activity of SZ is very low addition of Pt is necessary to promote activity and selectivity to isomerization of *n*-alkanes. Vaudagna *et al.* [41,42] found that SZ is active only with Pt and under hydrogen for *n*-hexane isomerization. They compared SZ and Pt/SZ under nitrogen and hydrogen atmosphere. Only Pt/SZ under hydrogen showed a good activity and stability with a high selectivity to C6 isomers, the other three samples showed a high initial activity and selectivity to cracking products but they are almost deactivated completely after 9 min TOS.

On SZ the dissociation of hydrogen is not favored and the carbenium ions, which are formed and isomerized on the acid sites remain long time at the surface where they are either oligomerized and then cracked or polymerized into coke. On Pt/SZ hydrogen can be easily activated and can form protons as a source of Brønsted acid sites and hydride ions, which can interact with carbenium ions giving isomerized alkanes. Therefore Pt is not directly involved in the isomerization process; it is more likely involved in the generation of active reaction sites on the surface. Metallic and acidic sites show a concerted action rather than acidic sites isomerizing alkenes formed on metallic sites.

When Pt/SZ becomes deactivated, i.e. after regeneration in an inert atmosphere, sulfate groups were lost. With decreasing concentration of sulfate groups the activity of *n*-heptane conversion decreases and the catalyst cannot be regenerated. But the *in situ* IR measurements showed that already after the first treatment at 500 °C in an inert gas after reduction the activity was completely lost and a further decrease of the SO band did not have any effect on the activity. In literature it was discussed that the loss of a small part of the sulfate groups is enough to deactivate the catalyst totally [32]. Kim *et al.* [43] determined the fraction of sulfate species possibly utilized as reversible adsorption sites to be only 0.2% or even lower of sulfate species available on the surface.

4. Conclusions

The first activation of Pt/SZ can be done in air or in an inert atmosphere, followed by reduction at 200 °C. Then Pt/SZ is active in the conversion of hydrocarbons independent of the activation atmosphere. The activity and selectivity in the isomerization of *n*-alkanes in hydrogen atmosphere is nearly the same. Regeneration in air restored the catalytic activity and selectivity of Pt/SZ completely.

If, however, regeneration of Pt/SZ is done in He or N_2 a remarkable loss of SO_2 was observed and the catalyst was irreversibly deactivated. The loss of SO_2 was detected by TG and TPE measurements and was observed by the decreasing intensity of the SO band and the increasing Zr–OH bands in the IR spectrum.

When the reaction was carried out in He or N_2 after activation or regeneration in air, Pt/SZ deactivated quickly and bands correlated to coke precursors or coke were found in the IR spectrum. Regeneration in air burned off the coke, no loss of sulfates was observed and the catalyst was active, whereas regeneration in an inert gas atmosphere is connected with decreasing amount of sulfates and leads to an inactive catalyst.

n-Heptane is converted to mono-methyl-, di-methyl-isomers and to propane and *iso*-butane over the active Pt/SZ, whereas over the inactive form only hydrogenolysis to propane and *n*-butane take place.

Independent of the activation and reaction atmosphere, H_2 or N_2, SZ without Pt deactivates very quickly due to coke formation. No loss of sulfate groups was observed and regeneration could restore the initial activity.

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