# Acid centers in sulfated, phosphated and/or aluminated zirconias

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On sulfated $ZrO_2$, the comparison of the effects of adsorbing water or ammonia on the infrared bands between 1400 and 1000 $cm^{-1}$ suggests that besides structural Lewis sites on the surface of $ZrO_2$, strong Lewis sites are made from chemisorbed $SO_3$. Upon adsorption of water, $SO_3$ is converted, partially, into a surface sulfated species which may act as strong Brønsted sites. At moderate surface hydration, both types of sites may coexist. The catalytic activity in the isomerization of isobutane is a function of the overall nominal surface density in $SO_4$. The acid sites on the surface of phosphated mesoporous zirconia are attributable to surface P–OH groups working as weak Brønsted sites. On both sulfated and phosphated zirconia, surface coating of alumina stabilizes the porosity, but it does not modify the nature of their acid centers.

**Keywords:** Lewis and Brønsted acid centers, zirconia

## 1. Introduction

The preparation and properties of mesoporous sulfated and oxophosphated zirconia obtained at low pH from dodecyl sulfate and phosphate, respectively, have been described recently [1,2]. The incorporation of up to 5% Al in the lattice of the phosphated zirconia prevents the crystallization of oxophosphate at 900 °C. On the surface of the sulfated material an alumina coating helps to preserve the surface area and the porosity up to 500 °C [3]. This contribution characterizes the nature of the acid sites on these materials.

Because of its catalytic properties the nature of the acid sites of non-mesoporous sulfated zirconia with specific surface area ca. 100 $m^2/g$ has gathered enormous interest. Excellent reviews have been published regularly, such as those of Tanabe et al. [4] in 1990, Corma [5] in 1995, Song and Saryari [6] in 1996 and, recently, Dumesic and coworkers [7]. Infrared spectroscopy has been, of course, of fundamental interest in detecting the nature of the centers [8,9]. Theoretical calculations [10,11] have also helped to define the material, but the problem of catalytic properties is still partially unsolved.

Several factors explain the difficulty in understanding how sulfated zirconia works. For instance, it has been shown that the catalyst's [10,12] performance depends "sharply" on the amount of residual water on the surface. The catalytic activity of a sample dried at 500 °C is one order of magnitude less than that of a sample dried at 315 °C, but the addition of water at 150 °C restores the activity [10]. Such an observation would suggest an interplay between Lewis and Brønsted acid sites, but the heat of ammonia adsorption is not altered by dehydration. Kobe et al. [12] suggested that the change in catalytic activity with drying temperature is related to the modification of a redox cycle. This cycle, initiated by a sulfate species, would activate the hydrocarbon (butane) allowing the acidic function to isomerize the activated butane [13].

This idea has been advocated, in particular, by Ghenciu et al. [14,15], who studied the isomerization of methylcyclopentane to cyclohexane at 65 °C. Using polycyclic saturated hydrocarbon they found that in the first step, which involves oxidation, no cleaved product was observed, which would be the case if superacid was present. Still, strong acidity is needed for the propagation steps. It was suggested [7] that this is achieved mainly by Brønsted sites, although the intervention of strong Lewis sites was not excluded.

The complexity of the surface of sulfated $ZrO_2$ is best illustrated by the $^{31}P$ NMR spectrum of chemisorbed trimethylphosphine [16]. Besides the proton adduct $TMPH^+$, typified by a $^{31}P$ MAS resonance at $-3$ ppm (with respect to $H_3PO_4$), a resonance near $-33$ ppm is assigned to TMP on Lewis sites. The preparation of the surface is very critical and discrepancies between results presented by different authors [17,18] can be traced to the technique employed for preparing the sample used in the $^{31}P$ NMR study. This is especially true for a narrow resonance near $+26$ ppm [16] which could be attributed to an oxidation product $TMPO_x$ [19]. It is noteworthy that $SO_4$–$Al_2O_3$ pretreated exactly as $SO_4$–$ZrO_2$ does not oxidize TMP. Riemer and Knözinger [18] have tried to elucidate the oxidative function by recording the ESR signal of $SO_4$–$ZrO_2$ outgassed at 450 °C. They observed an intense isotropic line at $g = 2.0038$ that they assigned to $SO_3^-$ or to an oxygen vacancy. This signal is absent in $ZrO_2$.

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As a consequence of our sample preparation procedure [1–3], the sulfate and phosphate anions are incorporated within the catalyst structure at low temperature (∼120 °C). In the classical preparations, the zirconia is first calcined at high temperature (>500 °C) and then impregnated by a solution of the corresponding anion before being thermally activated. The effect of aluminum is worthwhile investigating, since specific surface areas larger than 200 $m^2$/g are maintained above 500 °C in the presence of aluminum [3].

As far as the acidity of phosphated samples is concerned, the development of a relatively weak acidity could be anticipated if some POH groups are present on the surface. The sulfated materials described here will have to be enriched in sulfate in order to compete catalytically with non-mesoporous zirconias, because of the larger surface area exposed in the impregnation process.

In this contribution the main technique applied will be the infrared spectroscopic study of autocoherent films of compressed materials, as well as a powder, which are manipulated in a controlled atmosphere. The probe molecule will be $NH_3$ which has also been used in our lab to quantify the Lewis and Brønsted acidity in zeolites [20]. Water as a probe molecule (weak base) has been extensively studied by Morterra et al. [8] and Babou et al. [9], but surface reconstruction could occur with water. In addition, comparing the two probes is interesting, since the heats of adsorption of ammonia and water on alumina Lewis acid sites are comparable [21]. The variation of the heats of adsorption of $NH_3$ with coverage on different sulfated zirconias has been carefully examined [22], giving results between ∼200 and ∼60 kJ/mol. If we focus on sites with strength large enough to retain chemisorbed ammonia under vacuum at 110–120 °C, e.g., the sites with heats of adsorption larger than 120 kJ/mol [20,21], the corresponding coverage is about 1 $\mu$mol/$m^2$. This limit is also that assigned by Hong et al. [7] to the separation between sites with “poor” and “reasonable” activity.

In addition to the spectroscopic technique, we have also used the isobutane isomerization reaction as a test for strong acidity. Following the suggestion of Dumesic [23], the isomerization of isobutane is simpler to handle than that of butane, because there is no need to purify the gas from the olefins, and the rate of a catalyst deactivation is ten times less than in the case of butane isomerization.

## 2. Experimental

The preparations and properties of the materials have been reported earlier and will not be repeated here. Essentially, zirconium isopropoxide is slowly hydrolyzed in acid medium ($H_2SO_4$ or $H_3PO_4$) in the presence of an anionic surfactant. Table 1 summarizes the main data.

Table 1
Physical and chemical characteristics of the samples used in this work.[a]

| Sample[b] | Al (mmol/g) | (1/2)$P_2O_5$ or $SO_3$[c] (mmol/g) | $A$[d] ($m^2$/g) | |
|---|---|---|---|---|
| | | | 140 °C | 500 °C |
| $S_{12}$ (8) | 0 | 0.363 | 335 | 116 |
| $S_{16}$ (2) | 0 | n/a | 247 | 115 |
| $S_{12}$ (20) | 0.829 | 0.832 | 446 | 220 |
| $S_{12}$ (21) | 1.5160 | 1.2569 | 487 | 281 |
| $P_{12}$ (6) | 0 | n/a | 455 | 380 |
| $P_{12}$ (16) | 0.372 | 4.0223 | 540 | 401 |

[a] See [1] and [3] for preparation and characterization.
[b] Surfactant used in the synthesis; $P_{12}$ and $S_{12}$: dodecyl phosphate and sulfate; $S_{16}$: lauryl sulfate.
[c] Analysis carried out on samples calcined at 500 °C.
[d] $A$: $t$-plot specific surface after outgassing at 140 and 500 °C.

### 2.1. IR spectroscopy

The spectra were obtained with a Perkin–Elmer 1800 FTIR operating in the absorbance mode. One hundred scans were accumulated and the spectral resolution was 2 $cm^{-1}$. The Peakfit® program was sometimes used for deconvoluting the spectra.

Wafers weighing 14 mg/$cm^2$ were calcined in the IR cell at 500 °C and were exposed to 30 Torr dry $NH_3$. Spectra were recorded after outgassing for 30 min at 115 °C and for at least 30 min at higher temperatures.

In the regions of the asymmetric bending modes of ammonium (∼1450 $cm^{-1}$) and of ammonia (∼1605 $cm^{-1}$) the quantitative analyses were performed, as reported in [20].

Diffuse reflectance Fourier transform infrared spectroscopy (DRIFT Mattson Instrument, 500 scans, 4 $cm^{-1}$ resolution) was used to follow the dehydration of some sulfated zirconia up to a temperature of 500 °C. The DRIFT cell was continuously evacuated at $10^{-2}$ Torr.

### 2.2. Catalytic tests

The flow reactor was typically fed with a mixture of isobutane (15 ml/min) and helium (40 ml/min) at temperatures between 200 and 250 °C, and the yield in butane was characterized by on-line chromatography (Perkin–Elmer 8500 with an Alltech C-5000 98714 L column).

In order to achieve an activity with the mesoporous sulfated sample that is comparable to that of the MEI reference sample (see infra), the mesoporous samples dried at 140 °C were impregnated with $H_2SO_4$. Two different doses were added and the corresponding samples were called $S_{12}$ (8)a and $S_{12}$ (8)b, to be compared to $S_{12}$ (8)140, namely, the original samples. An aluminated sulfated sample $S_{12}$ (20)140 was treated likewise and called $S_{12}$ (20)a. All samples were calcined at 500 °C in the air, cooled down at room temperature and exposed to air overnight. They were redried in the flow of helium at 250 °C. The reaction temperature was 250 °C. Drying at lower (150 °C) or higher (325 °C) temperatures resulted in a lower activity.

## 3. Results

### 3.1. Phosphated zirconia

Figures 1 and 2 summarize the spectroscopic observation of the $NH_4^+$ or $NH_3$ bending vibrations (part (A), 1700–1100 cm$^{-1}$), and in the OH, NH stretching regions (part (B), 3800–3000 cm$^{-1}$) for sample $P_{12}$ (6), containing no aluminum, and sample $P_{12}$ (16), containing aluminum, respectively. Spectrum 0 is recorded after outgassing in the IR cell at 500 °C for several hours.

After calcination at 500 °C a narrow band with a half-height width of ~10 cm$^{-1}$ is observed at 3676 cm$^{-1}$, in agreement with the observations by Boyse and Ko [24] on a zirconia–phosphate aerogel. Another broader and weaker band is observed at 3773 cm$^{-1}$. The first band is not observed on zirconia. The intensity of the band at 3676 cm$^{-1}$ decreases strongly upon introduction of $NH_3$. Spectrum (1) is obtained after introduction of 30 Torr $NH_3$ and outgassing at 115 °C for 30 min.

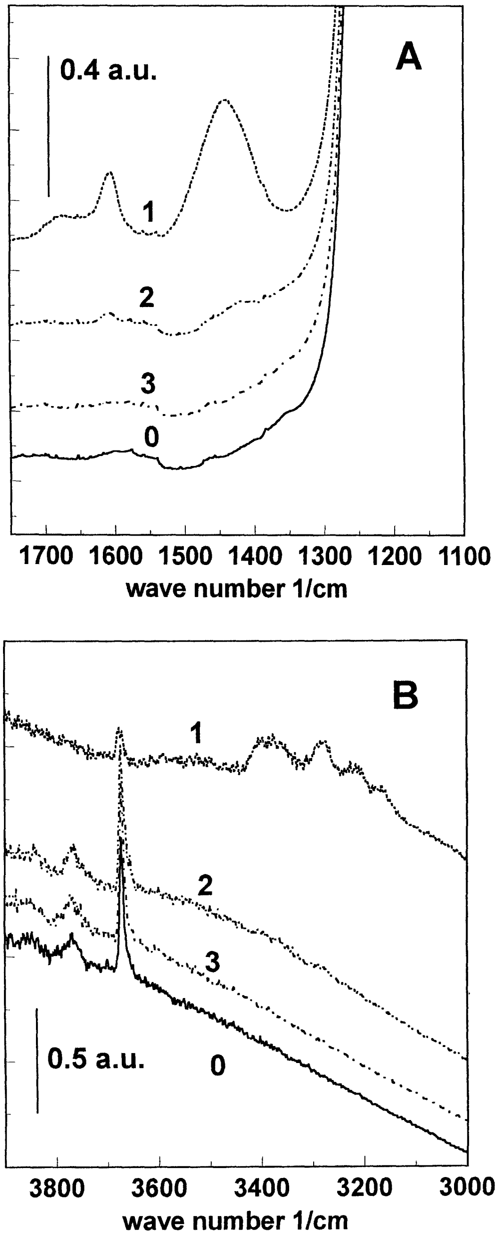

Figure 1. Sample $P_{12}$ (6) outgassed at 500 °C, exposed to 30 Torr $NH_3$ and outgassed for 30 min at (1) 115, (2) 175 and (3) 225 °C for the same time. (A) Bending region of $NH_3$ and $NH_4^+$; (B) OH and NH stretching region.

The bending vibration region shows three bands which can be assigned to adsorbed species in spectrum (1), at 1675, 1608 and 1450 cm$^{-1}$, respectively.

The band at 1608 cm$^{-1}$ is the asymmetric deformation of $NH_3$ and the band at 1450 cm$^{-1}$ can be assigned to the asymmetric deformation of $NH_4^+$. These bands find the corresponding stretching vibrations at 3376, 3277, 3215 and 3164 cm$^{-1}$ due to $NH_3$ (the two first ones) and $NH_4^+$, respectively.

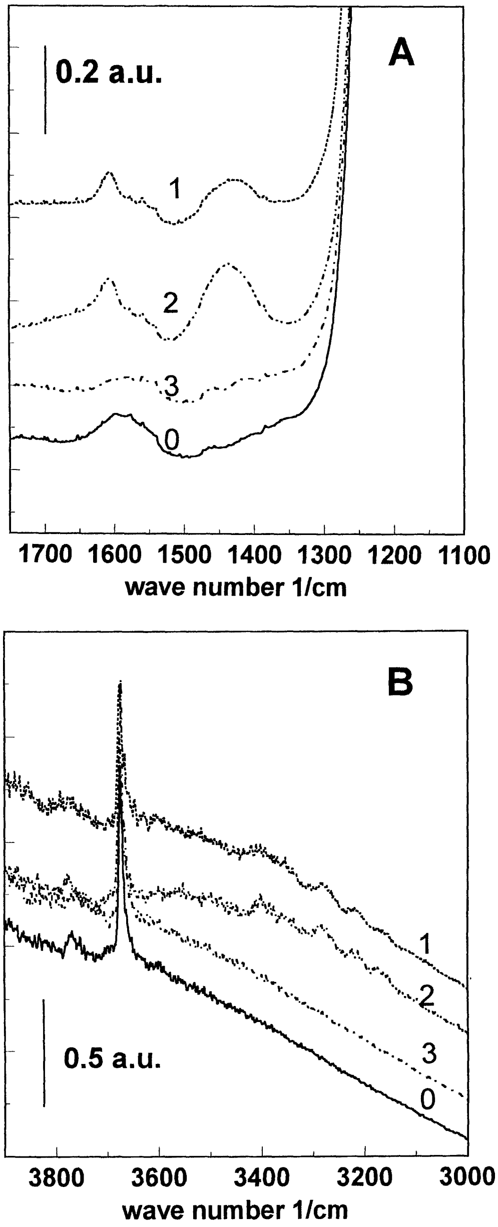

Figure 2. Sample $P_{12}$ (16). Same caption as in figure 1.

Table 2
Lewis and Brønsted sites in phosphated mesoporous zirconia ($NH_3$ chemisorption).

| Sample | Outgassing temperature[a] (°C) | Site ($\mu$mol/$m^2$) | |
|---|---|---|---|
| | | Lewis | Brønsted |
| $P_{12}$ (6) | 115 | 1.63 | 0.53 |
| | 160 | 0.184 | 0.05 |
| $P_{12}$ (16) | 115 | 0.65 | 0.12 |
| | 160 | 0.47 | 0.1 |

[a] Outgassing for 30 min at 115 °C and an additional 30 min at 160 °C.

Note that the characteristic vibrations of $PO_4$ are observed below 1300 $cm^{-1}$ [24]. They are very intense and no modifications due to adsorption of $NH_3$ are detectable.

After outgassing at 175 °C (spectrum (2)) and 225 °C (spectrum (3)) for 30 min, the spectral characteristics of chemisorbed $NH_3$ and $NH_4^+$ disappear and the intensity of the OH stretching vibration at 3676 $cm^{-1}$ is restored.

Assigning this band to acidic POH presents no ambiguity, since it is observed only when phosphorus is present. The Lewis sites exist either on the surface of zirconia or on the surface of the aluminum coating. The contents of the Lewis and Brønsted acid sites are shown in table 2. Less than 5 mol% P bear acidic OH. The incorporation of the phosphate in the zirconia structure accounts for this low rate. A similar situation should exist for sulfated samples.

### 3.2. Sulfated zirconia (figures 3–5)

In the following we support most of the assignments suggested by Babou et al. [9,11] and we will add more experimental evidence in their favor.

Upon calcination in vacuum at 500 °C a relatively weak and broad band is observed at 3655 $cm^{-1}$ in the OH stretching region. The shape and the intensity of this band are very different from those of the band at 3676 $cm^{-1}$ in the phosphated material. The adsorption of ammonia is marked by weak NH stretching modes at 3370, 3275, 3177 and 3047 $cm^{-1}$, the first three being very similar to the bands observed with the phosphated zirconia, but the band at 3655 $cm^{-1}$ is not affected by the $NH_3$ adsorption. The corresponding OH is, therefore, not acidic.

In the 1700–1100 $cm^{-1}$ region the main feature is a band which shifts from 1390 $cm^{-1}$ towards a lower frequency upon $NH_3$ adsorption. The shift is accompanied by a broadening and a splitting into two bands at ~1360 and 1270–1300 $cm^{-1}$. These modifications are reversible upon outgassing at 350 °C. Similar features are observed with the zirconia synthesized through the mediation of hexadecyl sulfonate (compare figure 4 (A) and (B)). In the material doped with aluminum, the band at 1393 $cm^{-1}$ is narrower than in the undoped sulfated zirconia. This band has been assigned [9] to the $\nu_3$ vibration of adsorbed $SO_3$.

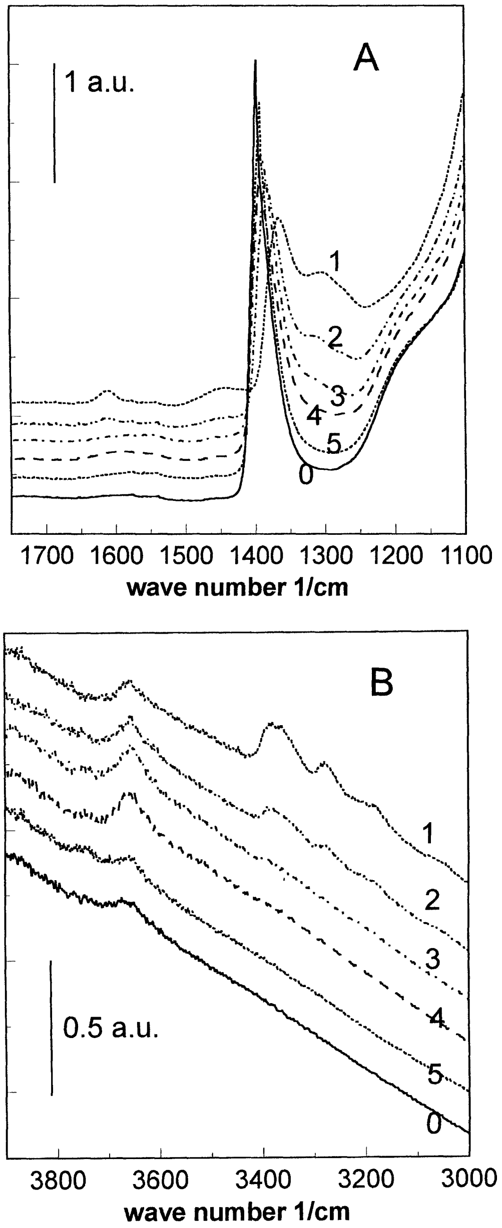

Figure 3. Sample $S_{12}$ (21) outgassed at 500 °C (0), exposed to 30 Torr $NH_3$ and outgassed for 30 min at (1) 115, (2) 160, (3) 215, (4) 275 and (5) 350 °C.

Similar spectacular modifications are observed upon adsorbing or desorbing water [8,9] and they are very much the same as those reported by Dumesic and his group [21].

Figure 5 represents the DRIFT spectra obtained with samples $S_{12}$ (21) and $S_{12}$ (8) calcined at 500 °C, exposed to atmospheric moisture and outgassed under vacuum at increasing temperatures up to 500 °C. This set of spectra mimics the state of hydration of the catalysts as there are used for the catalytic test, see infra. The bands at about 1150, 1100 and 1050 $cm^{-1}$, which are moderately affected by rehydration, can be assigned to bidentate bridging $SO_4^{2-}$ with symmetry $C_{2v}$ in which $\nu_3$ splits into three bands [25,26]. It should be recalled that the intensities in reflectance spectra are affected by different factors includ-

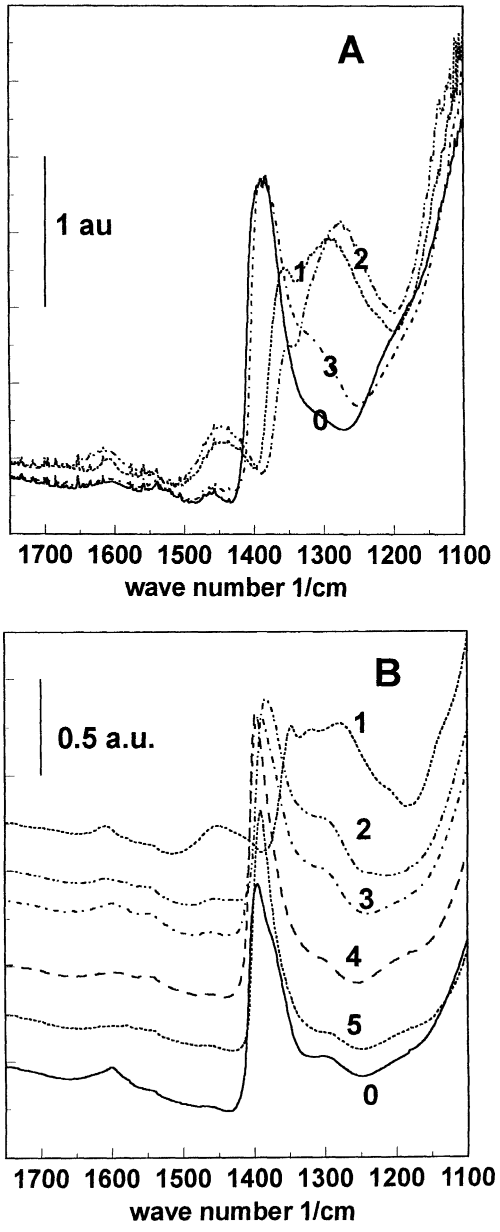

Figure 4. (A) Sample $S_{12}$ (8) and (B) sample $S_{16}$ (2). Same caption as in figure 3.

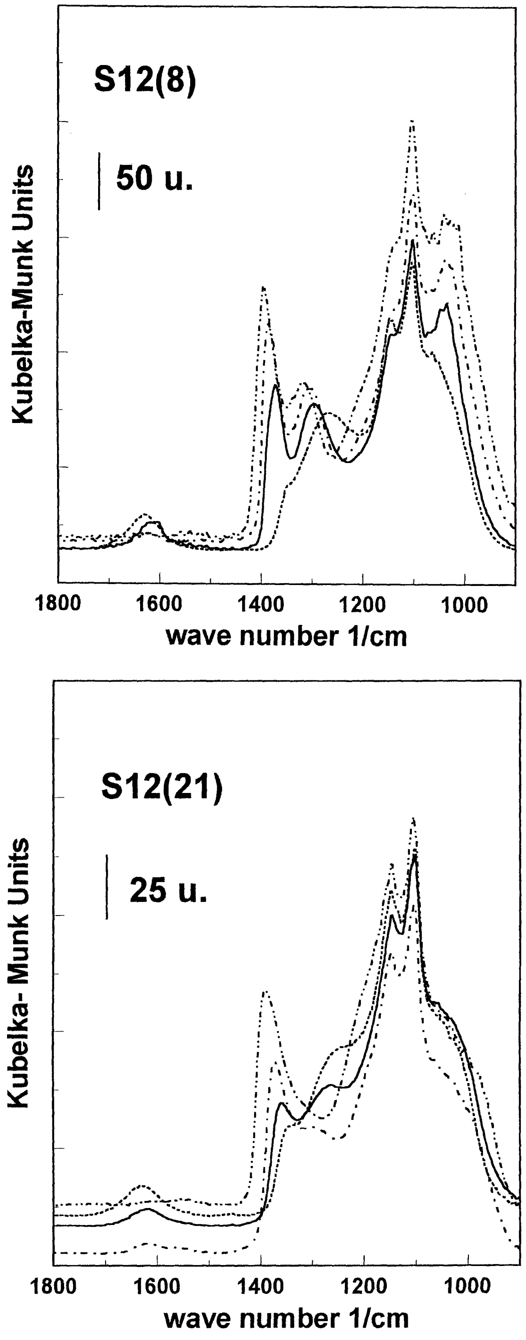

Figure 5. DRIFT spectra obtained by outgassing rehydrated samples $S_{12}$ (8) and $S_{12}$ (21) at increasing temperatures. The solids were precalcined at 500 °C and exposed to air before outgassing (- - -). Outgassing at 130 (—), 350 (- · -) and 500 °C (- · · -).

ing the particle size. The intensities in spectra of $S_{12}$ (8) and $S_{12}$ (21) are not proportional to the sulfate content (table 1).

In the hydrated sample a broad band is observed at 1200 $cm^{-1}$, which shifts towards higher frequency upon outgassing, but it is still present after calcining at 500 °C, probably due to water remaining at a residual pressure of $10^{-2}$ Torr.

It has been shown [9] that the intensity of the band at 1395 $cm^{-1}$ decreases linearly with the surface density in chemisorbed water expressed as the amount of adsorbed species divided by the number of sulfate groups. The extrapolation to a zero optical density is achieved for $H_2O/S \approx 1$, suggesting that the dehydrated sulfate species could adsorb one $H_2O$ per S atom. From the $^1H$ broad-line NMR of the system containing two $H_2O/SO_4$, Semmer et al. [27] concluded that there is *one* $H_3O^+$ per Brønsted acid site, this number being considered equal to the number of available $SO_4^{2-}$ (one site per $SO_4^{2-}$).

The main difference between the ammonia and water adsorption is the complete disappearance of any shifted line near 1360 $cm^{-1}$ upon removing ammonia in the IR cell under residual pressure close to $10^{-6}$ Torr. The band at $\sim$1360 $cm^{-1}$ observed upon adsorbing $NH_3$ and $H_2O$ is the SO (of $SO_3$) stretching shifted by hydrogen bonding and the band observed in the hydrated state below $\sim$1260 $cm^{-1}$ is

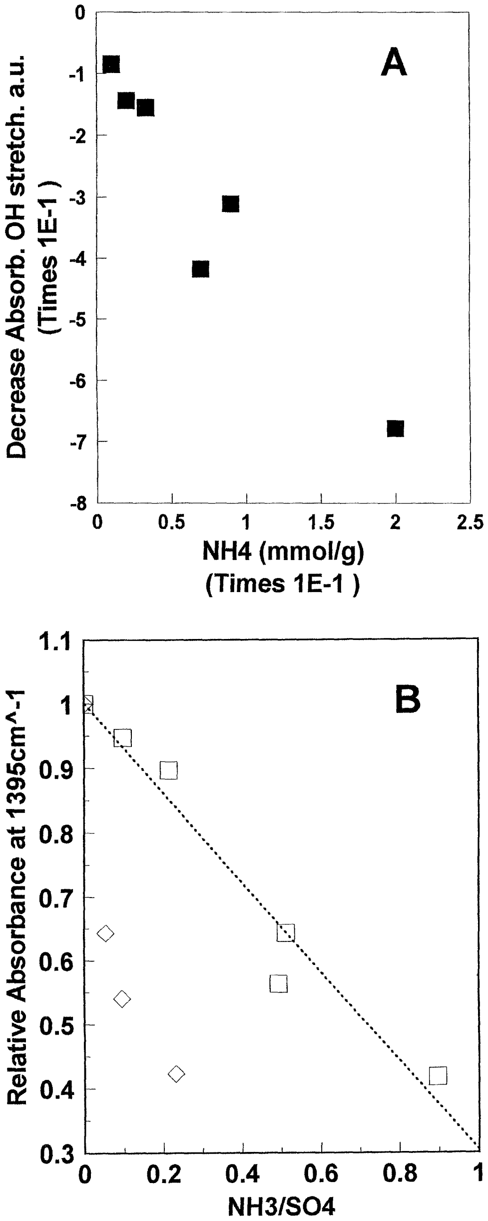

Figure 6. (A) Titration of the acid OH on the surface of $P_{12}$ (6) and $P_{12}$ (16) by $NH_3$, which is transformed into $NH_4^+$. (B) Titration of the $SO_3$ species in $S_{12}$ (8) and $S_{16}$ (2) (□) or in $S_{12}$ (21) (◇) by $NH_3$ chemisorbed on Lewis sites.

due, probably, to $SO_4H^-$ species, since it is not observed by adsorbing $NH_3$.

In figure 6(B) we have plotted the relative absorbance of the band at 1395 $cm^{-1}$ (referred to the absorbance of the clean surface obtained after outgassing at 500 °C) with respect to the ratio $NH_3/SO_4$ for the sulfated mesoporous zirconia. $NH_3$ is the chemisorbed ammonia content calculated from the band at 1608 $cm^{-1}$ ($NH_3$ on Lewis site). As this ratio approaches one, the relative intensity approaches 0.3. For the aluminated mesoporous solid, a similar intensity is obtained for $NH_3/SO_4 \approx 0.3$. While these asymptotic values are approximated, they tend to show that on the sulfated sample, one $NH_3$ "neutralized" somewhat less than one $SO_4$ species. On the aluminated and sulfated zirconia, the number of neutralized sites is much less than the number of $SO_4$, suggesting that an important fraction of $SO_4$ is linked to aluminum and unable to form a strong acid center. This conclusion will be supported by the catalytic test, as shown later.

$NH_4^+$ and $NH_3$ asymmetric deformations are observed at 1440 and 1610 $cm^{-1}$, respectively, upon adsorbing $NH_3$ at 115 °C on the calcined sample and outgassing for 30 min at 115 °C.

The bending bands of $NH_3$ and $NH_4^+$ disappear after outgassing at temperatures higher than 200 °C and, accordingly, above 300 °C the $SO_3$ stretching is back to its original position before the chemisorption of ammonia. The number of chemisorbed $NH_3$ remaining after outgassing at 115 °C for 30 min is about 0.2 mmol/g. Fogash et al. [22] indicate that the number of ammonia retained with a differential heat larger than 120 kJ/mol is about 0.1 mmol/g for a sample having an approximate BET surface area near 140 $m^2/g$.

The results reported here for the mesoporous sulfated sample agree with observations by other authors on the most important points. In particular, the "titration" by $NH_3$ (figure 3) or by water support the idea of the formation of $SO_3$ through the calcination $H_2SO_4$ supported on zirconia.

### 3.3. Catalytic test: isomerization of isobutane

The main goal was to test the catalytic performance of the mesoporous zirconia, treated or not, with aluminum, with respect to those of a "classical" sulfated zirconia in the isomerization of isobutane into butane. Note that all the sulfated or phosphated catalysts, aluminum doped or not, are made from tetragonal zirconia [1–3].

From the description of the spectroscopic results, the mesoporous sulfated zirconia was not expected to behave differently. In addition, the introduction of aluminum should not qualitatively affect the result, since its sole role is to maintain a large surface area above 500 °C [3].

However, Gao et al. [28] have studied the influence of aluminum on the catalytic performance of a sulfated catalyst obtained by coprecipitation of zirconyl chloride and aluminum nitrate by ammonia. At an aluminum content larger than 0.5 mol%, they observe a gain in activity for the isomerization of butane at 250 °C after 1 h and up to 6 h. Microcalorimetry of $NH_3$ adsorption shows that doping with 3 mol% $Al_2O_3$ increases the number of acid sites with heats of adsorption larger than 135 kJ $mol^{-1}$. We did not observe an enhancement of the catalytic activity, but the $Al_2O_3$ content in our samples is less.

The acidity of phosphated zirconia, aluminated or not, is obviously weaker, the source of surface acidity being P–OH groups. Lewis sites due to coordinately unsaturated zirconium are in small concentration. The phosphated zirconias were completely inactive in the isomerization of isobutane under the conditions used for the sulfated sample, but some activity in 1-butene isomerization at 150 °C [24] was reported for zirconia–phosphate aerogels.

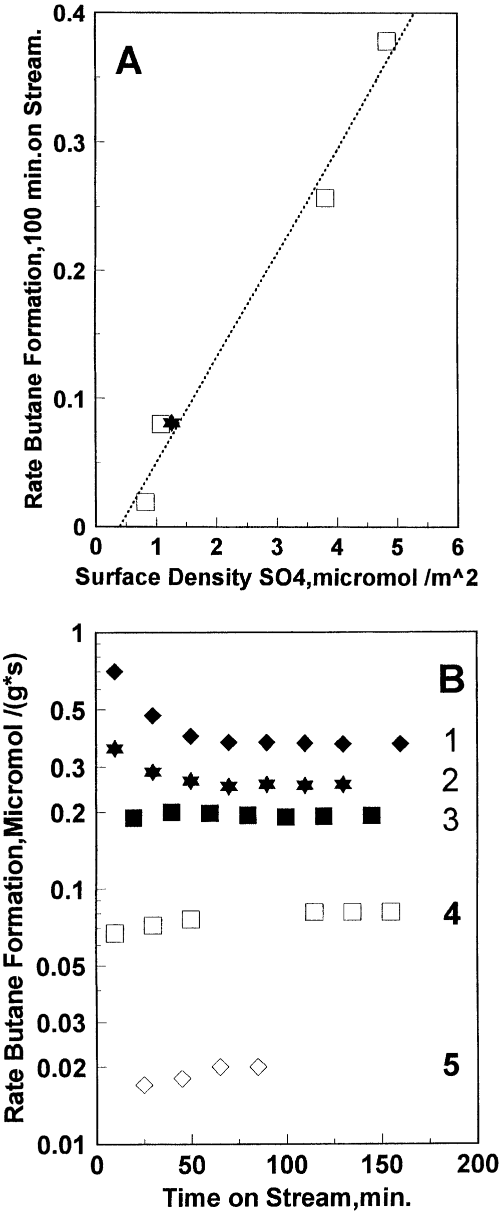

Figure 7. Catalytic test. Isomerization of isobutane into butane in a flow of 26% isobutane/(isobutane + He) over sulfated zirconia (table 3). (A) Reaction rate vs. the surface density in $SO_4^{2-}$ ($\mu$mol/m$^2$). (B) Reaction rate with respect to time on stream. The curve label refers to table 3. The $\star$ is the interpolated value for the aluminized sample.

Table 3
Catalytic performance of sulfated mesoporous zirconia.[a]

| Catalyst | S content (wt%) | $SO_3$ or $SO_4$[b] ($\mu$mol/m$^2$) | Steady-state rate (100 min) | Figure 6, curve no. |
|---|---|---|---|---|
| $S_{12}$ (8)140 | 0.88 | 0.82 | 0.019 | (5) |
| $S_{12}$ (8)a | 4.08 | 3.80 | 0.257 | (2) |
| $S_{12}$ (8)b | 1.16 | 1.08 | 0.08 | (3) |
| $S_{12}$ (20)a | ~4 | 1.26[c] | 0.081 | (4) |
| MEI (XZ0.682) | 1.52 | 4.85[d] | 0.378 | (1) |

[a] Calcination at 500 °C, exposed to air overnight, dried at 250 °C. Reaction at 250 °C; flow: isobutane/He ~26%.

[b] The sulfur analysis was performed on the sample dried at 140 °C, following the impregnation by $H_2SO_4$. The surface coverage is calculated using the surface area (table 1) measured after drying at 140 °C.

[c] Coverage obtained through interpolation in figure 7(A) ($\star$). It cannot be calculated because an appreciable fraction of the sulfate is bound to the aluminum coating. This sample behaves as if ~1.8 wt% S was bound to zirconia. The molar ratio $SO_4$/Al would be 0.83.

[d] The impregnation is carried out after calcination at 500 °C.

In order to achieve with the mesoporous sulfated sample an activity that is comparable to that of the reference MEI sample (containing about 1.5 wt% S on a surface of ~100 m$^2$ g), the mesoporous zirconia samples were impregnated with 5 wt% $H_2SO_4$. The activity of the original preparation ($S_{12}$ (8)140) was about 10% that of the reference MEI sample.

The experimental data are summarized in figure 7(B) and table 3. First, and in agreement with Dumesic et al., it can be seen that the catalyst deactivation is small.

The calculation of the $SO_4$ or $SO_3$ surface density is an interesting challenge. For the mesoporous $S_{12}$ (8) samples (table 3), the surface density is calculated by dividing the molar S content (10/32 wt%) by the surface area measured for the samples dried at 140 °C. It is, indeed, at that stage that the samples were impregnated with $H_2SO_4$. For the reference sample which is impregnated after calcination, the surface density is obtained from the $SO_4$ content divided by the area of the samples at the impregnation (98 m$^2$/g).

As seen in figure 7(A), a satisfactory linear correlation exists between the surface density ($SO_4$ or $SO_3$) expressed in $\mu$mol/m$^2$ and the steady-state rate measured after 100 min on stream. However, the catalytic run is carried out on the samples calcined at 500 °C, prior to being rehydrated and redried (at 250 °C). Thus, it must be concluded that, upon calcination, an appreciable amount of sulfate is no longer available on the surface (table 1). The surface area available after calcination of $S_{12}$ (8) at 500 °C is 29% of that measured after drying at 140 °C, but this surface contains per unit area the same $SO_4$ density as before calcination. As to the aluminated sample $S_{12}$ (20)a, enriched in sulfate, the $SO_4$ (or $SO_3$) surface density should be 2.8 $\mu$mol/m$^2$. The interpolated value, from the linear regression in figure 7(A), yields a surface density of 1.26 $\mu$mol/m$^2$. Thus, ~0.69 mmol $SO_4$ per gram are probably linked to the aluminum in the alumina coating. The surface molar $SO_4$/Al is then 0.83. $SO_4$ linked to aluminum would not provide catalytic sites for the isomerization reaction. Sulfated alumina alone does not show the IR spectral features exhibited by sulfated zirconia in the ~1400 cm$^{-1}$ region.

## 4. Discussion

The surface of $ZrO_2$ outgassed at high temperature contains Lewis sites created by oxygen vacancies. The IR spectrum of phosphated $ZrO_2$, $P_{12}$ (6), exposed to $NH_3$, shows bands at 1608 and 1425 cm$^{-1}$ assigned to $NH_3$ on Lewis sites and to $NH_4^+$ on Brønsted sites, respectively. These acid sites are (table 2) relatively weak, as shown by the sharp depletion in $NH_3$ or $NH_4^+$ after outgassing at 160 °C. In HZSM-5, for instance, the band at 1425 cm$^{-1}$ persists up to about 350 °C. The Brønsted sites are most likely surface POH groups. The aluminization of the phosphated zirconia depletes both the number of Lewis and Brønsted sites.

The IR study of the acidity of sulfated and, eventually, aluminated zirconia has not shown any fundamental differences with what was known from parallel studies of zirconia obtained from precipitation and sulfated by impregnation. However, because the mesoporous sample has a high specific surface area, the infrared spectra of the chemisorbed species were well-defined. In addition, the comparison of the spectral modifications brought about by the chemisorption of ammonia and water (figures 4 and 5) is of prime importance for understanding the enhancement of the catalytic activity due to residual water [12].

Amazingly, in the study of the acidity of sulfated zirconia, the interaction with ammonia has rarely been studied by itself, but $NH_3$ was used to poison the catalytic sites. The interesting point in the comparison is the similarity of the effects. $NH_3$ and $H_2O$ shift the bands at 1395 to $\sim$1360 $cm^{-1}$ at low coverage. At a higher coverage by $NH_3$ a band at $\sim$1270 $cm^{-1}$ increases in intensity, but the shifted band near 1360 $cm^{-1}$ does not disappear. At high coverage with water the band near 1210–1240 $cm^{-1}$ is dominant. These transformations are reversible.

The comparison of the effects of water and $NH_3$ supports the assignment of the line at 1395 $cm^{-1}$ to the $\nu_3$ vibration of adsorbed $SO_3$. $SO_3$ is a strong Lewis acid and it should form stable adducts with $NH_3$ and with $H_2O$. The $\nu_3$ band in the adsorbed state is remarkably narrow, especially on the aluminated and sulfated $ZrO_2$. The narrowness of the band suggests that the molecules reorient rapidly on the surface. Judging from the width of the shifted line, the $NH_3$ or $H_2O$ adducts reorient more slowly.

After the first chemisorption step, additional water reacts to form ($HSO_4^-$). At that stage a strong $NH_4^+$ bending vibration is an indication of the formation of the Brønsted sites (not shown).

It is important to point out that the maximum catalytic activity is observed after drying a material hydrated in the air at about 300 °C. In this temperature range $SO_3$ and, thus, Lewis sites still subsist, but the Brønsted sites resulting from the rehydration of $SO_3$ are abundant. Their numbers are comparable.

The coexistence of strong Lewis and Brønsted sites on zirconia calcined at 500 °C having chemisorbed dry, gaseous $SO_3$ at 250 °C and further outgassed at 500 °C has been confirmed recently by Zhang, Nicholas and Haw in a straightforward manner [30]. The $^{15}N$ MAS NMR of adsorbed pyridine shows two lines corresponding to N on Lewis sites or protonated N. On silica having chemisorbed $SO_3$ in a similar way, pyridium- and hydrogen-bonded pyridine are observed.

The coexistence of both kinds of acid sites in a relatively broad domain of temperature may explain the distribution of the heats of $NH_3$ chemisorption studied by Dumesic's group [22]. The sites with heats of adsorption larger than 120 $kcal\,mol^{-1}$ represent less than 20% of the amount of $SO_4$ on the surface. Referring to figure 6(B), this number of sites may easily represent the amount of $SO_3$ present on the surface of a sulfated material with residual water.

In addition to its role as a Lewis site, $SO_3$ may work as an oxidant [29]. The importance of this role has been recalled in the introduction (see [10]).

## 5. Conclusion

The acidity of the phosphated zirconia is due to the simultaneous presence of P–OH Brønsted sites and to weak Lewis sites located on the $ZrO_2$ lattice.

The acidity of the sulfated zirconia is more complex and it can be assigned essentially to $SO_3$ acting as a Lewis site and to a Brønsted site like a surface ester of sulfuric acid, as suggested by Haw and Nicholas [30]. The unique role of $ZrO_2$ is to provide a lattice on which $SO_4$ and $SO_3$ can be anchored.

The activity of sulfated zirconia in the isomerization of isobutane is maximized by a residual hydration that provides comparable numbers of Lewis and Brønsted sites. The mesoporous character of the support, in noticeably increasing the surface area, also requires a larger, formal concentration of sulfate groups. The aluminization of the support increases the surface area, but the sulfate groups linked to the surface aluminum do not seem active in the isomerization of isobutane.

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