RESEARCH NOTE

Free Radical Formation in ZrO$_2$–SiO$_2$ Sol–Gel Derived Catalysts

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Zirconia–silica mixed oxides have been prepared by the sol–gel method using zirconium butoxide and tetraethoxysilane as starting materials. The samples were sulfated using sulfuric acid as alkoxide hydrolysis catalyst or by impregnation with sulfuric acid of a sample previously prepared using HCl as alkoxide hydrolysis catalyst. In thermally treated samples, an intense EPR signal was observed for the sample prepared using HCl, while the EPR signal was lower in the sulfated samples. FTIR–pyridine adsorption spectra showed that Brønsted and Lewis acidity is developed in the sulfated samples. The formation of two types of Brønsted sites depending upon the sulfating method used is proposed. The catalytic activity of the samples was evaluated in isopropanol and *n*-butanol dehydration. The mechanism by which sulfation is achieved and the Brønsted-type site formed are discussed. © 1999 Academic Press

Key Words: **sol–gel ZrO$_2$–SiO$_2$; EPR of zirconia–silica; iso-propanol dehydration; 2-butanol dehydration; zirconia free radicals; zirconia Brønsted and Lewis acidity.**

INTRODUCTION

An important research area in catalysis laboratories is the study of sulfated zirconia catalysts. Sulfated zirconia exhibits a high potential for use in reactions involving acidic catalysts. Its acid strength, measured by Hammett indicators, reaches values of $H_0 = -16.0$, as has been reported by Ino and Arata (1). Its characterization and catalytic properties have been studied by many authors (see, e.g., Monterra (2), Corma (3) and Ko (4, 5)). The strength of the acidic sites increases notably if the sulfate ion is incorporated during the zirconia preparation step (4, 5).

Pure zirconia sinters and its specific surface area is drastically diminished by temperature effects. Alternative methods of preventing zirconia from sintering include supporting zirconia on a stable oxide such as silica and preparing zirconia–silica mixed oxides (6–12).

In a recent paper, it has been reported that mixed titania–silica oxides showing high acidity were obtained after cogellation of tetraethoxysilane and titanium isopropoxide using sulfuric acid as hydrolysis catalyst (13). In the present paper the synthesis of sol–gel zirconia–silica mixed oxides with sulfuric acid as the gelling catalyst is reported. The interaction between the zirconium oxide and the sulfate ion will justify using sulfuric acid as the hydrolysis catalyst. The dispersion of the sulfated zirconia will be accomplished by simultaneous cogellation with the support. The role of the zirconium alkoxide and that of the hydrolysis acid (sulfuric or hydrochloric), as well as their correlation with the formation of paramagnetic species, are discussed. Brønsted and Lewis acidic sites were determined by FTIR–pyridine adsorption. Isopropanol and 2-butanol dehydration were used as the acidic reactions test.

EXPERIMENTAL

Sample Preparation

The solids were prepared by cogellation of tetraethoxysilane (TEOS) and zirconium *n*-butoxide. The cogellation was accomplished using HCl or H$_2$SO$_4$ as hydrolysis catalysts. The zirconia content in silica was maintained at 10 wt% in all the samples. The general procedure for the preparation of the samples was as follows: in a flask containing 148 ml of TEOS, 150 ml of ethanol, and 25 ml of distilled water, the pH was adjusted with 0.5 mL of HCl (Baker AR, 35% vol.) to a value of 3.0. The flask was put under reflux at 70°C until the solution became opaque and was immediately cooled at 5°C. Then a solution containing 10 ml of zirconium butoxide in 25 ml of ethanol was added drop by drop. When the addition of zirconium alkoxide was accomplished, the reaction system was again put under reflux at 70°C until a gel was formed. The sample was labeled AlcZrSi–HCl. For sulfation, the sample was dried overnight at 70°C and then impregnated with 50 mL of sulfuric acid solution (2 M). After constant stirring for 3 h the sample was again dried at 70°C overnight. This sample was labeled as AlcZrSi–HCl–SO$_4$. Following the same preparation method described above but instead of HCl as the hydrolysis catalyst a third sample was prepared by adding 0.5 mL of H$_2$SO$_4$ acid (Baker 99% A.R.) to adjust the pH

of the initial solution to a value of 3.0 (sulfating *in situ*). The sample was labeled AlcZrSi–H$_2$SO$_4$.

Characterization

Bulk sulfur was quantified in a Model SC 444 LECO S analyzer by calcining the solid samples at 1300°C, followed by gas analysis in a S detector (UV–Vis).

The specific surface areas of the ZrSi mixed oxides were determined in samples thermally treated at 400°C for 4 h. An automated ASAP 2000 Micromeritics apparatus was used to determine the nitrogen adsorption isotherm. The specific areas and the pore size diameter were calculated from the slope of the BET isotherm and by using the BJH method, respectively.

The EPR signal of the samples was obtained at room temperature. A JEOL JES-RE3X spectrometer, using a cylindrical cavity (TE$_{011}$ mode) with 100-kHz field modulation was used to obtain the EPR spectra. The microwave frequency was in the X band ($\approx$9.3 Ghz). The *g* (paramagnetic resonance spectroscopic factor) values were obtained by measuring the resonance field using a JEOL ES-FC5 NMR gaussmeter and an HP-5350B frequency counter. EPR signal intensity evolves as a function of the thermal treatments given to the gels. The maximum signal intensity was obtained in samples calcined in air at 600°C for 15 min.

The FTIR spectra of the samples were obtained in a Nicolet 710 apparatus (resolution 2 cm^{-1}). Self-supported waffles were mounted in a quartz IR cell in which thermal treatments can be done. For the adsorption of pyridine, the samples were reactivated at 500°C in vacuum for 2 h. After cooling, the temperature was stabilized at room temperature and the cell was flushed with a flow of nitrogen saturated with pyridine. The gaseous and weakly adsorbed pyridine was evacuated under vacuum. The adsorbed pyridine was followed at different temperatures from room temperature to 500°C. After each treatment the spectra were recorded at room temperature.

Before activity tests, the samples were treated at 400°C in air for 4 h. The isopropanol decomposition was determined at atmospheric pressure in a flow reactor and at low conversion to avoid mass and heat diffusion effects. The reaction conditions were as follows: isopropanol pressure, 22 Torr; nitrogen carrier, 738 Torr; temperature of reaction, 150°C. The catalytic system was coupled to a gas chromatograph analytical apparatus and the analysis of products was made on line. Under these working conditions, propene and isopropyl ether were the only products detected. The 2-butanol dehydration was carried out at atmospheric pressure under the same procedure used for the isopropanol dehydration. The work conditions were as follows: 2-butanol partial pressure, 8.1 Torr; temperature of reaction, 150°C. The detected products were 1-butene and *tran*- and *cis*-2-butenes.

RESULTS

Specific Surface Area

The hydrolysis rate of TEOS is lower than that of zirconium alkoxide. The formation of multiple Si–O–Zr bonds will be greater if the hydrolysis rate of both alkoxides are comparable. To obtain comparable condensation rate on both alkoxides the solution underwent TEOS prehydrolysis and subsequent cooling.

The nitrogen isotherms of the samples are shown in Fig. 1. It can be seen that when HCl is used for alkoxide hydrolysis the isotherm corresponds to Type I. On the other hand, when the Zr–Si mixed oxide is prepared using sulfuric acid, the isotherm is of Type IV, showing an important hysteresis loop. The surprising result is that observed in the isotherm corresponding to the sulfated HCl preparation AlcZrSi–HCl–SO$_4$: the corresponding isotherm is of Type IV. The sulfation was carried out in the sample dried at 70°C; at this drying temperature the sample is a highly hydroxylated gel. The modification of the isotherm then could be due to subsequent hydrolysis induced by the sulfuric acid used for the sulfation of the sample; the textural properties will not be very different from those, obtained for the sulfuric preparation (AlcZrSi–H$_2$SO$_4$). The corresponding mean pore size diameter is shown in Fig. 2. A narrow distribution for the three samples can be seen.

The BET areas, as well as the pore size distributions, are reported in Table 1 for the various samples. An important effect is observed in the relationship between the BET areas and the hydrolysis catalysts used. The higher specific surface area is shown by the catalyst prepared with HCl 629 m^2/g. For the catalysts sulfated *in situ* the specific surface area was 423 m^2/g. Sulfation of the HCl prepared sample by impregnation with sulfuric acid results in a notable diminution of the specific area from 629 to 324 m^2/g. The second acid treatment done by the sulfation will be responsible for the specific area diminution. The gellation of TEOS in acidic medium produces silica showing a high specific surface area (14). When zirconium alkoxide is added to a prehydrolyzed TEOS using a mineral acid (HCl or H$_2$SO$_4$), the large specific area preestablished in the silica gel is maintained in the mixed oxide. The diminution of the BET area by sulfation of the HCl preparation could be due to additional hydrolysis

TABLE 1

Zirconia–Silica Sol–Gel Mixed Oxides Characterization

Catalyst	EPR intensity (a.u.)	BET area (m^2/g)	Mean pore diameter (nm)	Sulfur content (wt%)
AlkZrSi–HCl	20.0	629	2.5	0.00814 (blank)
AlkZrSi–H$_2$SO$_4$	8.0	423	4.2	5.55
AlkZrSi–HCl–SO$_4$	1.0	324	3.6	4.47

is clear that the mineral acid (HCl or H_2SO_4) used as hydrolysis catalyst, as well as the sulfation of the samples, is an important variable in the textural properties of the final ZrO_2–SiO_2 mixed oxide.
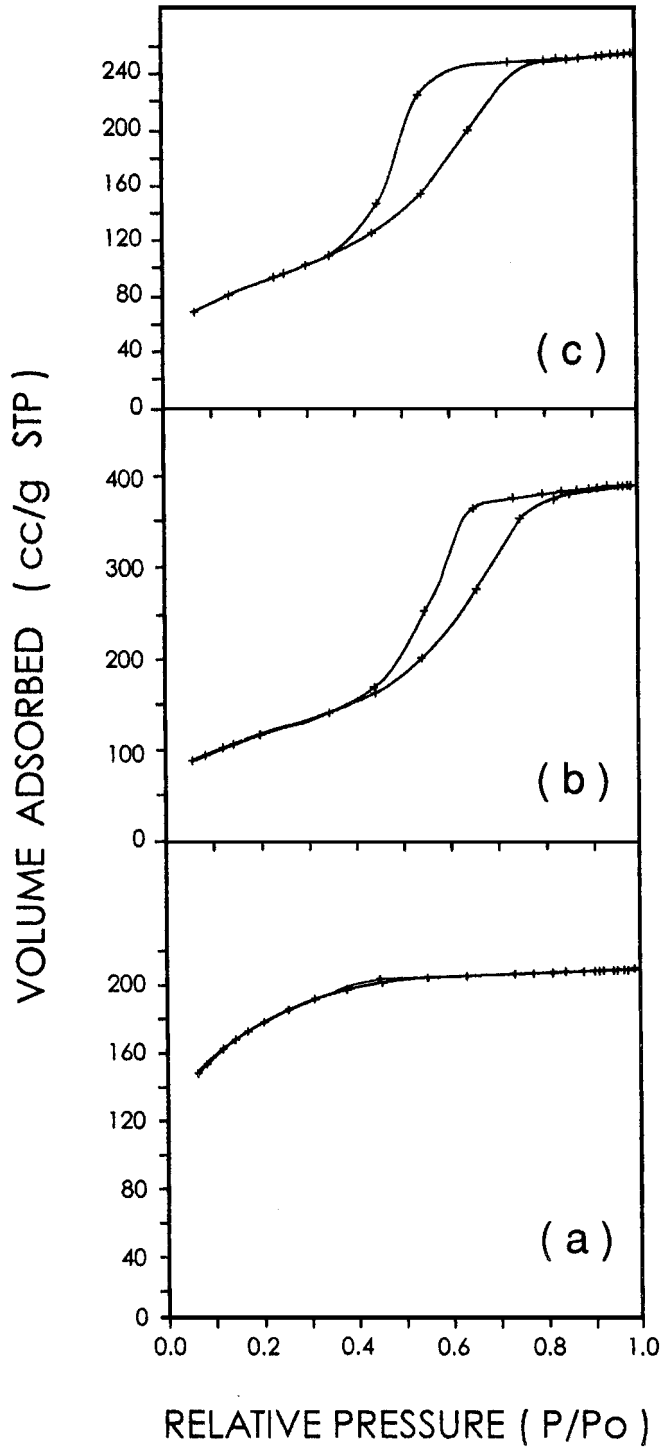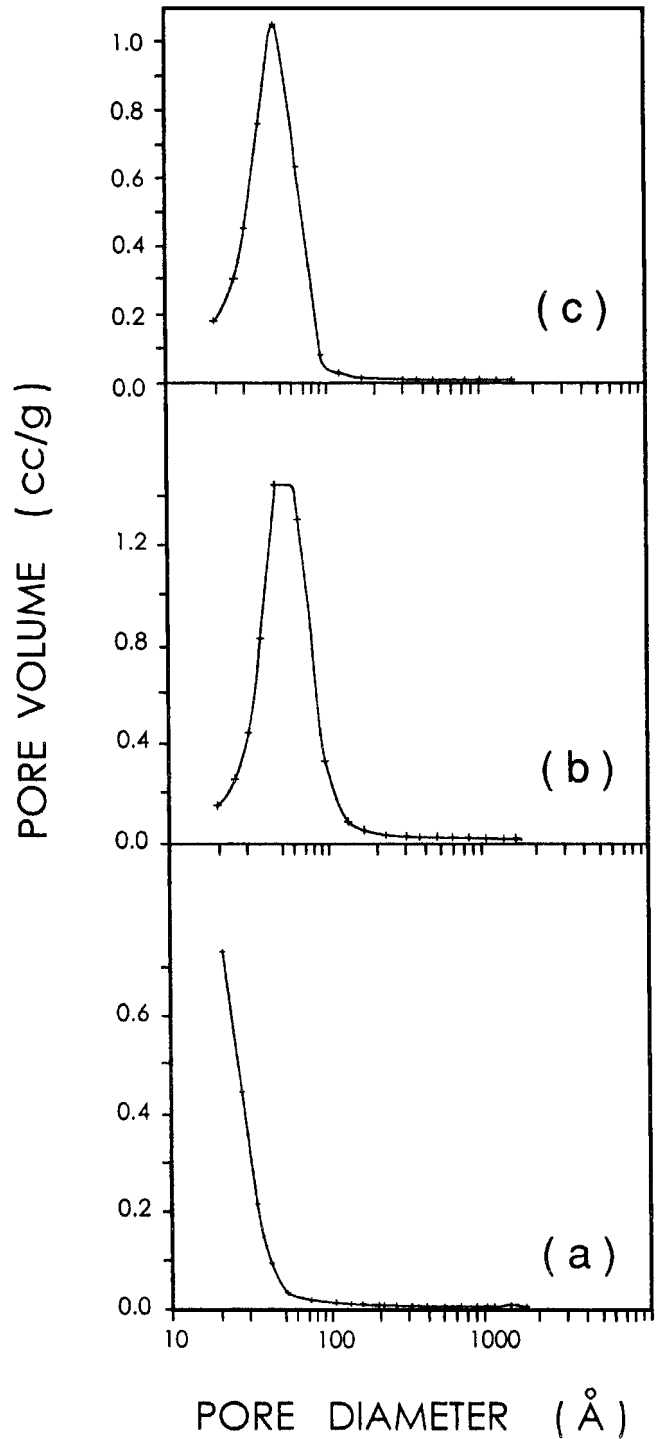

FIG. 1. Nitrogen isotherms for zirconia–silica mixed oxides. (a) AlkZrSi–HCl, (b) AlkZrSi–H_2SO_4, (c) AlkZrSi–HCl–SO_4 catalysts.

FIG. 2. Mean pore size distribution for the zirconia–silica mixed oxides. (a) AlkZrSi–HCl, (b) AlkZrSi–H_2SO_4, (c) AlkZrSi–HCl–SO_4 catalysts.

produced by the sulfuric acid solution. The Si–O–Zr bonds previously formed can easily be hydrolyzed by contact with sulfuric acid and some extraction of Zr from the silica network will result. The effect will be comparable to that of a silica oxide covered by highly dispersed zirconium oxide. It

FIG. 3. Room temperature EPR signal of ZrO_2–SiO_2 sol–gel catalysts calcined at 400°C in air.

EPR Characterization

Dehydroxylation is an important step in stabilizing gels. During this process a large number of structural defects can be produced. If paramagnetic species are formed, EPR is an adequate spectroscopy technique for detecting the formation of free radicals and other kinds of paramagnetic sites. The formation of paramagnetic centers in thermally treated ZrO_2–SiO_2 mixed oxides has been identified by the EPR signals obtained in the different samples. The EPR spectra show a signal of variable intensity depending on the sulfation process and on the catalysts used for the alkoxide hydrolysis. The EPR spectroscopic parameter g has a value of $g = 2.0034(2)$ in all cases. The signals do not show appreciable microwave power saturation over the whole operation range (0.04–4 mW), and these results (Fig. 3) account for the presence of a free radical center in these sol–gel mixed oxides. In Table 1, the different EPR signal intensities of the mixed oxides are reported. It should be noted that the EPR signal intensity of the AlkZrSi–HCl sample is higher than that observed for the *sulfated in situ* and HCl-sulfated preparations. In such samples the EPR signal intensity is notably diminished, suggesting that the sulfate is preferentially located in the vacancies.

FTIR-Pyridine Adsorption Study

Sulfated zirconia has been reported as a strong acid. Its acidity would be comparable to that of sulfuric acid. The strong acidity is related to the sulfate ions retained on the zirconia. High acidity is reported in small zirconia crystallites (15). This observation supports an interpretation in which the low coordination of zirconium atoms of small crystallites is responsible for a strong sulfate–zirconia interaction. Low zirconium atom coordination can be obtained by dispersing zirconia in silica as well as by insertion of zirconium into Si–O–Si bonds [6]. When zirconium alkoxides are cogelled with silicon alkoxides, a high probability of zirconium atom insertion on the silica network is expected and sulfating them will produce solids showing a high acidity. In our mixed oxides the acidity of the samples was determined by the adsorption of pyridine, since it is the most frequently reported technique for determining either Brønsted or Lewis acidity. The higher the temperature at which the pyridine is retained adsorbed, the higher will be the acidity of the sample. The bands which characterize the Lewis or Brønsted sites (6) are the following: the band at 1445 cm^{-1} is attributed to pyridine adsorption in Lewis sites; the band at 1490 cm^{-1} is assigned to both Lewis and Brønsted sites; and the band at 1545 cm^{-1} is assigned to Brønsted sites. In the following discussion we will treat only the bands mentioned above.

In Fig. 4, the FTIR pyridine adsorption spectra of the Zr–Si prepared with HCl is shown. At room temperature an intense band at 1445 cm^{-1} (Lewis sites), a medium intensity band at 1490 cm^{-1} (Brønsted and Lewis sites), and a very low band at 1545 cm^{-1} (Brønsted sites) are observed.
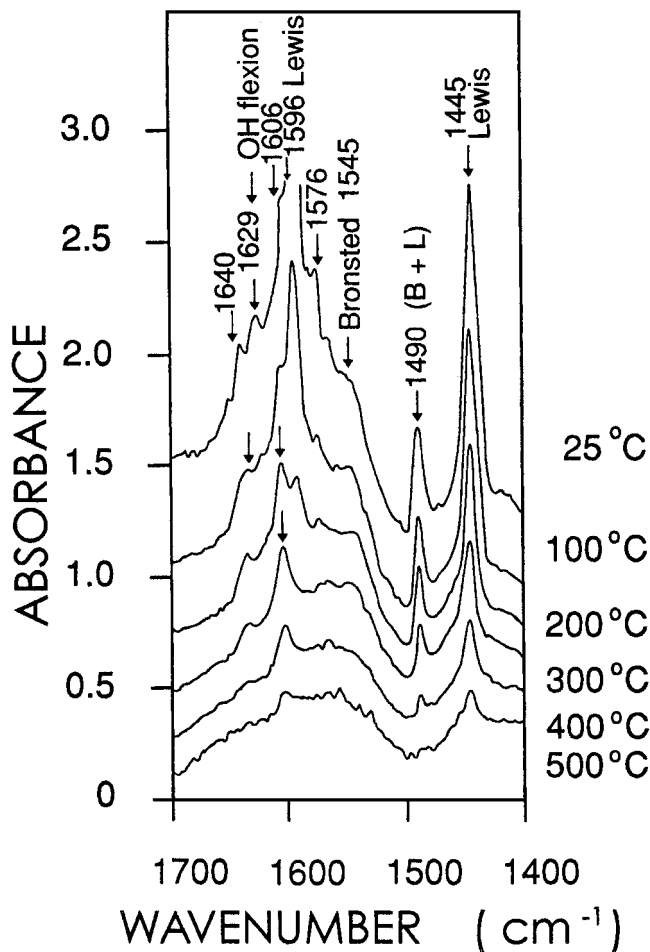
FIG. 4. FTIR–pyridine adsorption spectra for the AlkZrSi–HCl catalyst.

sulfur in the *in situ sulfated* sample can be explained by the method used during the preparation since the sulfur content is a "bulk" determination and sulfur could be trapped in the bulk, replacing some zirconium atoms, as proposed by Ward and Ko (16).

Catalytic Activity Determination

The catalytic activity of the various samples for isopropanol decomposition is reported in Table 2. The highest activity is observed for the catalysts sulfated *in situ* and for HCl-prepared sulfated catalyst. In contrast, very low activities are obtained for the nonsulfated catalysts prepared with HCl. On the other hand, we can see from the product selectivity that the formation of acetone is not observed for any of the catalysts studied here. The only products detected were propene and isopropyl ether. The absence of acetone is an important fact, since acetone is usually the main product of isopropanol decomposition on pure zirconia (12). A wide range in activities is observed in Table 2; the activity values are between 6.2 to 206×10^{-7} mol/g s.
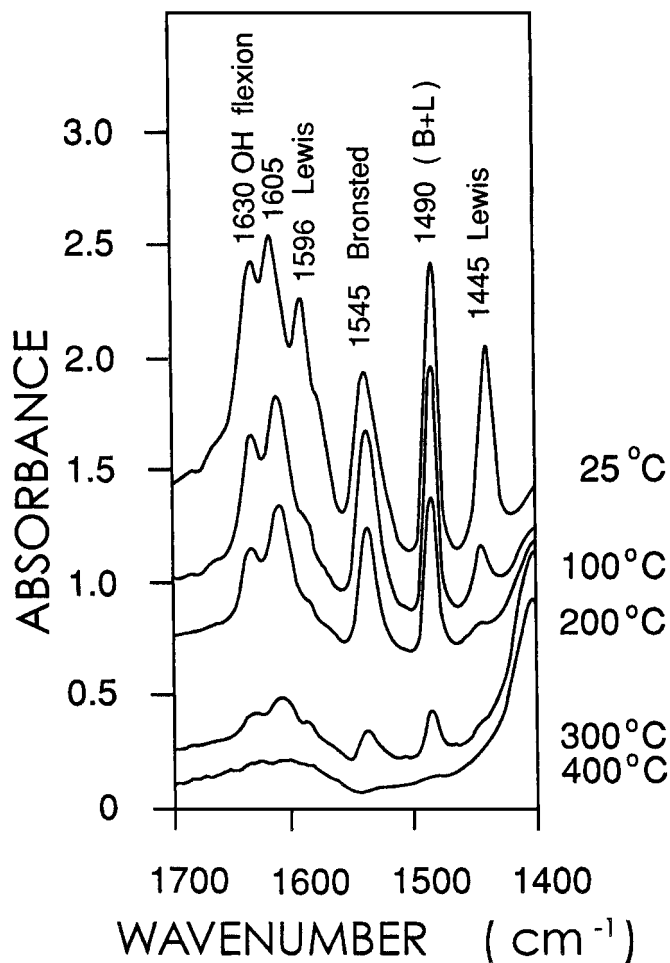
After thermal desorption the intensity of the bands notably diminishes; at desorption temperature 400°C only the Lewis band at 1445 cm^{-1} and the B+L band are observed. Compared with HCl preparation, when the sample was prepared with sulfuric acid (AlkZr–Si–H$_2$SO$_4$) the pyridine adsorption spectra show a different intensity of the Lewis and Brønsted bands (Fig. 5). First, the Lewis band (1445 cm^{-1}) is of lower intensity; second the B+L sites band is notably higher in intensity; and third, the Brønstend band at 1545 cm^{-1} shows high intensity. The Brønsted and B+L bands are still observed at desorption temperature 300°C. However, the most important result is that obtained for the sulfated HCl-prepared sample. The FTIR pyridine adsorption spectra show Brønsted and B+L site adsorption bands with unusual intensity, and moreover the adsorption bands are still observable in the spectra obtained after evacuation at 500°C (Fig. 6).

The amount of sulfur in the samples is 20% higher in the sulfated *in situ* sample AlkZr–Si–H$_2$SO$_4$ (5.55% S) than in the HCl-sulfated ones (4.47% S). The higher amount of

FIG. 5. FTIR–pyridine adsorption spectra for the sulfated *in situ* AlkZrSi–H$_2$SO$_4$ catalyst.
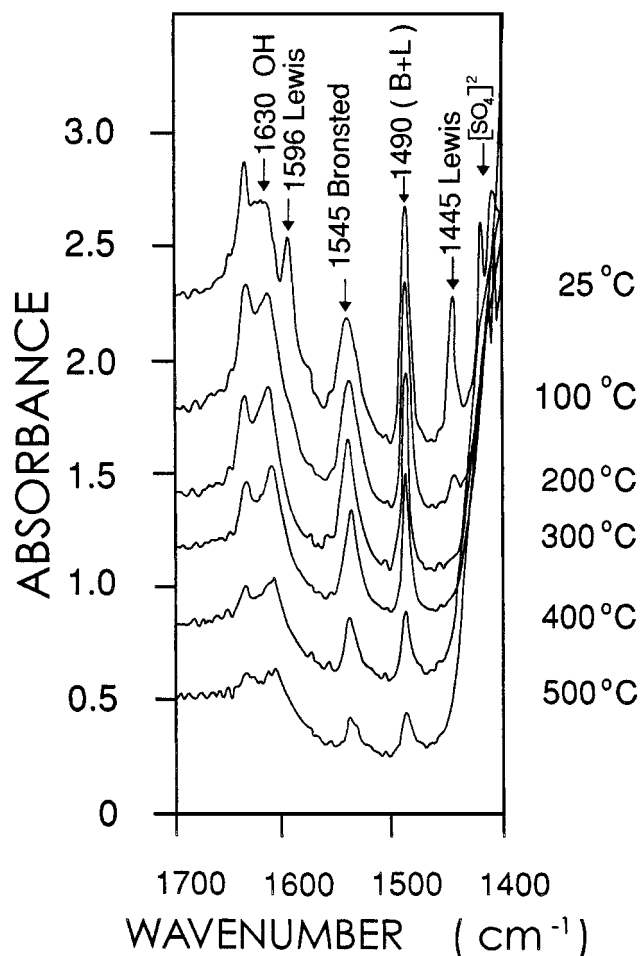
FIG. 6. FTIR–pyridine adsorption spectra for the AlkZrSi–HCl–SO$_4$ catalyst.

For 2-butanol dehydration the activity shows the same behavior observed for the isopropanol dehydration. The most active catalysts are the sulfated ones, either sulfated *in situ* or sulfated by impregnation with sulfuric acid. The activity for the sulfated catalysts is higher (240 and 159×10^{-7} mol/g S) than that obtained for the nonsulfate one (46×10^{-7} mol/g s). These results confirm the behavior observed in the isopropanol dehydration.

DISCUSSION

Two mechanisms occur during the hydrolysis and sulfating of the sol–gel preparations. When HCl acid is used, the dehydration mechanism occurs in a similar manner as happens in a thermal dehydration process; [O$^-$] radical is formed when water is removed (Fig. 3). This [O$^-$] species would be responsible for the EPR signal. On the other hand, when the cogellation is done in a sulfuric acid medium the dehydration step occurs as a protonic attack on the hydroxyls, leaving a vacancy into which the sulfate ion is inserted. Consistently, the EPR signal will be relatively diminished in intensity. It is well known that H$_2$SO$_4$ acid is a good dehydration agent, while HCl acid is not so efficient for dehydration. The mechanisms for the formation of vacancies and the insertion of the sulfate ion occurring during the gel dehydration step are illustrated in Figs. 7–9.

The catalytic activity measurements for isopropanol and 2-butanol dehydration support the proposed mechanisms. The higher activity corresponds to the catalysts showing the lower EPR signal intensity. In general it can be seen that when the zirconia–silica mixed oxides are sulfated either *in situ* or by sulfating the gel a high activity is obtained (206, 148×10^{-7} mol/g s), while for the nonsulfated sample the activity is 6.4×10^{-7} mol/g s. Alcohol dehydration is used to test the acid–base properties of a catalyst (17–19). Olefin formation is considered a function of the overall acidity of the samples. In Tables 2 and 3, a high selectivity to propene and to 2-*cis*- and *trans*-2-butene is observed. Acetone formation is not detected in isopropanol dehydration. Pure zirconia, being an acid–base catalyst, would normally give acetone as an important product during isopropanol decomposition (20, 21). Indeed, the absence of acetone in the products of the decomposition of isopropanol establishes that the zirconia in the ZrO$_2$–SiO$_2$ sol–gel catalysts in practice will be found as a part of Si–O–Zr bonds in HCl acid preparations and as sulfated zirconia (because of its high activity) in the sulfated catalysts.

To complete the study it is necessary to explain the different pyridine adsorption intensities observed in the sulfated samples. In the catalyst sulfated *in situ* a large number of Brønsted acidic sites are observed; however, they desorb

TABLE 2

IsoPropanol Dehydration of the Zirconia–Silica Mixed Oxides at 150°C

Catalyst	Rate $\times 10^7$ (mol/g s)	Selectivity (%mol)	
		Propene	Iso-propylether
AlkZrSi–HCl	6.4	86	14
AlkZrSi–H$_2$SO$_4$	206	95	5
AlkZrSi–HCl–SO$_4$	148	98	2

TABLE 3

Dehydration of 2-Butanol on the Zirconia–Silica Mixed Oxides at 150°C

Catalyst	Rate $\times 10^7$ (mol/g s)	Selectivity (mol%)		
		1-Butene	*Trans* 2-butene	*cis* 2-butene
AlkZrSi–HCl	46	11.7	44.3	44.0
AlkZrSi–H$_2$SO$_4$	240	8.1	47.9	44.0
AlkZrSi–HCl–SO$_4$	159	7.9	54.1	38.0

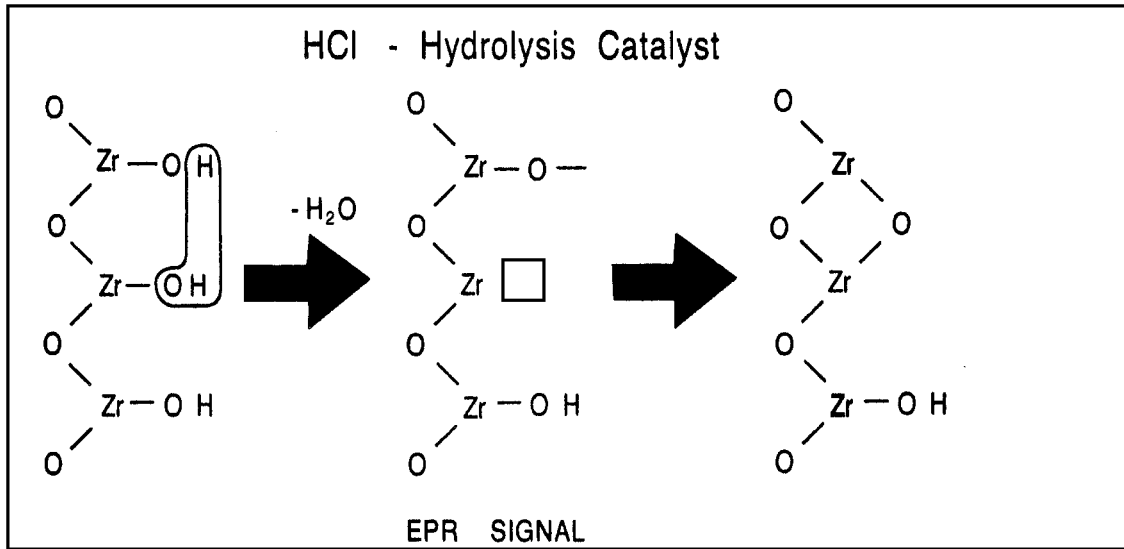**FIG. 7.** Dehydration mechanism for ZrO_2–SiO_2 sol–gel mixed oxides prepared with HCl acid as hydrolysis catalyst (AlkZrSi–HCl).
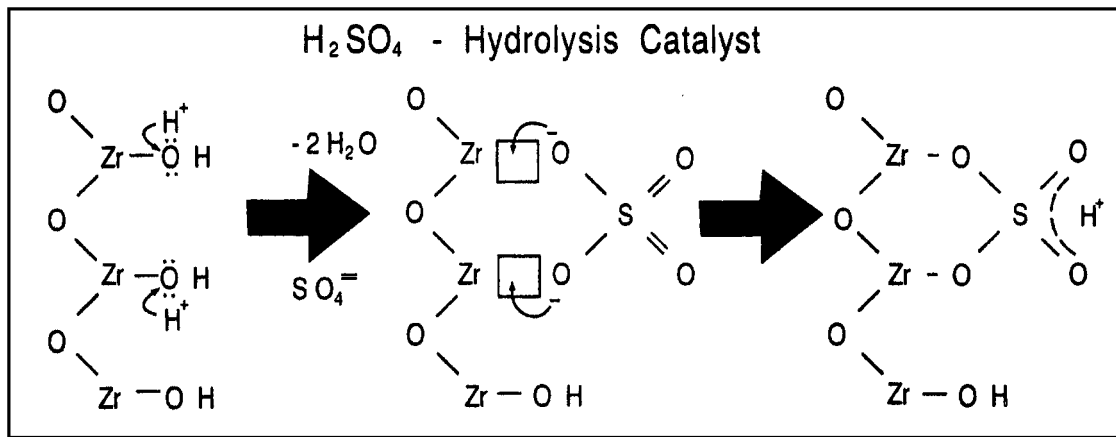

FIG. 8. Dehydration and sulfating mechanism for ZrO_2–SiO_2 sol–gel mixed oxides prepared with H_2SO_4 as hydrolysis catalyst sulfated *in situ* sample (AlkZrS–H_2SO_4).

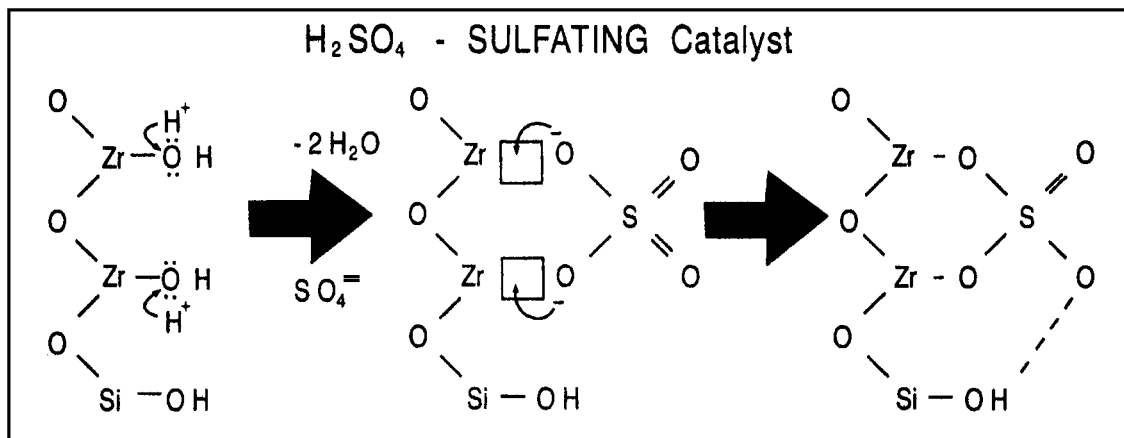**FIG. 9.** Dehydration and sulfating mechanism for ZrO_2–SiO_2 sol–gel mixed oxides prepared from the AlkZrSi–HCl catalyst and sulfated by impregnation with H_2SO_4 acid (AlkZrSi–SO_4).

at lower temperature (300°C) than those observed in the HCl-prepared sulfated sample (500°C). The FTIR pyridine adsorption spectra show that two types of Brønsted acidity are developed. Here we propose two models for the origin of the Brønsted acidity. First, for *in situ* sulfated samples, we can assume a large formation of Si–O–Zr–O–Zr–Si. In this case the Brønsted acidity can be explained using a model similar to that proposed by Ward and Ko (16), in which the interaction between the Si–OH neighboring the Zr–O–Zr sulfated zirconia atoms occurs at the Brønsted site (Fig. 8). This model assumes that silica (even highly hydroxylated) does not develop important acidity after sulfation; i.e., the Si–OH bonds are not exchanged by the $SO_4^=$ ions. On the other hand, when the zirconia–silica gel is sulfated by impregnation with sulfuric acid, the Si–O–Zr–O bonds previously formed can be hydrolyzed and the zirconia will be extracted from the network, giving zirconia highly dispersed in a silica support. The sulfated zirconia in this case could be represented by the model reported by Ward and Ko in any of its multiple representations (16, 22), in which the proton is found between the two oxygens of the sulfate as shown in Fig. 9. Two types of Brønsted acidic sites certainly give two types of strong acidity, defining the strong acidity as the resistance of adsorbed pyridine to being removed as a function of the desorption temperature. The present hypotheses propose that, in spite of the low temperature at which the pyridine is desorbed in the *in situ* sulfated catalyst, the proton interacting with the Si–OH neighboring site acts faster during the alcohol dehydration than when the proton is found in the sulfate oxygens. Certainly, the latter remains in the surface at higher temperatures but its ability to attack hydroxyls is limited by its difficult to be removed. We focused our attention on the Brønsted acidic sites; the Lewis acidity is not discussed in the present paper. The reactions tested are dehydration reactions; because they were determined at low temperature and of course water is a product of the reaction, the most important sites involved in the reaction are without a doubt the Brønsted sites.

To prove the importance of the zirconium precursor hydrolysis, experiments were carried out using acetylacetonate as a zirconium precursor (10 wt% ZrO_2). The cogellation was done by adding to an ethanol TEOS solution an acetonic acetylacetonate zirconium solution and completing the hydrolysis with HCl (AcAcZrSi–HCl) or sulfuric acid sulfated *in situ* (AcAcZrSi–H_2SO_4) or by impregnating the AcAcZrSi–HCl with sulfuric acid (AcAcZrSi–SO_4). The difficulty in hydrolyzing the zirconium acetylacetonate under the conditions used, and hence the difficulty in developing acidity, is shown in Fig. 10, where in the FTIR–pyridine adsorption spectra nonadsorption pyridine bands corresponding to Brønsted or Lewis acidity can be observed. These initial studies support that the hypothesis the hydroxyls (from the zirconia hydrolyzed precursors) are of great importance for its sulfation (16, 22).
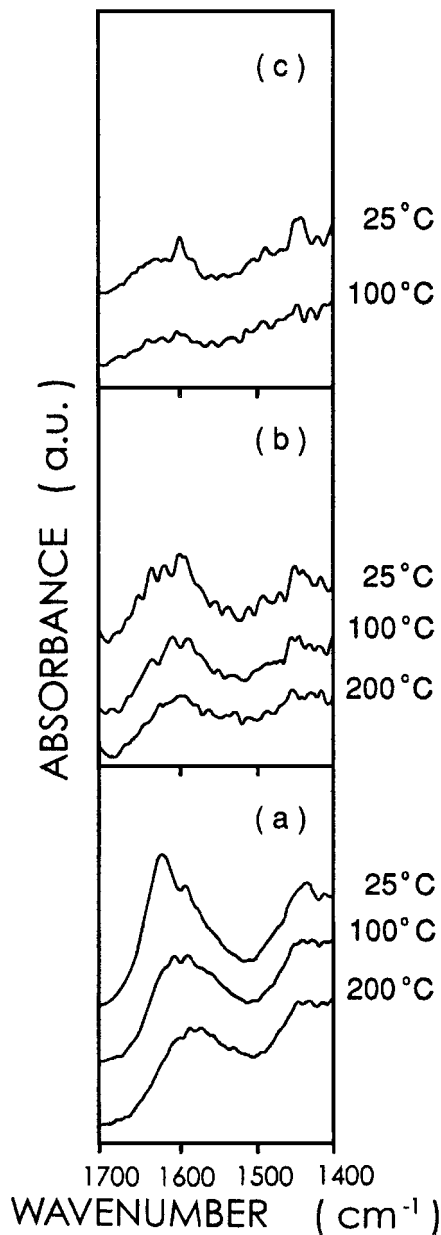

FIG. 10. FTIR–pyridine adsorption of the zirconium acetylacetonate–TEOS samples. (a) Hydrolyzed with HCl, (b) hydrolyzed with sulfuric acid sulfating *in situ*, and (c) HCl hydrolyzed sample sulfated with sulfuric acid.

CONCLUSIONS

We conclude that sol–gel ZrO_2–SiO_2 mixed oxides were obtained with structural defects formed during their preparation. The defects were detected through the EPR signal at $g = 2.0032$. When HCl acid is the hydrolysis catalyst, the EPR signal is related to the formation of $[O^-]$ radicals during the dehydroxylation step. On the other hand, when the hydrolysis of the zirconium precursors is performed with sulfuric acid, the low EPR signal intensity led us to

assume that dehydroxylation occurs by proton attack on the hydroxyls, followed by sulfate ion insertion in the oxygen vacancies. In this case the Brønsted acidity developed is related to the sulfated zirconia model in which Si–OH neighboring sites are present. When sulfation is done by impregnating the mixed oxide with sulfuric acid, zirconia extraction will occur. The sulfated catalyst obtained would be similar to that obtained in pure sulfated zirconia, where the proton is localized in the sulfate oxygen. Depending upon the method used for sulfating the formation of two types of Brønsted sites in zirconia–silica mixed oxides obtained by the sol–gel method is proposed.

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