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An in situ DRIFTS study of the deactivation and regeneration of sulfated zirconia

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Abstract

Changes in the surface structure of sulfated zirconia prepared by sol–gel method were studied using nitrogen adsorption, XRD, TGA and in situ DRIFTS. These studies were performed following deactivation and regeneration of the catalyst. The physical properties of sulfated sol–gel zirconia were unchanged as a result of reaction and catalyst regeneration. The isomerization of *n*-butane was used as a probe reaction. Both Brønsted and Lewis acid sites as determined using pyridine adsorption at 100°C were observed on sulfated zirconia. Only Lewis acid sites were observed on non-sulfated zirconia. The ratio of Brønsted to Lewis acid sites was found to be strongly dependent on catalyst pre-treatment temperature prior to reaction. The Brønsted to Lewis acid ratio was observed to decrease from a value of 0.466 to 0.127 following the removal of the catalytically active surface sulfur. The total catalyst acidity was observed to decrease only slightly following removal of this surface sulfur species. An infrared band, centered at 1370 cm^{-1}, was observed for the catalytically active material. This band appeared following activation in N_2 at 375°C and was assigned to S=O. A Brønsted/Lewis acid site ratio of approximately 0.5 was found to be optimum for the isomerization of *n*-butane. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Sulfated zirconia; In-situ DRIFTS; Diffuse reflectance; Deactivation; Brønsted

1. Introduction

The development of environmentally acceptable processes, such as alkylation and isomerization using strong solid acid catalysts as a replacement for HF and H_2SO_4 is needed. Sulfated zirconia has attracted much attention as a potential replacement catalyst because of its strong acidity. Although, sulfated zirconia has been shown to be active for the isomerization of *n*-butane, a rapid decrease in activity with reaction time is observed. Because sulfated zirconia, including metal promoted sulfated zirconia, deactivates so rapidly, it has not yet been successfully used as a substitute for strong liquid acids. For this reason, this study is focused on obtaining a better understanding of the deactivation process and how a deactivated catalyst can be regenerated to its initial activity. To do so, we have purposely avoided the promotion of sulfated zirconia by the addition of metals in order not to complicate the reaction mechanism by providing competing pathways. Possible reasons for the deactivation of sulfated zirconia can be summarized as follows: (1) reduction of the oxidation state of sulfur in the surface sulfate from S^{6+} to lower oxidation states resulting in a decrease in acid strength [1,2]; (2) coke formation

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[3–5]; (3) possible removal of sulfur as H_2S [6]; (4) the transformation of the catalytically active surface tetragonal phase into the inactive monoclinic phase [7]; and (5) changes in the surface acidity [8,9].

In a previous TGA/FT-IR study [10], only two weight losses were observed when a fresh sulfated zirconia catalyst (previously calcined at 600°C) was heated in a TGA furnace interfaced with an FTIR using N_2 as the purge gas. The two weight losses were assigned to the desorption of surface water (at 100°C) and to the decomposition of sulfate (above 600°C with a maximum at 800°C), respectively. An additional weight loss, associated with a sample deactivated in the isomerization of *n*-butane at 200°C occurred at 600°C. The species evolved at 600°C were identified as SO_2 (hereafter referred to as low temperature SO_2 to distinguish it from the SO_2 evolved at 800°C) and CO_2. Concomitant with this low temperature SO_2, a weight loss due to the formation of CO_2 was observed to occur at the same temperature. Because the evolution of both SO_2 and CO_2 were observed at the same temperature, it was speculated that perhaps an organo-sulfur complex might be formed on surface sites that had a high activity in the isomerization of *n*-butane. We suggested that the formation of this surface complex might be responsible for the rapid deactivation of sulfated zirconia. However, it was determined that this organo-sulfur complex formed during reaction did not have a well-defined stoichiometry.

The use of oxygen O_2 as a purge gas resulted in weight loss curves that were essentially identical to both the fresh and deactivated samples. The weight loss occurring at 600°C was no longer evident. Recent TGA/FT-IR studies [11] made it possible to quantify the amount of coke deposited on the surface and the related sulfur as a function of both reaction time and temperature. For example, when sulfated sol–gel zirconia was deactivated in the isomerization of *n*-butane at 200°C for 180 min, the carbon deposited amounted to only 0.06 wt.% of the total catalyst weight. However, the catalyst was totally deactivated. The low-temperature sulfur associated with this carbon was 14% of the total sulfur. The atomic ratio of carbon to this low-temperature sulfur was found to be $C/S=0.56$.

These observations suggest that two different regeneration procedures might be tried in order to restore the deactivated catalyst to its initial activity. On the one hand, carbon could be selectively burnt off in O_2 at temperatures below 450°C. Under these conditions, the low temperature sulfur would be left on the surface. On the other hand, treatment of the deactivated catalyst in N_2 at 550°C would remove not only the carbon, but also the low temperature sulfur. This study clearly showed that regeneration in N_2 at 550°C resulted in a complete loss of catalytic activity while regeneration in O_2 at 450°C essentially restored the catalytic activity to that of a fresh catalyst. From these studies, we concluded that there were two different types of sulfur present on the surface. The catalytic activity of the sulfated zirconia catalyst, is tied to the sulfur species which is evolved at 600°C. Loss of this sulfur resulted in a catalyst which was completely inactive.

It was visualized that in nitrogen, carbon atoms deposited on the active surface sites during catalyst deactivation, reacted with oxygen atoms from the surface sulfate groups to form CO_2. The evolution of CO_2 destabilizes the surface sulfate groups due to a change in the coordination of the surface sulfur atoms. This change in the coordination of surface sulfur results in the immediate evolution of SO_2. For this reason, both CO_2 and SO_2 are evolved at the same temperature. Under oxygen flow, oxygen from the gas phase reacts directly with surface carbon atoms to form CO_2. Under these conditions, the surface sulfate species can be restored to their original structure without the loss of oxygen atoms from the catalyst.

The nature of the surface of sulfated zirconia during the reaction and regeneration remains unanswered. The aim of this study is to address this unanswered puzzle through the use of in situ DRIFTS techniques.

2. Experimental

2.1. Sample preparation

Sulfated zirconia catalysts were prepared by a 2-step sol–gel synthesis method described in reference [12]. The sulfated sol–gel zirconia used in this study was prepared using 0.5 N H_2SO_4. The physical properties of the resulting sulfated zirconia together with those of a commercial sample are summarized in Table 1. The sol–gel sulfated zirconia had a sulfur content of 2.90 wt.% following calcination at 600°C

Table 1
Physical properties of sulfated zirconia[a]

Sample	BET (m^2/g)	Pore volume (ml/g)	Average pore diameter (nm)
Sol–gel, fresh	180.3	0.24	3.3
Sol–gel, deactivated for 180 min at 200°C	181.0	0.24	3.3
Sol–gel, regenerated in N_2 at 550°C	183.0	0.23	3.3
Commercial MEI, fresh	130.0	0.15	3.1

[a] After calcination at 600°C for 1 h.

for 1 h. The commercial sample, having a product code MEIC at XZ0682/01 (Magnesium Elecktron), was used for comparison. The commercial sample was prepared from the precipitation of zirconium hydroxide. It had a sulfur content of 1.32 wt.% following calcination at 600°C for 1 h.

2.2. Catalytic test reactions

The catalytic properties of the resulting materials were studied using the isomerization of *n*-butane as a reaction probe [12]. These studies were performed in a single pass, downward flow, quartz microreactor under atmospheric pressure and isothermal reaction conditions. Approximately 200 mg of the sample, calcined at 600°C, was charged to the reactor without dilution. Because the materials were rather hygroscopic, they were activated in dry N_2 (20 ml/min) at 500°C prior to reaction. The temperature was increased from ambient to 500°C using a heating schedule of 5°C/min. The isomerization of *n*-butane was performed at 200°C. The carrier gas, N_2, was controlled through the use of Tylan mass flow controllers. The total flow rate was 20 ml/min, with a fixed 10% *n*-butane content in the mixture. Product gas analysis was performed using a Hewlett Packard 5890A gas chromatograph equipped with a flame ionization detector. The first reaction data point was obtained after 15 min time on stream.

The BET surface area and pore size distribution was obtained using nitrogen adsorption at -196°C. Surface area characterization studies were performed using a Coulter Omnisorb 100 instrument.

Sulfur analysis on the resulting catalysts was performed by the Galbraith Laboratory (Knoxsville, Tennessee). A combustion method using a Leco induction furnace was used to perform these analyses.

X-ray diffraction (XRD) was performed using a Scintag XDS2000 X-ray diffractometer with Cu K_α radiation at 45 kV and 40 mA and a scan range of 2θ from 5 to 60°.

2.3. Acid-base measurement

A diffuse reflectance infrared fourier transformation spectroscopy (DRIFTS) accessory and an in situ heatable sample cell were designed and constructed to selectively collect the diffuse reflectance while minimizing the specular reflectance. The details of this design will be forthcoming in a future publication [13]. Briefly, the accessory was composed of three mirrors: a concave spherical reflector with a paraxial focal length of 68.5 mm, and two flat square reflectors of 7 cm and 5 cm, respectively. Adjustment slides and screws were used for three-dimensional positioning of the three mirrors to achieve optimum performance.

The sample cell was positioned on a platform where the IR beam could be focused. A heatable reactor cell was designed in our laboratory and manufactured by the Bryon Lambert (Franklin Park, Illinois). It was made of stainless steel and had a gas inlet and outlet. An insulated thermocouple was inserted through the gas outlet and positioned in the catalyst bed. The reactor also featured a 16 mm×2 mm optical windows which could be NaCl, KBr or CaF_2 depending on the wavelength cutoff necessary. A cartridge heater (Odgen) was placed underneath the well.

A 50 mg sample was diluted to 4 wt.% in KBr powder (1200 mg) which was stored in an oven at 140°C at all times. In order to ensure the best possible reproducibility the same weight of sample plus KBr was used in each experiment. The experimental error was estimated to be less than 4%. The first spectrum was recorded at room temperature with a background spectrum of pure KBr at the same temperature. The sample was then heated in flowing N_2 using the built-in cartridge heater. The UHP grade N_2 was dried using a gas purifier (All Tech) in order to maintain moisture levels in the ppm range. The N_2 flow rate was controlled at 60 ml/min. The sample was then increased to the desired temperature at a rate of 7°C/min and then cooled back down to 100°C. At 100°C, a spectrum of pure KBr was recorded in order to perform a background correction. A pulse of 50 μl of pyridine (Spectroscopic grade, Alfa) was injected into the N_2 flow through a three-way union upstream of the cell. Another spectrum was taken at 100°C 2 h following the injection of pyridine to ensure that physically adsorbed pyridine was not present. The ratio of Brønsted to Lewis acidity was determined from the spectra of adsorbed pyridine following the method of Basila and Kantner [14].

2.4. Total acidity measurements

The total acidity was measured using pyridine adsorption-desorption. In these measurements a thermogravimetric analyzer (TGA 2950, TA instruments) was used. The method was similar to that described by Alerasool et al. [15] with some modification. The sample temperature was linearly increased to 375°C using a temperature ramp of 7°C/min under N_2 flow (UHP grade, Doussan). The temperature was reduced to 100°C and then maintained at this temperature until the weight remained constant (approximately 45 min). The 375°C temperature was chosen for two reasons: (i) it was low enough to ensure that neither carbon or sulfur would be evolved in a N_2 flow and, (ii) the 375°C temperature duplicated that of the DRIFTS study. Following the attainment of constant weight, the N_2 flow was redirected through a saturator containing pyridine. The pyridine was then contacted with the sample situated in the TGA sample pan. The saturator was maintained at 0°C through the use of an ice-water bath. This configuration resulted in a constant flow of nitrogen/pyridine ($P_{\text{pyridine}}=5.3$ mm Hg) at an adsorption temperature of 100°C. The adsorption of pyridine was continued until a constant weight was observed (usually about 0.5 h). At this point, the flow of pyridine was discontinued and was replaced by N_2 at 100°C. This step was necessary in order to insure the desorption of physically adsorbed pyridine. The flow of N_2 at 100°C was continued until a constant weight was obtained. Values of total acidity were obtained from the equation: $\Delta W/(W_i \cdot M_W)\times 10^6$, where ΔW was the net weight gain of the catalyst as a result of adsorption of pyridine. W_i is the initial weight of the catalyst and M_W is the molecular weight of pyridine. The total acidity was also expressed in terms of μmoles of pyridine/m^2 of surface.

3. Results

Initial *n*-butane isomerization activities were high. However, deactivation as a function of time on stream was substantial for all of the catalysts studied [10–12]. In order to understand this rapid deactivation, surface properties, acid–base properties, crystal structure, coke formation and the characterization of surface sulfate species were studied in detail.

3.1. Physical properties

The BET surface areas, pore volume and pore size distribution (Table 1), did not change as a result of deactivation under reaction conditions or regeneration in either oxygen or nitrogen. Changes in surface area following reaction at 200°C for periods of 3 h during which time the catalyst was totally deactivated were not observed. We, therefore, conclude that deactivation is not due to a surface area loss. Regeneration in O_2 at 450°C resulted in a complete restoration of the initial activity. Regeneration in N_2 at 550°C resulted in a complete loss of catalytic activity. However, this loss in catalytic activity cannot be attributed to a either a loss in surface area or pore plugging by carbon deposition at the pore mouth.

3.2. XRD studies

The XRD patterns clearly show that the bulk structure of sulfated zirconia is not changed as the result of deactivation and regeneration in either O_2 or N_2 (Fig. 1). However, XRD is a bulk technique. We cannot rule out changes which may occur at the surface of sulfated zirconia as a result of catalyst deactivation.

3.3. In situ DRIFTS studies

The adsorption of pyridine is an ideal probe to study changes in the acid–base properties of surfaces which

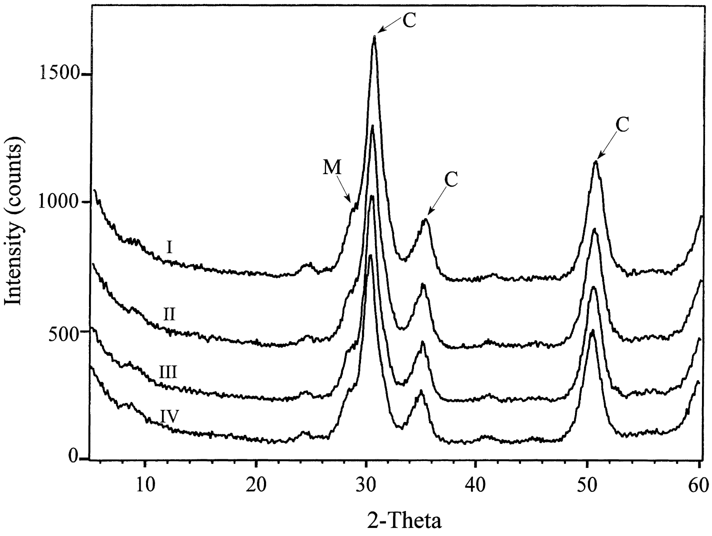

Fig. 1. X-ray diffraction patterns for fresh, deactivated and regenerated sulfated sol–gel zirconia catalysts. C and M denote the characteristic peaks of the cubic and monoclinic phases of zirconia, respectively. Curve I – the fresh sample. II – deactivated in the isomerization of *n*-butane at 200°C for 3 h. III – regenerated in O_2 at 450°C. IV – regenerated in N_2 at 550°C.

contain both Brønsted and Lewis acid sites. The design of the infrared cell used in this study is such that changes in the surface structure which occur during deactivation and regeneration of the catalyst can be probed under in situ conditions. In addition to this capability, changes in the distribution of acid sites, can be monitored by following the thermo-desorption of pyridine.

The two spectral regions of interest on sulfated zirconia include the hydroxyl stretching region (3000–3800 cm^{-1}) and the sulfate stretching region (900–1400 cm^{-1}). The interaction between sulfate and surface hydroxyl groups has a strong bearing on the sulfate groups which are generated on the surface. In addition to this, the activation of surface species can be conveniently followed by means of DRIFTS. Sulfated zirconia rehydrates following calcination. The moisture content of the catalysts plays an important role in the activity of the catalyst following pre-treatment. This change in catalytic activity may be closely related to changes in the ratio of Brønsted to Lewis acid sites. Through the progressive elimination of water, an optimum ratio of *B/L* sites can be generated. For this reason, important information concerning changes in the *B/L* ratio which may occur during deactivation, regeneration and pre-treatment can shed light on the activity of sulfated zirconia catalysts. In this study, particular attention is given to regeneration in N_2 because a small loss in sulfur content results in a complete loss in catalytic activity.

The infrared spectra of both sulfated and non-sulfated zirconia are shown in Fig. 2. The characteristic bands at 1640, 1607, 1540 and 1490 cm^{-1} are assigned to pyridinium ions adsorbed on Brønsted acid sites [16]. The bands at 1604, 1574, 1490 and 1445 cm^{-1} correspond to pyridine adsorbed on Lewis acid sites. Inspection of the spectra clearly shows that while both Brønsted acid sites and Lewis acid sites are present on sulfated zirconia, only Lewis acid sites are observed on non-sulfated zirconia.

Since sulfated zirconia is hygroscopic, considerable rehydration occurs following calcination at 600°C and storage at room temperature. For this reason, reactivation prior to reaction is essential. The spectral changes which occur during activation are shown in Fig. 3. Pre-treatment at 375°C, followed by cooling to 100°C results in the formation of four IR bands centered at 1272, 1154, 1022, and 999 cm^{-1}, respectively. These bands are assigned to the structure of a bidentate sulfate ion coordinated to Zr^{4+} [1,17]. They are due to the reduction in the C_{2v} symmetry as a result of the splitting of the triply degenerate ν_3 and ν_1 normal modes. Upon dehydration, the in situ DRIFTS spectrum shows the formation of a new infrared band

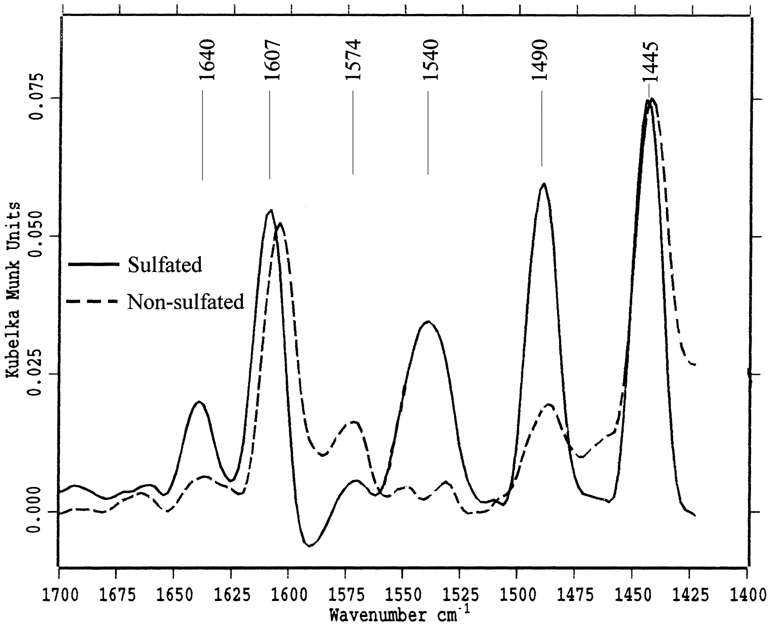

Fig. 2. In situ DRIFTS spectra of sol–gel zirconia following the adsorption of pyridine. The samples were pretreated at 375°C in N_2 prior to the adsorption of pyridine. The spectra were taken at 100°C. The spectrum of the sample prior to pyridine adsorption was substracted.

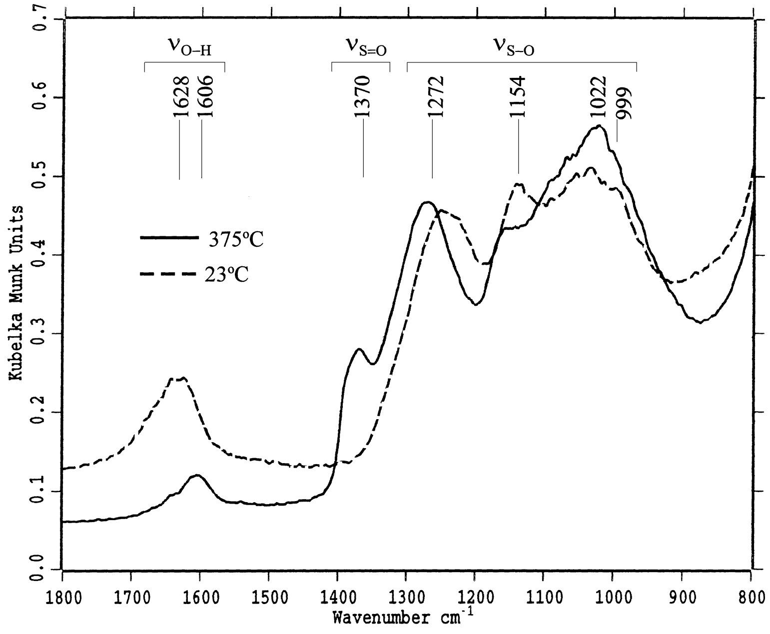

Fig. 3. In situ DRIFTS spectra of fresh sulfated sol–gel zirconia as a function of pre-treatment temperature. Top: prior to pretreatment. The spectrum was taken at room temperature. Bottom: following pre-treatment at 375°C. The spectrum was taken at 100°C.

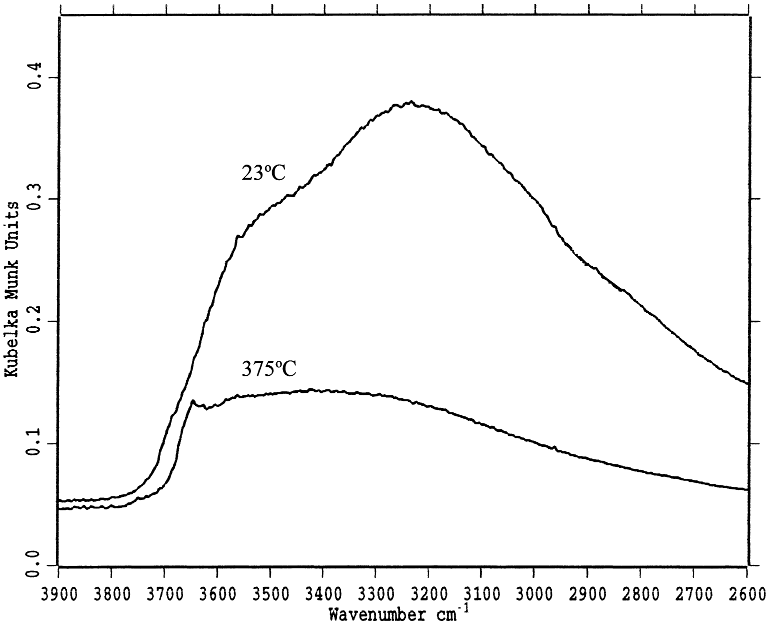

Fig. 4. In situ DRIFTS spectra of fresh sulfated sol–gel zirconia as a function of pre-treatment temperature. Top: prior to pretreatment. The spectrum was taken at room temperature. Bottom: following pretreatment at 375°C. The spectrum was taken at 100°C.

centered at 1370 cm^{-1}. This band is tentatively assigned to an S=O stretching vibration. The decrease in the water content of the catalyst could be observed by following the decrease in the intensity of the OH bending vibration centered at 1628 cm^{-1}. A red shift to 1606 cm^{-1} was observed as a result of the dehydration. Fig. 4 shows the corresponding decrease in the intensity of the OH stretching region of the spectrum due to the loss of hydrogen bonded adsorbed water.

The Brønsted to Lewis acid ratio of fresh sulfated zirconia as a function of dehydration temperature is shown in Fig. 5. A gradual decrease in the *B/L* ratio was observed when the temperature was increased from 100°C to 375°C. The optimum dehydration temperature for the maximum conversion of *n*-butane to isobutane [12] was shown to be between 375°C and 400°C. This optimum dehydration temperature resulted in a *B/L* ratio of approximately 0.5. When the catalyst was regenerated in O_2 at 450°C, the *B/L* acid ratio was 0.474 (Table 2). However, regeneration in N_2 at 550°C resulted in a *B/L* ration of 0.127 and a catalyst that was completely inactive and could not be restored to its initial activity. The *B/L* acid ratio following deactivation at 200°C for 3 h was essentially equal to that of the fresh catalyst (0.466). Because the activity of the deactivated catalyst could be fully restored by treatment in oxygen at 450°C this result was expected.

When pyridine was added to a freshly activated sample of sulfated zirconia, a strong interaction between pyridine and the S=O bond was observed (Fig. 6). The most noticeable change in the infrared spectrum of sulfated zirconia was the disappearance of the S=O which appeared only as a weak shoulder on the 1272 cm^{-1} band. This downward shift has been attributed to a weakening in the ability of S=O to attract electrons from Zr^{4+} due to the adsorption of pyridine [18]. A comparison of the infrared spectrum of deactivated sulfated zirconia to that of a fresh

Table 2
The *B/L* ratio of sulfated sol–gel zirconia following pretreatment at 375°C determined by pyridine adsorption

Sample	*B/L* ratio
Fresh	0.466
Deactivated for 180 min at 200°C	0.464
Regenerated in O_2 at 450°C	0.474
Regenerated in N_2 at 550°C	0.127

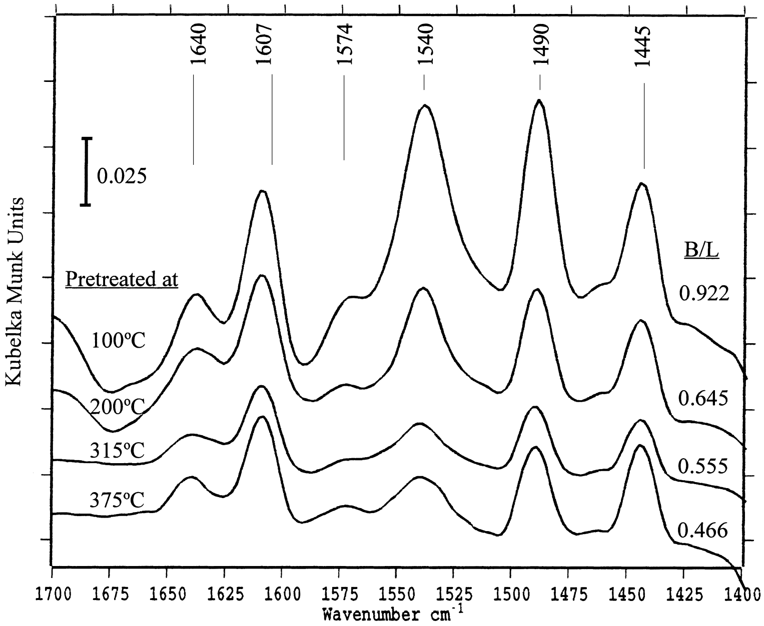

Fig. 5. In situ DRIFTS spectra and *B/L* ratios of fresh sulfated sol–gel zirconia following the adsorption of pyridine as a function of pretreatment temperature. The spectra were taken at 100°C. The spectrum of the sample prior to pyridine adsorption was subtsracted.

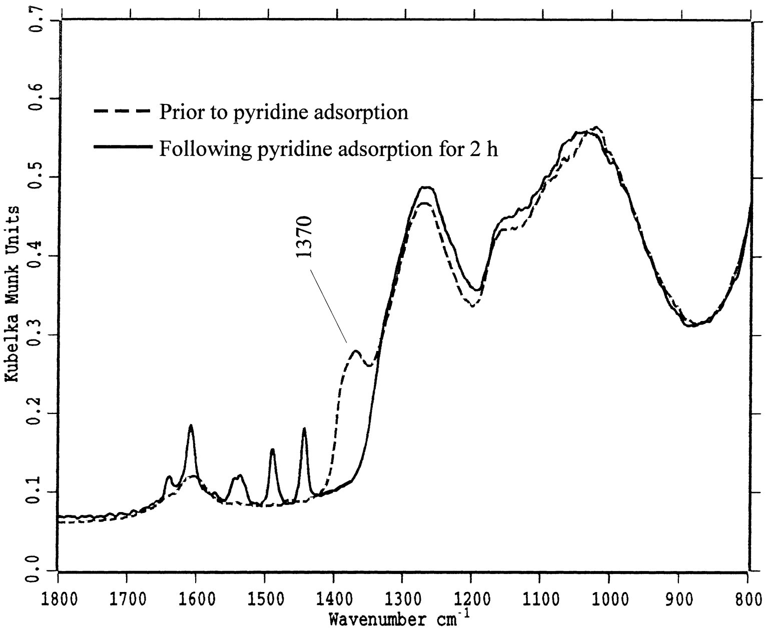

Fig. 6. In situ DRIFTS spectra of fresh sulfated sol–gel zirconia before and after the adsorption of pyridine. The sample was pretreated at 375°C in N_2 prior to the adsorption of pyridine. The spectra were taken at 100°C.

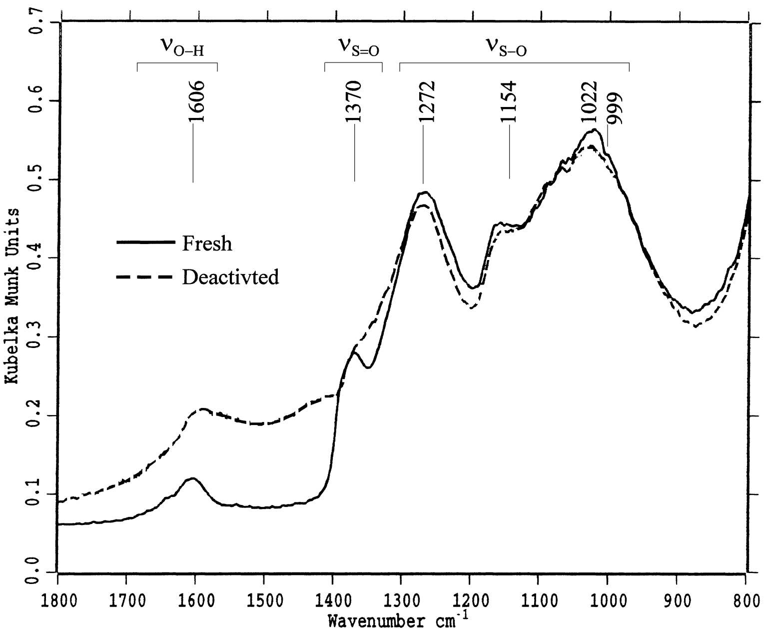

Fig. 7. In situ DRIFTS spectra of fresh and deactivated sulfated sol–gel zirconia. The samples were pretreated at 375°C in N_2. The spectra were taken at 100°C. The sample was deactivated in the isomerization of *n*-butane at 200°C for 3 h.

sample is shown in Fig. 7. The most important feature in the spectra is the decrease in the intensity of the 1370 cm^{-1}, which is most likely due to the formation of carbon on the S=O site.

The fresh, active zirconia catalyst is compared to the deactivated catalyst regenerated in N_2 at 550°C (Fig. 8). There is a marked decrease in the intensity of all of the sulfate bands and a slight shift to lower wavenumber. The most noticeable difference between the two spectra is the decrease in the intensity of the S=O bond. Regeneration in O_2 at 450°C (not shown) essentially reproduces the spectrum of the fresh catalyst.

3.4. *Total acidity measurement*

Total acidity measurement were performed using a TGA balance and pyridine adsorption. The results are summarized in Table 3 both as total pyridine adsorption and normalized in terms of μmoles of pridine/m^2 of BET surface area. The total acidity of fresh sol–gel sulfated zirconia was 336 μmol/g or 1.86 μmol/m^2. The non-sulfated sol–gel zirconia had a total acidity of 90 μmol/g or 0.94 μmol/m^2, about half that of the sulfated zirconia which had both Lewis and Brønsted acid sites. It should be recalled that only Lewis acid sites were present on the non-sulfated zirconia. The total acidity of fresh MEI catalyst is also included in Table 3. Its total acidity was slightly less than that of the sol–gel sulfated zirconia catalyst. However, when the acidity was normalized per m^2 of surface area, the total acidity was comparable to that of the sol–gel catalyst. Fogash et al. [19] reported a saturation ammonia coverage of 230 μmol/g on the MEI sample

Table 3
Total acidity of sulfated zirconia as measured by pyridine adsorption using TGA[a]

Sample	Total acidity (μmol/g)	Total acidity (μmol/m^2)
Fresh sulfated sol–gel	336	1.86
Deactivated for 180 min at 200°C	315	1.74
Regenerated in O_2 at 450°C	322	1.79
Regenerated in N_2 at 550°C	298	1.63
Nonsulfated sol–gel	90	0.94
Fresh commercial MEI, sulfated	227	1.74
Commercial MEI, non-sulfated	80	0.93

[a] Measured at 100°C following pretreatment at 375°C in N_2.

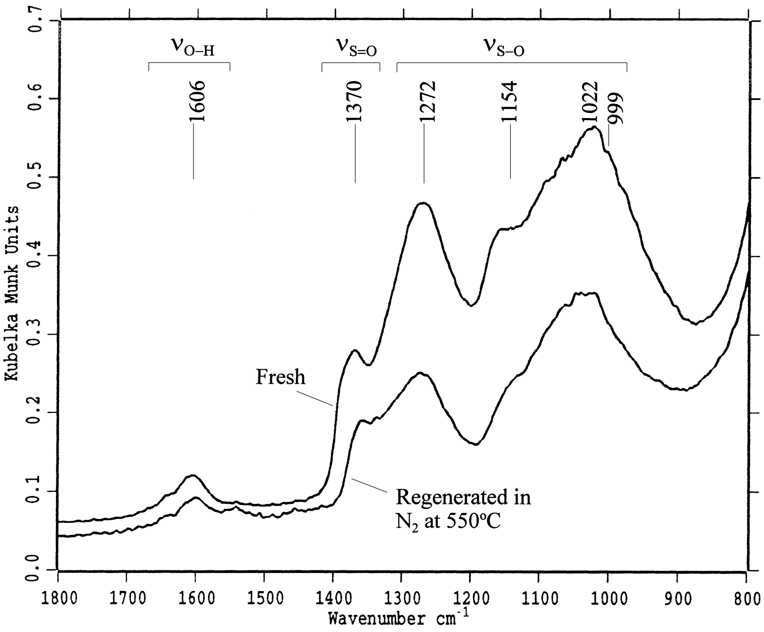

Fig. 8. In situ DRIFTS spectra of fresh and regenerated sulfated sol–gel zirconia. The samples were pretreated at 375°C in N_2. The spectra were taken at 100°C. The sample was regenerated in N_2 at 550°C.

which is comparable to the result reported in this study.

The results shown in Table 3 are rather surprising in that regeneration in N_2, which results in a catalyst which is totally inactive, has a total acidity which is only 11% lower than that of a fresh active catalyst. The error in these measurements is estimated to be about 2%. This observation leads one to conclude that the number of active sites for the isomerization of *n*-butane is rather small. The measurement of total acidity when taken together with the relatively small amounts of coke required to poison the isomerization of *n*-butane, suggest that the reaction may occur on a very small number of acid sites. These active sites, when poisoned by coke, may be sufficient to reduce the catalytic activity but may not change the total acidity of the catalyst significantly.

4. Discussion

Sulfated zirconia has shown a remarkable low temperature activity in the isomerization of hydrocarbons. Unfortunately, this high initial activity decreases rapidly with time severely reducing its usefulness in commercial applications. In a previous study [10], we observed that this decline in catalytic activity was linearly related to the formation of coke on the surface of the catalyst. In a separate study [11] the weight of coke deposited on the surface of sulfated zirconia during the isomerization of *n*-butane was quantified using a sensitive TGA/FTIR technique. In this study, it was determined that 0.06 wt.% carbon was deposited on the surface of the catalyst during the isomerization of *n*-butane at 200°C over a 3 h period. The deposition of as little as 0.02 wt.% carbon was sufficient to reduce the conversion to 10% of the initial isomerization activity. This observation leads one to conclude that the number of active sites required to actually catalyze the isomerization reaction must be very small. The purpose of this study was to attempt to understand the surface changes which lead to this rapid deactivation.

A number of models of the structure of sulfated zirconia have been proposed [8,20–31]. In order to discuss the nature of active sites of sulfated zirconia, a model proposed by Clearfield et al. [31] is included as Fig. 9. The uncalcined catalyst contains protons as bisulfate groups and as hydroxyl groups bridging two Zr ions. During heating, an adjacent hydroxyl interacts

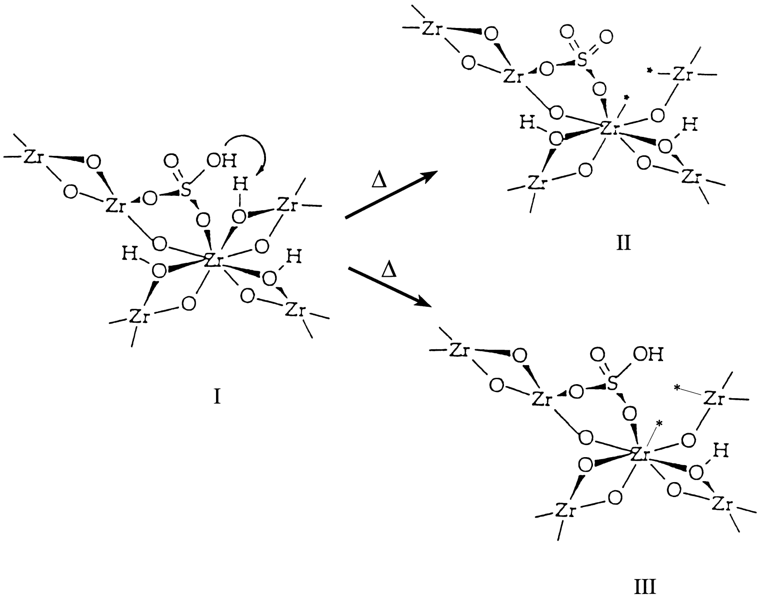

Fig. 9. Schematic of the effect of heating sulfated zirconia (from reference [31]).

with the bisulfate ion to split out water and lead to structure II. However, the hydroxyl group could also interact with an adjacent -ol bridge to split out water and leave the bisulfate ion intact (structure III). This would place strong Lewis acid sites adjacent to a permanent S–O–H group. The Lewis acid sites are marked by asterisks. These bisulfate groups act as Brønsted acid sites. These Brønsted acid sites are highly acidic because the Lewis acid sites tend to withdraw electrons from the sulfate group, thus weakening the SO–H bond.

The XRD and surface area measurement presented in Table 1 show that changes in the physical properties of the sulfated zirconia catalyst cannot be responsible for the drastic changes in catalytic activity which are observed as a result of deactivation. Again we emphasize that changes in the surface phase of sulfated zirconia cannot be detected by the bulk XRD measurements made in this study. Sulfur was not evolved from the surface under the reaction conditions used in this study. This results is in agreement with those of Yori et al. [32], and Spielbauer et al. [5], but not with that of Ng et al. [6]. These authors claimed that sulfur was evolved as H_2S from the surface and that this sulfur loss was related to the decline in catalytic isomerization activity. Because the catalytic activity could be completely restored by burning of the coke selectively in the presence of oxygen, we reject sulfur loss during reaction as a reason for deactivation. The deposition of coke does not appear to inhibit the adsorption of pyridine. However, there appears to be a strong interaction between adsorbed pyridine and the S=O site on the surface. Because this surface site appears to be related to the initial isomerization activity and is also lost following the initial deposition of carbon (Fig. 7), its role may be significant in the loss of catalytic activity. Comelli et al. [33] point out that the total acidity does not appear to be related to the catalytic activity. These results agree with the conclusions obtained in this study (see Table 3). Of considerable significance is the observation that an optimum ratio of Brønsted to Lewis sites is essential in order to generate a high isomerization activity. This ratio is approximately B/L=0.5. Regeneration in N_2 at 550°C results in a loss of the surface sulfur species which is related to this high isomerization activity. The B/L ration of 0.147 obtained following regeneration in N_2 will not sustain any isomerization activity. Regeneration in O_2 at 450°C restores the B/L ratio to that of the fresh catalyst, i.e., B/L=0.46 without the loss of sulfur. We should also point out that the initial catalytic activity can also be restored by regeneration in air at 450°C. The *B/L* ratio of about 0.5 appears to be very important. The optimum *B/L* ratio of 0.5 agrees well with that reported by David and Ko [8]. *B/L* ratios of 0.147 are completely inactive while higher *B/L* ratios obtained by activation at lower temperature are considerably less active than the 0.5 ratio obtained following activation between 375 and 400°C. In this study, both Brønsted and Lewis sites were observed on sulfated zirconia. However, only Lewis acidity was observed on non-sulfated zirconia.

The relatively small amount of surface sulfur responsible for the high-low temperature activity (14% of the total sulfur) is puzzling. In this study, the sulfated sol–gel zirconia was prepared by a two-step method. In the first step, zirconia was made by drying the gel followed by pre-treatment in He at 385°C. Sulfuric acid (0.5 N) was added in the second step. From this, we might surmise that a major percentage of this sulfur is located at the surface although we cannot completely rule out the fact that a portion of this sulfur may be located in the bulk. This is in accord with similar observations made by Yori et al. [32] and Sarzanini et al. [34]. In the case of a one-step sol–gel method preparation [8], the sulfur was trapped in the pores of the gel network and was expelled onto the surface in the catalyst activation step. Attempts were made to recalcine the deactivated catalyst regenerated in N_2 at 600°C in O_2 to redistribute the sulfur on the surface. Only a slight improvement in activity was obtained supporting the idea that the sulfur was primarily on the surface. An important question as to the nature of the sulfur species which contains the active site remains.

It was seen that the bulk crystal structure of nitrogen regenerated sulfated sol–gel zirconia was basically identical to that of the fresh catalyst. Surface area changes were not observed in nitrogen regenerated catalyst. In other words, the removal of the low temperature sulfur did not cause the crystal structure and physical structure to change. However, it resulted in a change in the acid sites and strength, and so in the activity of the catalyst.

Morterra et al. [35] reported that at low surface coverages of sulfur (less than 0.8 sulfur atom/nm^2) only Lewis acid sites are observed. Sulfur coverage up to approximately to 2.0 sulfur atoms/nm^2 produce primarily Lewis sites with some Brønsted sites. An increase in the sulfur loading to an amount exceeding half a monolayer (equal to about 2.0 sulfur atoms/nm^2) results in the formation of a pyrosulfate species with a concomitant increase in the number of Brønsted sites. In the present study, calcination at 600°C results in the formation of sulfate coverage consisting of 3.03 S atoms/nm^2 for the sol–gel sample and 1.91 S atoms/nm^2 for the MEI commercial sample.

It is still a matter of some debate as to whether Brønsted or Lewis acid sites are responsible for the higher isomerization activity. For example, Yaluris et al. [36] suggest that Brønsted acid sites are responsible for normal isomerization activity while the presence of Lewis acid sites are responsible for enhancing this activity. Adeeva et al. [37] showed that the acid sites on sulfated zirconia catalysts were probably not stronger than the Brønsted sites found on acid zeolites or the Lewis acid sites on γ-alumina. Bolis et al. [38] suggested that perhaps two Lewis sites of differing acid strength were present. While not excluding the contribution from Brønsted sites, Morterra et al. [39] proposed that Lewis sites were vital for the generation of higher isomerization activity,. Yori and Comelli [32,40] concluded that Lewis sites were responsible for generating a higher activity in the isomerization of *n*-butane.

Using ^{31}P-NMR spectroscopy and trimethylphosphine as a probe, Lunsford et al. [41] found evidence for the presence of both Brønsted and Lewis sites and suggested that Brønsted sites are essential for high isomerization activity. Fogash et al. [19] reported that sulfated zirconia catalysts that had a high isomerization activity, had differential heats of ammonia adsorption between 125 and 140 kJ/mol. They proposed that Brønsted acid sites of intermediate strength were active for *n*-butane isomerization while not discounting a possible role of stronger acid sites.

We believe that both Brønsted and Lewis acid sites are needed to catalyze the isomerization of *n*-butane. A suitable ratio of Brønsted to Lewis sites is essential and an optimum *B/L* ratio of 0.5 was determined under the reaction conditions in this study. The results of this study show unequivocally that the elimination of a small percent of sulfate species results in a catalyst that is totally inactive in the isomerization of *n*-butane. The *B/L* acid site ratio of this deactivated catalyst is 0.147. The ratio cannot be increased by catalyst manipulation.

5. Conclusions

The following important conclusions emerge from this study:

1. An optimum Brønsted/Lewis acid site ratio of 0.5 was found for the isomerization of *n*-butane.
2. A reduction of *B/L* acid site ratio to a value of 0.147 results in a catalyst which is completely inactive in the isomerization of *n*-butane.
3. Catalysts regenerated in N_2 result in the elimination of surface sulfate species which are inactive in the isomerization of *n*-butane, while catalysts in which coke is selectively burned off in O_2 can be restored to its initial activity.
4. Catalysts deactivated in N_2 cannot be reactivated by catalyst manipulation.
5. Catalytic activity does not appear to depend on total acididty.
6. Regeneration in N_2, O_2 or deactivation during *n*-butane isomerization does not have effect on physical properties such as pore size distribution, crystal structure or BET surface area.

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