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Synthesis of Catalytically Active Sulfated Zirconia Aerogels

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Sulfated zirconia aerogels were synthesized by a sol-gel method followed by high temperature supercritical drying. Aerogels with sulfur introduced during the gelation step had high surface areas and pore volumes. Their textural properties could be tuned by variation of the preparation conditions. Samples synthesized by this procedure and those obtained by incipient wetness impregnation of zirconia aerogels with $(NH_4)_2SO_4$ were shown to exhibit catalytic activity in the isomerization of n-butane comparable to conventional precipitated zirconia. Maximum catalytic activity of impregnated aerogels was observed at lower nominal sulfur loadings. They were shown to retain more surface sulfates after calcination compared to samples prepared by two other methods. The most active samples had close to monolayer surface coverage with sulfates with the decomposition peak at 820–830°C. Over-monolayer surface sulfates hindered the isomerization activity whereas bulk sulfates had little effect. © 1998 Academic Press

INTRODUCTION

Sulfated metal oxides have attracted the attention of many researchers in the last decade due to their high activity in acid catalyzed reactions. Sulfated oxides of zirconium, titanium, iron, tin and hafnium have been shown to be solid superacids (1), that is to possess surface acid sites stronger than pure sulfuric acid. They were shown to be active in reactions requiring exceptionally strong acidity such as isomerization and cracking of paraffins, alkylation, and acylation of aromatics (1, 2).

These solid super acids have two major advantages over liquid Lewis acids or Pt on chlorinated alumina that are currently in use: first, they are much more environmentally friendly and, second, they allow the reaction to proceed at lower temperatures, which thermodynamically favors the formation of branched alkanes.

Despite intensive study (3–11), there is no universally accepted theory as to what type of sites account for the unique catalytic activity of SO_4/ZrO_2. Lewis (2, 12) and Brönsted acid (1, 3) sites as well as one-electron acceptor sites (4, 13) have been proposed. Preparation conditions, such as type of precursor, sulfur content, and activation temperature were shown to have major influences on the catalytic activity.

Most of the previous studies used catalyst preparation techniques similar to the original one (14). Namely, hydrous zirconia formed by precipitation with ammonium hydroxide was promoted (impregnated) with ammonium sulfate or sulfuric acid of variable concentration. It has been generally accepted that for the catalyst to be active, the support had to be amorphous before promotion (1, 2).

Development of new procedures for the catalyst preparation may be important for understanding these unusual materials. Among recent studies noteworthy from this point of view, the preparation of active catalysts by impregnation of crystalline aerogel (15) or yttria-stabilized (10) tetragonal zirconia and one-step aerogel synthesis (5) should be mentioned.

Aerogels are materials obtained by controlled hydrolysis of metal alkoxides with the formation of polymerous gels and subsequent supercritical drying of the latter. Under supercritical conditions, the liquid–vapor interface that produces the collapse of the initial gel framework during conventional drying is eliminated. The removal of the supercritical fluid leaves the gel structure intact (16).

The materials obtained by aerogel procedures have high surface area and pore volumes. The method is known to be versatile and allows controlling texture, composition, and structural properties of the materials (17). All these factors are important for the development of active catalysts, so the number of catalytic materials prepared by this method has increased rapidly in recent years (18, 19).

In the present study we synthesized catalytically active sulfated zirconia by a sol-gel method. Catalysts obtained by sulfation of zirconia during the gelation step and after supercritical drying have been compared to conventionally prepared samples. We employed a high temperature supercritical drying step. This method is known to yield aerogels with properties different from those obtained by low-temperature drying with supercritical CO_2 as done in previous studies (5, 15). Compared to low-temperature SCD, high-temperature SCD is believed to lead to thermodynamically more stable aerogel materials, which is reflected by prominent structural and chemical changes (19). Earlier we have studied in detail the effect of preparation

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conditions on textural properties of zirconia aerogels dried at high temperatures (20) and found them significantly different from those obtained with the low-temperature SCD (21).

EXPERIMENTAL SECTION

A. Aerogels and Sulfated Aerogels

Zirconia alcogels (without sulfate) used in this study were prepared as follows: 26 ml of zirconium butoxide–butanol complex (Alfa-Aesar) were dissolved in 60 ml of ethanol (McCornick, dehydrated, absolute—200 proof). The amount of the precursor was calculated to ensure zirconium concentration in the gel 0.5 mol/L. Nitric acid (0.48 moles per mole of the precursor) was added as a catalyst. In another beaker hydrolysis water was dissolved in 30 ml of ethanol. Total water concentration was 4 mol/mol Zr, including water from nitric acid. Both solutions were stirred for 10 min for homogenization and then quickly mixed under intensive stirring. Time required for the vortex created by the stirring to disappear was called gel time. Gels made by this procedure had gel times in the range of 20–25 s. Then they were covered and aged for 2 h at room temperature.

Aerogels (AP-ZrO_2) were made by high temperature supercritical drying of the alcogels in a standard 1-liter autoclave (Parr). The autoclave with the gel was first flushed with nitrogen for 10 min. Then it was filled with nitrogen at an initial pressure of about 100 psi and sealed. The autoclave temperature was slowly increased up to a desired value at a rate 1 K/min and maintained at temperature for 10 min. The final pressure was about 1200 psi. After completion of the procedure, the pressure was quickly released by venting of solvent vapor. The sample was again flushed with nitrogen for 10 min and allowed to cool down in nitrogen. After drying the aerogels had surface areas 350 ± 5 m^2/g.

Sulfated zirconia aerogels (AP) were prepared by a similar procedure. The desired amount of sulfuric acid (96 wt%, Fisher, Reagent A.C.S.) was added to the precursor solution before gelation. (Amounts of nitric acid remained the same as in the nonsulfated preparations.) Some of the sol-gel parameters were varied to study their effect on textural characteristics of the aerogels.

B. Conventionally Prepared ZrO_2

$ZrOCl_2 * 8H_2O$ (Alfa Aesar, 99.9% metals basis) was used as a starting material in the preparation of conventional zirconium hydroxide. Thus, 32.2 g of the precursor were dissolved in 200 ml of distilled water. Aqueous ammonium hydroxide (Fisher, 28–30 wt%) was added dropwise under continuous stirring up to pH ∼ 10. The precipitate was filtered, thoroughly washed with hot distilled water, and dried at 120°C overnight, yielding CP-ZrO_2.

C. Impregnated CP-ZrO_2 and AP-ZrO_2

Precipitated and aerogel ZrO_2 were sulfated by the incipient wetness technique to give CP and IAP sulfated zirconia, respectively. Appropriate amounts of ammonium sulfate (Fisher, Certified A.C.S.) was dissolved in distilled water to give the desired sulfur loading. A predetermined amount of the solution (3 ml/g aerogel and 0.8 ml/g for precipitated zirconia) was added dropwise to dry powders to fill the pores just below incipient wetness. Then the impregnated powders were dried at 120°C for 5 h. Calcination in open air at 600°C for 2 h was the final preparation step.

The sample names used in this paper include the preparation method (AP, IAP, or CP) and the nominal sulfur loading in mol%. For example, CP9 means conventional (precipitated) sulfated zirconia with 9 mol% of sulfates. The nominal sulfur loading was calculated as the molar amount of sulfur used during the sulfation procedure divided by the sum of this amount with the molar amount of zirconia. For AP samples, the latter was calculated from the weight of the precursor used. For CP and IAP samples, it was calculated from the weight of CP or AP hydrated zirconia, which was used for the preparation, after calcination at 500°C for 2 h.

Textural characterization of the samples was performed on a NOVA 1200 gas sorption analyzer (Quantachrome Corp.). Prior to the analysis the samples were outgassed at 180°C for 1 h. Seven point BET surface areas, total pore volumes, and pore size distributions (BJH method) were calculated from 40 point nitrogen adsorption–desorption isoterms.

X-ray powder diffraction experiments were conducted on a Scintag-XDS-2000 spectrometer with Cu Kα radiation. Scans were made in the 2Θ range 20–80° with a scanning rate 1°/min. Crystallite sizes were determined from X-ray line-broadening using Scherrer's equation. Volume fractions of zirconia tetragonal and monoclinic phases were calculated from integrated peak intensities.

Thermogravimetric analysis (TGA) was performed on a Shimadzu TGA-50 instrument. The samples were heated in platinum crucibles up to 1000°C with a heating rate 10°C/min in 30 ml/min dry air flow.

Isomerization of n-butane was performed in a stainless steel pulse reactor. A catalyst (0.1 g) mixed with glass wool and held in place with a glass wool plug was pretreated in O_2 (30 ml/min) at 500°C for 2 h. Then it was cooled to 300°C and the flow gas was changed to helium. After subsequent cooling to 170°C, 0.15 ml gaseous butane (Alltech, 99.8%) was injected every 10 min. An on-line Gow-Mac 580 gas chromatograph with a thermal conductivity detector and Chemipack C18 column (Alltech) was used to determine the product composition. The initial reagent contained 0.2% of isobutane as the only detectable impurity. Catalytic activity was determined as an average conversion in the first five pulses.

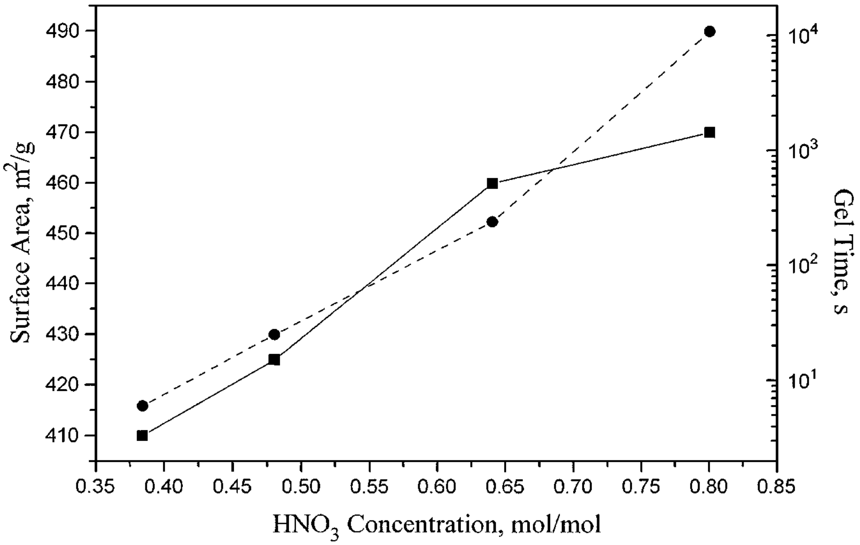

FIG. 1. Dependence of sulfated zirconia aerogel gel times (dashed line, right axis) and surface areas after supercritical drying (solid line, left axis) on the concentration of nitric acid. The aerogels contained 10 mol% sulfuric acid.

RESULTS AND DISCUSSION

Textural Properties

Recently we have reported the influence of sol-gel parameters on the textural properties of zirconia aerogels (20). In this study sulfated zirconia aerogels were prepared according to a procedure similar to the one used there. Sulfuric acid was added to the precursor solution before gelation. We have studied the influence of some sol-gel parameters on textural properties of aerogels with a 10 mol% nominal sulfur loading. Previously, this loading was shown to be sufficient to give rise to catalytic activity in butane isomerization after calcination at high temperatures (5).

We observed only a small effect of the H_2SO_4 addition on gel times. Gels with 10% sulfuric acid had gel times only slightly higher than pure zirconia.

Nitric acid concentration had a similar effect on textural properties of sulfated zirconia aerogels before calcination as for pure zirconia (20). Gel times and surface areas (Fig. 1) increased with acid concentration.

Hydrolysis of zirconium alcoxides is very fast. The rate of the sequential condensation can be effectively influenced by the concentration of an acid. Four main types of products can be obtained (22). If no acid or not enough acid is added, immediate precipitation occurs. The precipitates usually do not possess desirable porous structure and surface area (21). In a certain concentration range, quick formation of a hard polymeric gel containing precipitate is observed. Further increase of the acid amount progressively results in the increase of the gel time and formation of clear hard and, then, soft alcogels. Obviously, if the acid concentration is sufficiently high, condensation can be completely suppressed.

Figure 2 shows the dependence of surface areas and pore volumes after calcination at 600°C for 2 h in air. This treatment is known to be required for the formation of active catalytic materials. In different studies maximum activity was reported after calcination at temperatures from 550°C to 650°C, depending on the preparation method and reaction conditions. But sulfated zirconia catalysts precalcined

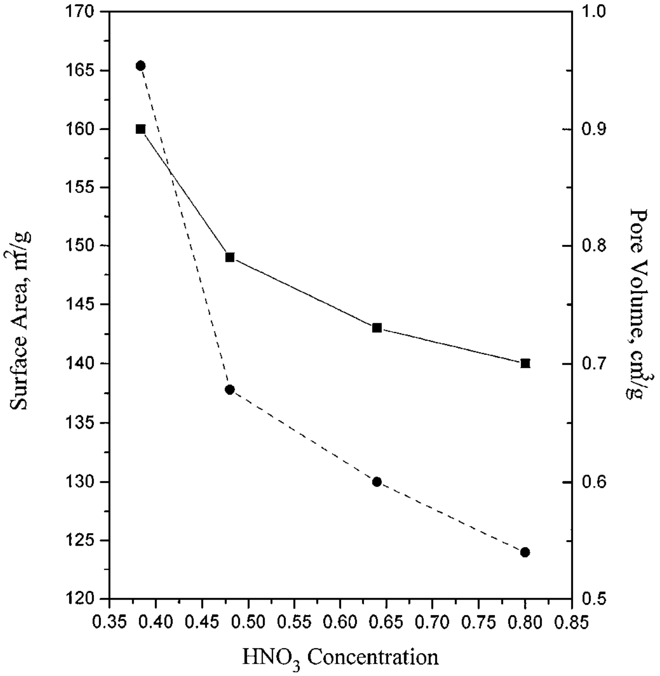

FIG. 2. Dependence of surface areas (solid line) and pore volumes (dashed line) of sulfated aerogels calcined at 600°C on the concentration of nitric acid.

at 600°C were always active if the samples exhibited catalytic activity after any heat treatment. Based on this literature background, we chose 600°C as the calcination temperature, and then compared samples prepared by different methods and having different sulfur contents. Effect of the calcination temperatures on the catalytic and morphological properties will be reported later.

Comparing Figs. 1 and 2, one can see that the calcination inverts the surface area trend. Now surface areas and pore volumes decreased with the acid concentration. The highest surface area was observed for the sample with the gel time as low as 6 s. These results are not in complete agreement with the results obtained on pure zirconia aerogels (20) where definite maxima were observed for samples with gel times of 40–60 s. Pore size distributions of aerogels with different HNO_3 concentrations after the calcination are presented in Fig. 3. As in the case of pure zirconia aerogels, monodispersed distributions were obtained, with maxima shifting toward smaller pore radii with the acid concentration.

Some results showing the influence of other sol-gel parameters on the textural properties of sulfated zirconia aerogel are presented in Table 1. When higher amounts of hydrolysis water equal to 6 molecules per Zr atom were used, the acid concentration required to obtain similar gel time increased by a factor of 1.5, surface areas before and after calcination were lower than for aerogels with normal water concentration (4 mol/mol). The use of 1 mol/L precursor concentration gave rise to a higher surface area before calcination but substantially lower after calcination, compared to the concentration of 0.5 mol/L used in other preparations. Higher drying temperature (275°C) resulted in the surface area decrease before calcination and its increase after calcination.

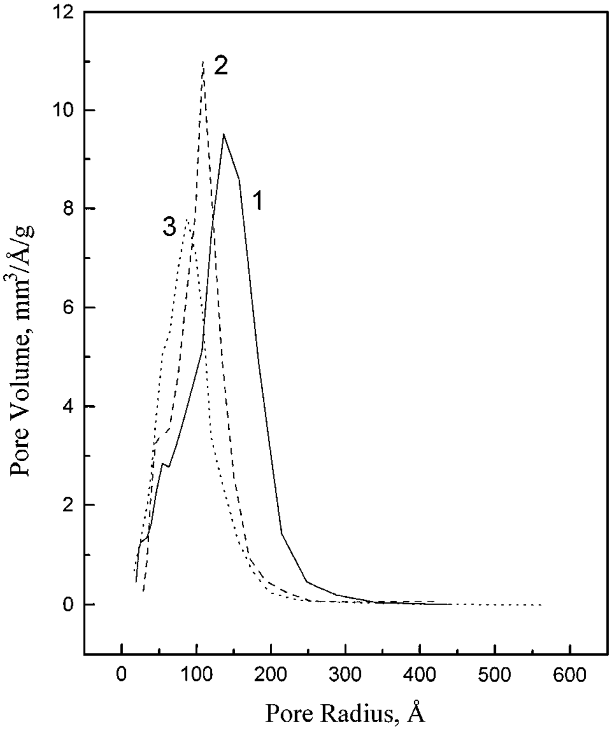

FIG. 3. Pore size distributions of sulfated zirconia aerogels calcined at 600°C. Concentrations of nitric acid were 0.64 (1), 0.48 (2), and 0.39 (3) moles per mole of the zirconium precursor.

TABLE 1

Properties of Some Sulfated Zirconia Aerogels Containing 10 mol% of Sulfuric Acid

	$Zr(OBu)_4$ conc., mol/L	H_2O conc., mol/mol	HNO_3 conc., mol/mol	Autoclave temperature, °C	Gel time, s	Surface area,[a] m^2/g	Surface area,[b] m^2/g
1	0.5	4	0.48	255	25	425	143
2	0.5	6	0.72	255	35	420	133
3	1	4	0.86	255	30	480	102
4	0.5	4	0.5	275	25	385	174

[a] After supercritical drying.
[b] After calcination at 600°C for 2 h.

Based on the above data and our study of pure zirconia aerogels (20), the following guidelines for tuning the textural properties of sulfated zirconia aerogels (with the sulfur content ≤20%, see below) can be suggested. To obtain aerogels with the highest surface area after calcination, one should use the precursor concentration of 0.25–0.5 mol/L, water concentration 4 mol/mol Zr and high drying temperature (295°C, or, probably, more). The nitric acid concentration should be adjusted to get short, but not zero, gel times. Ethanol seems to be the best solvent among normal alcohols.

In this work we varied sulfur loading from 0 to 33 mol%. No apparent effect of the H_2SO_4 concentration on the gel times was observed, which ranged from 12 to 25 s when the HNO_3 concentration was kept constant at 0.48 mol/mol. The dependence of the surface areas and pore volumes of uncalcined samples on the sulfur loading is shown in Fig. 4. Both curves look very similar, with maxima at the sulfur loading equal to 17 mol% and a drastic drop at higher loadings.

Gels with H_2SO_4 concentration up to 17% were clear and apparently homogeneous. Higher loadings disturbed the structure of zirconia gels, and it was not possible to prepare a gel without a precipitate. The apparent amount of the precipitate seemed to increase with the sulfur loading increase. We also prepared a gel with 50 mol% of sulfur. This sample had a very low surface area (2 m^2/g) and obviously could not be used as a catalytic material.

Pore size distributions for aerogels with different sulfur contents are presented in Fig. 5. Zirconia aerogel without sulfur had a broad distribution in the mesoporous region with the only detectable peak at pore radius equal to 70 Å. This sample, as well as all the others, contained also some micropores but their impact on total pore volume and

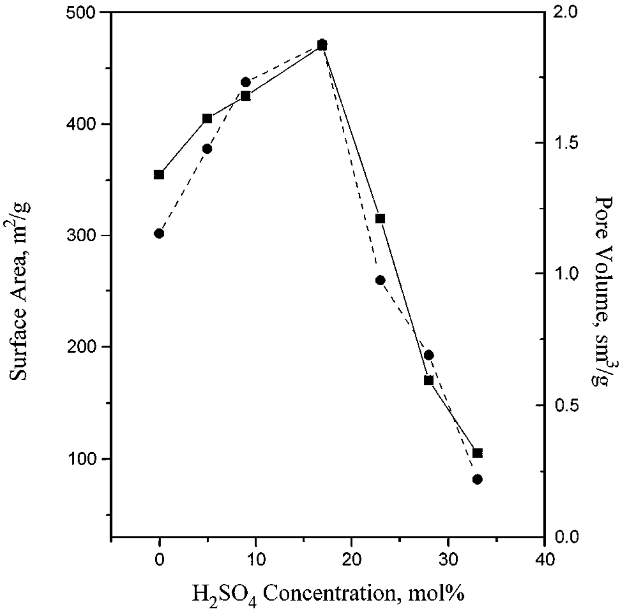

FIG. 4. Dependence of surface areas (solid line) and pore volumes (dashed line) of sulfated aerogels on the concentration of sulfuric acid.

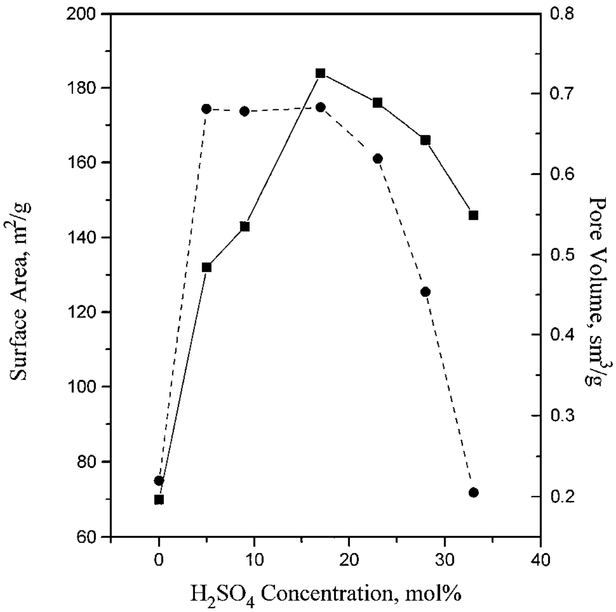

FIG. 6. Dependence of surface areas (solid line) and pore volumes (dashed line) of calcined sulfated aerogels on the concentration of sulfuric acid.

surface area was not large. With the increase in the sulfur loading, a new peak centered at 160–180 Å appeared, resulting in a substantial increase of the pore volume. The distribution and volume of pores smaller than 100 Å remained constant in this region of the sulfur concentration. At higher sulfur loadings, when the initial alcogels contained a precipitate, mesopores gradually vanished, the AP33 sample being mainly microporous with a very low pore volume.

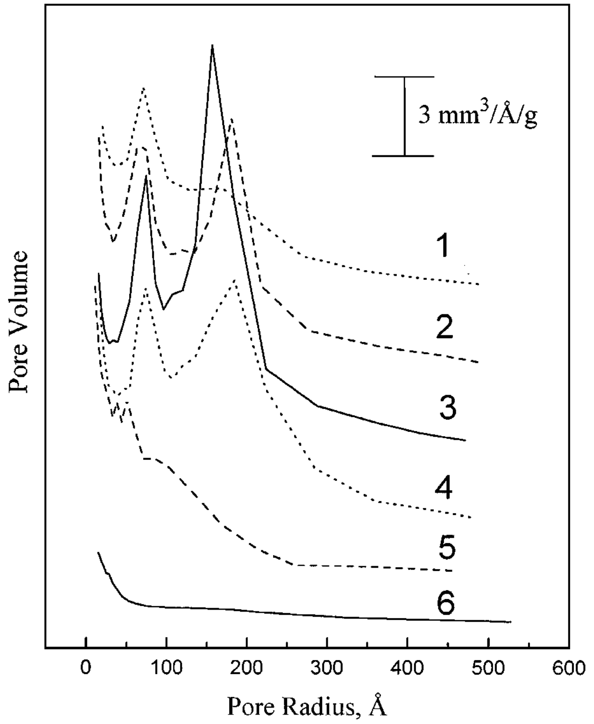

FIG. 5. Pore size distributions of sulfated zirconia aerogels: 1, AP0; 2, AP5; 3, AP9; 4, AP17; 5, AP28; 6, AP33.

Calcination at 600°C resulted in a substantial decrease of the surface and pore volume, except for the samples with the highest sulfur loading (Fig. 6). All sulfated samples had surface areas in the range of 130–185 m^2/g, the sample with 17 mol% SO_4 still exhibiting the highest surface area. It is notable that surface area of the sample with the highest sulfur loading even increased after the calcination. The calcination equalized pore volumes of the samples with the loading from 5 to 23 mol%.

From pore size distributions presented in Fig. 7, one can see that the calcination practically eliminated micropores. The distributions were then dominated by pores larger than 100 Å if they were present in the initial aerogels. Even 5 mol% of sulfur was enough to prevent the pore network from collapse and make the sample retain a large pore volume, surface area, and almost homogeneous pore size distribution.

Effects of the sulfur loading on surface areas of IAP and CP sulfated zirconia is shown in Fig. 8. In both series the areas increased with the loading, CP23 being the only exception. We were able to obtain samples with reasonably high surface areas (up to 170 m^2/g) by incipient wetness impregnation of our aerogels with $(NH_4)_2SO_4$ followed by calcination in air at 600°C. These areas were quite comparable to those of AP sulfated zirconia. The pore volumes and average pore radii of IAP and CP samples were much smaller than those of AP samples.

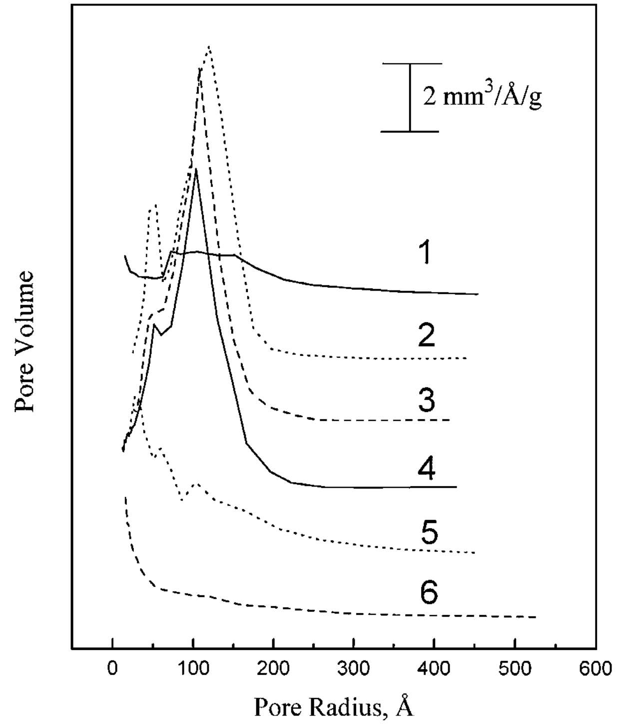

FIG. 7. Pore size distributions of calcined sulfated zirconia aerogels: 1, AP0; 2, AP5; 3, AP9; 4, AP17; 5, AP28; 6, AP33.

X-Ray Diffraction Data

At room temperature zirconia can exist in a thermodynamically stable monoclinic crystalline phase and a metastable tetragonal phase. Sulfation of ZrO_2 is known to stabilize the latter form (14, 23). In our experiments unsulfated precipitated zirconia (CP-ZrO_2) contained a mixture of the two phases after calcination at 600°C. AP and IAP samples were mainly tetragonal under the same conditions although small amounts of the monoclinic phase still could be detected. These results are similar to those previously reported (20).

Sulfur addition in the concentration as low as 2 mol% was sufficient to stabilize the tetragonal phase in all the samples. No peaks typical of the monoclinic phase were detected in all sulfated samples studied except AP33, and in this sample it was present in the concentration of about 35%. Additional study has shown that it was present in the sample even before calcination, whereas all the other samples were initially X-ray amorphous. This gel was not homogeneous and contained some quickly formed precipitate. Probably, the precipitate crystallized into the monoclinic phase in the autoclave.

Figure 9 presents XRD crystalline sizes of calcined samples with different sulfur loadings. The smallest crystalline size in all the methods was obtained at sulfur concentrations of 23 mol%. Most likely, this amount was sufficient to completely inhibit the particle growth during the calcination,

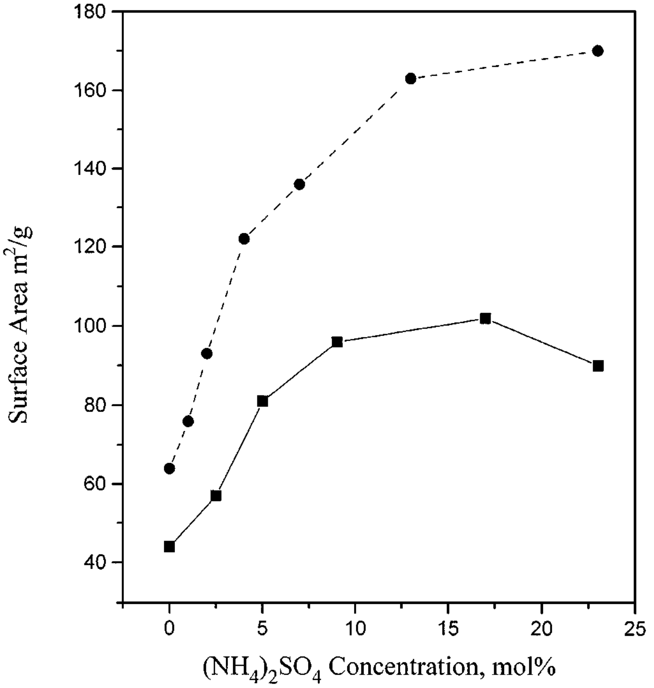

FIG. 8. Dependence of surface areas of sulfated zirconia prepared by IAP (dashed line) and CP (solid line) methods after calcination at 600°C on the $(NH_4)_2SO_4$ concentration.

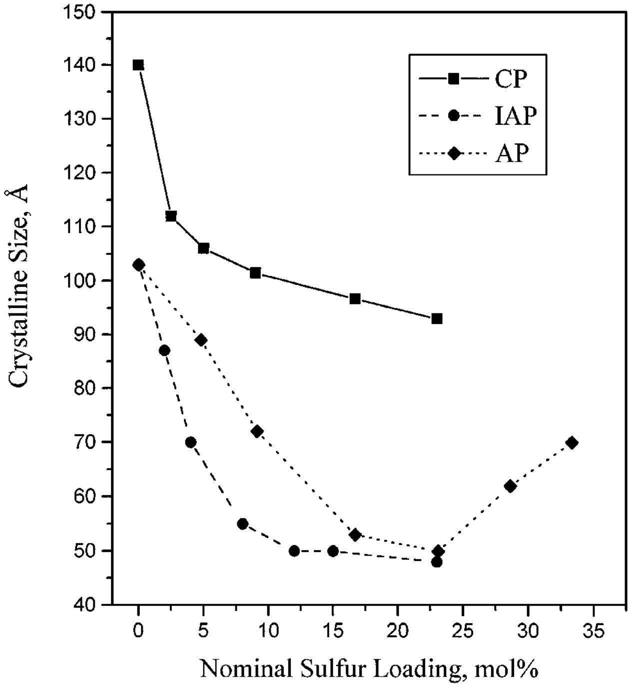

FIG. 9. Dependence of XRD crystalline sizes for sulfated zirconia prepared by different methods on the nominal sulfur loading. The samples were calcined at 600°C.

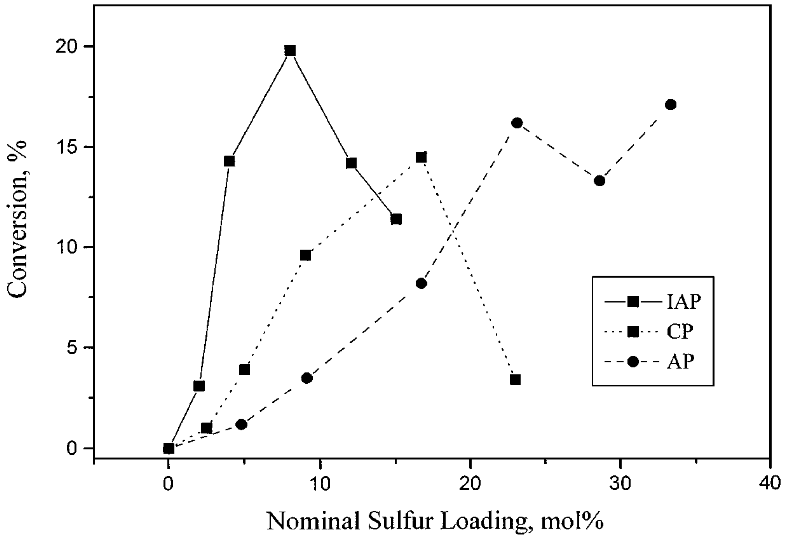

FIG. 10. Isomerization activity of sulfated zirconia as a function of the nominal sulfur loading.

and the sizes thus obtained correspond to the initial particle size achieved by the preparation method. For AP and IAP zirconia, this size was almost the same—about 50 Å. CP particles were almost twice as large. The increase of the average particle size of AP samples at higher sulfur loadings is likely to be the result of the presence of precipitates in these gels.

Catalytic Activity

Figure 10 presents the results of the catalytic experiments. All the sulfation methods gave rise to catalytic activity in butane isomerization. The activity dependence on the nominal loading had the same trend for all the methods. Unsulfated samples were not active at all. Samples with small amounts of sulfur also did not have appreciable activity, but then large activity increases were observed as the loading went up. Further increase in the loading resulted in smaller activities, except for AP series. Maximum activity was observed at intermediate sulfur concentrations. One should note that maximum activity on AP and IAP samples was somewhat higher than on CP ones. This is apparently due to the higher surface area of the former. For example, the reaction rate over IAP8 was 2.2 μmol g^{-1} s^{-1}, or 1.65×10^{-8} mol m^{-2} s^{-1}. This value ranks it among the most active sulfated zirconia catalysts (not modified with metals) reported.

Another striking feature is that maximum activities were obtained at very different nominal sulfur loadings. Indeed, 8 mol% was enough for the impregnated aerogels, whereas 23 mol% was required for AP samples. In the latter case AP33 was even slightly more active. Conventional samples were between the two in terms of the loading required.

Obviously, the preparation method must influence greatly the properties of surface sulfates resulting in differences in isomerization activities. We used TGA in an attempt to understand this.

Thermogravimetric Data

Figure 11 presents DTGA spectra of CP sulfated zirconia with different amounts of sulfur. Pure conventional zirconia has two peaks. The low temperature peak at 80°C belongs

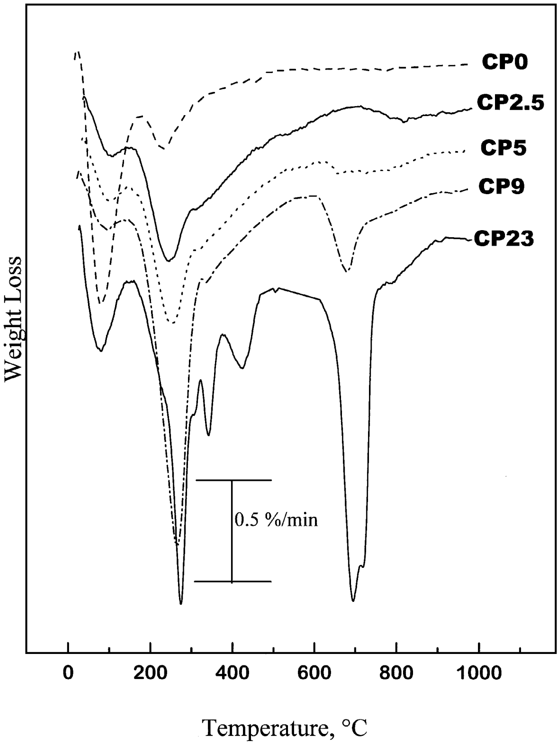

FIG. 11. Derivative TGA spectra of precipitated sulfated zirconia.

to physically adsorbed water. Peak size depended only on the time the samples were in contact with atmosphere and so is apparently due to atmospheric water adsorption. The peak centered at 230°C corresponds to water belonging to the hydrous zirconia framework.

Incipient wetness impregnation with a water solution of $(NH_4)_2SO_4$ resulted in the growth of the second peak with sulfur concentration and its slight shift to higher temperatures. Most likely, it is due to the decomposition of incorporated ammonium ions and increased zirconia hydration.

The CP2.5 sample exhibited a broad peak centered at 835°C. On CP5 it became even broader and extended to lower temperatures. A new large peak centered around 700°C appeared with samples with higher sulfur loadings, whereas the 835°C peak remained as a shoulder. As sulfur incorporation into the bulk seems unlikely in this method, the peak at 835°C probably corresponds to the decomposition of surface sulfates in the first monolayer, whereas the peak at 700°C is due to the decomposition of sulfates located in additional layers above. The sulfur monolayer for conventional sulfated zirconia has been reported to correspond to approximately 4 wt% (7). In our experiments the changes in the spectra were observed in the same concentration region.

DTGA spectra of the samples precalcined at 600°C for 2 h are shown in Fig. 12. As one would expect, no peaks at temperatures below 600°C were observed, except the low temperature water peak. (Calcined zirconia is known to be hygroscopic.)

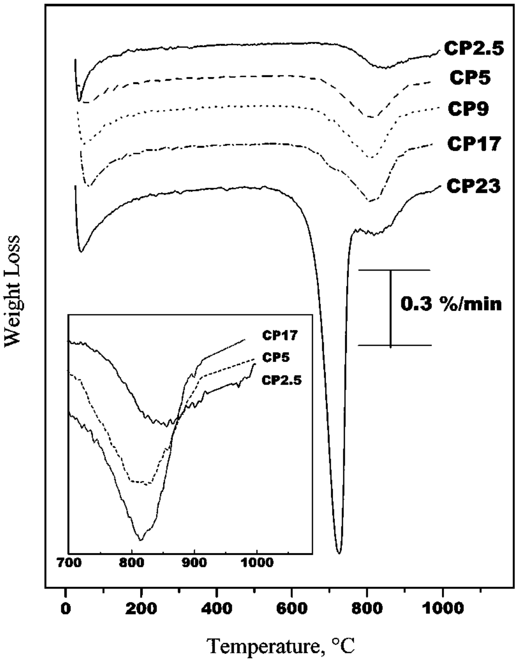

FIG. 12. Derivative TGA spectra of precipitated sulfated zirconia precalcined at 600°C (insert presents the high-temperature region of the spectra in the overlapping mode).

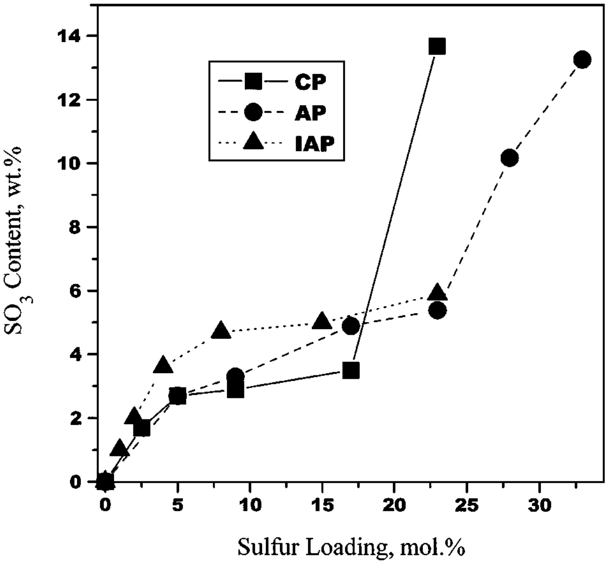

FIG. 13. Concentration of sulfates retained after calcination at 600°C on the surface of catalysts prepared by different methods as a function of the initial sulfur loading.

The CP2.5 sample exhibited a high temperature peak at 860°C. It increased in size and shifted toward lower temperatures with the sulfur loading increase, suggesting that the average interaction energy between sulfates and the surface decreased with increased loading. As one can see from Insert to Fig. 12, the actual amount of sulfates decomposing at very high temperatures (>900°C) decreased with the sulfur loading increase. Still some sulfates adsorbed, probably, on some structural defects remaining on the surface up to the highest temperatures.

Figure 13 presents the amount of sulfates retained by the catalyst prepared by different methods depending on the initial sulfur loading. These amounts were obtained as weight losses in the 600–1000°C temperature range. One can see that the CP17 sample retained after the calcination only twice as much sulfate as CP2.5—3.7 wt%. But its isomerization activity was almost 15 times higher. This means that only sulfates with relatively low interaction energy, which are practically not present in CP2.5, induce the catalytic activity. The sample with the highest loading retained much of its overmonolayer sulfur observed as a peak at 730°C. Obviously, in this case the calcination temperature (or time) was not enough to form the active surface species, and its catalytic activity was lower.

Based on IR data (2, 24, 25), it is generally believed that active sulfated zirconia catalysts contain sulfates in a highly covalent form. The position of the ν_3 band of the S=O bond observed in "*in situ*" IR spectra is known to depend on the degree of the electron transfer (24). In general, the higher the wavenumber, the less ionic are the sulfates.

It is very interesting that the position of this maximum for conventional sulfated zirconia catalysts has been shown to shift to higher wavenumbers with the sulfur loading increase. For example, Morterra *et al.* (25) found that the position of the peak shifted from 1374 to 1406 cm^{-1} with the sulfur loading increasing from 0.65 to 2.6 sulfur atoms per nm^2. Note that even the highest loading is quite far from the nominal monolayer estimated to be at 4 atoms/nm^2. These transformations were observed in the same range of the surface sulfur contents as changes in the TGA spectra registered in the present study. Therefore, it is natural to suggest that sulfates with a lower bonding energy which decompose at about 820°C are in a highly covalent form, whereas sulfates decomposing at higher temperatures, which are formed at low sulfur loadings, are more ionic.

Figure 14 presents DTGA spectra of IAP sulfated zirconia. The unsulfated sample had a spectrum very similar to those of zirconia aerogels (20). Besides the low temperature peak, it exhibited a water peak at 350°C with a shoulder at 420°C belonging to carbonaceous residues. No weight loss above 600°C was observed. Sulfation with 1–6 mol% of $(NH_4)_2SO_4$ led to the gradual lowering of the water peak due to the consumption of surface hydroxyls with sulfate ions. Two new peaks similar to those observed on the CP sample appeared. The peak at 230–250°C was due to the ammonium decomposition. The high temperature peak located at 900°C for IAPI gradually shifted to 800°C in the case of IAP6. Additional increase in the sulfate concentration results in the formation and fast growth of another peak at 720°C, corresponding to overmonolayer sulfates.

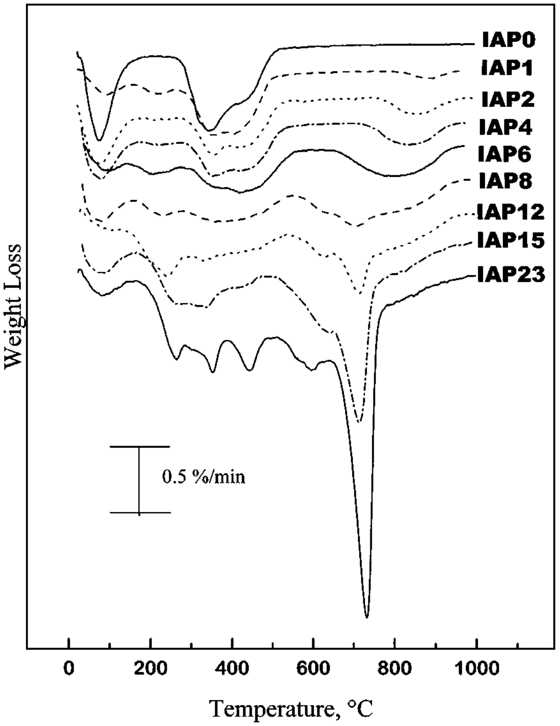

FIG. 14. Derivative TGA spectra of impregnated aerogel zirconia.

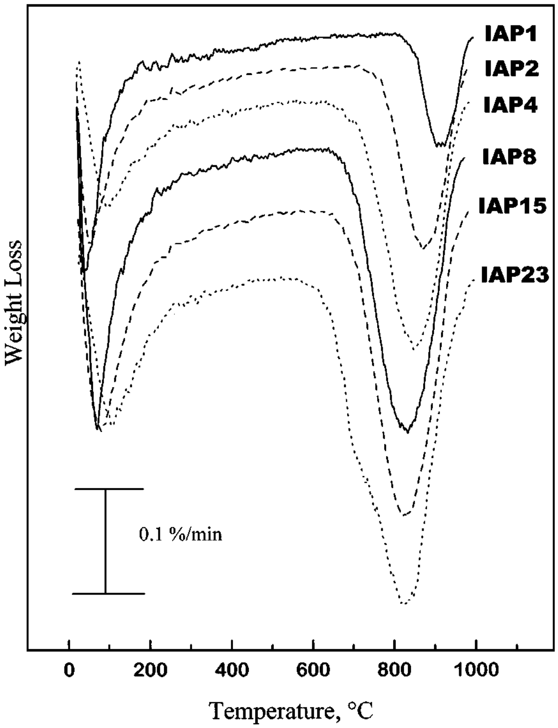

FIG. 15. Derivative TGA spectra of impregnated aerogel zirconia precalcined at 600°C.

An overall behavior similar to the CP series was observed for calcined IAP zirconia as well (Fig. 15). However, one should note that catalytic behavior of the IAP4 sample was similar to that of CP16—the most active conventional sample in the study. The unique IAP preparation method enabled it to retain nearly all of its sulfur (3.6 wt%, Fig. 13), and both the concentration and type of sulfates of these two samples were similar.

Thus, IAP samples retain more sulfur after calcination than CP and AP (Fig. 13) at any given initial loading not higher than 10 mol%. It results in higher catalytic activity (Fig. 10) and smaller crystalline size (Fig. 9). Basically, using this preparation method one does not need to overload the sample with sulfur that will be lost during the calcination step.

The TGA of the sulfate region of the AP samples is slightly more complex (Fig. 16). In this case sulfur can be incorporated into the zirconia network in the gelation step. At sulfur concentrations up to 9 mol% they behave similar to CP and IAP samples. However, at concentrations of 16 and 23 mol% a new peak was observed at 670°C. We believe that in this case overmonolayer sulfates decompose at lower temperatures due to the open structure of the aerogels. At higher sulfur concentrations resulting in certain precipitation on the gelation step and lower surface areas, this peak shifted to 720°C, similar to that formed for CP and IAP samples. Also a new peak centered at 760°C appeared in this case, and this peak may be due to decomposition of bulk sulfates. Sulfates are likely to be trapped during the AP preparation procedure, and this peak is not observed for CP and IAP series. These alcogels contained some precipitates of, presumably, zirconium sulfate. Additional sulfate incorporation into the bulk could occur in the autoclave in the presence of large amounts of sulfuric acid.

Spectra of the AP samples precalcined at 600°C are shown in Fig. 17. More ionic sulfates are formed in this method. The peak of AP9 was observed at 890°C. This temperature is higher than for the IAP2 and CP2.5 samples. It might be caused by sulfation with H_2SO_4 rather than $(NH_4)_2SO_4$, although most likely it is associated with the structure of the aerogels. Due to this fact, at any given sulfur loading below 20 mol% the aerogels were less active than CP and IAP samples. The 23 mol% nominal loading was required to shift the peak to 835°C and obtain appreciable activity.

These data are in a good agreement with the results obtained by Ward and Ko who synthesized sulfated zirconia aerogels using the low-temperature supercritical drying (5). In their case, a sample with 5 mol% H_2SO_4 exhibited no catalytic activity and had the IR peak at 1360 cm^{-1}. The 10 mol% sample was active, with the peak located at 1375 cm^{-1}. The activity of the 20 mol% sample was somewhat higher, with the peak at 1380 cm^{-1}. Note that in active conventional samples the peak is located at wavenumbers above 1400 cm^{-1}. These data correlate with our observations that high sulfur loadings are required for the generation of the catalytic activity, and surface sulfates formed using this method are more ionic than those made with the use of other preparation methods, as judged form the positions of the decomposition peak.

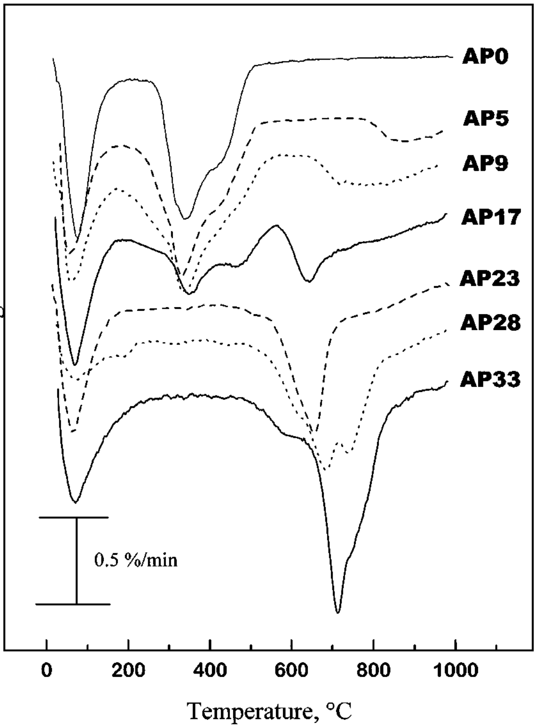

FIG. 16. Derivative TGA spectra of sulfated zirconia aerogels.

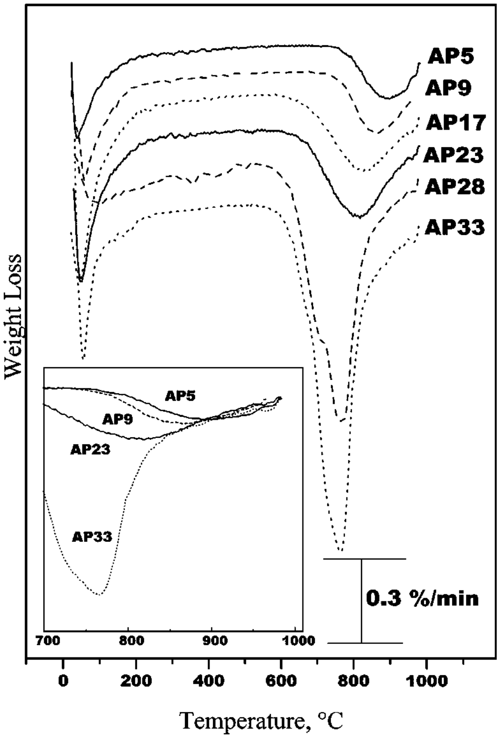

FIG. 17. Derivative TGA spectra of sulfated zirconia aerogels precalcined at 600°C (insert presents the high-temperature region of the spectra in the overlapping mode).

Samples with higher sulfur concentrations showed a large peak at 770°C. As the presence of these sulfates did not strongly affect the catalytic activity, this peak is likely to represent sulfates trapped into the bulk during the gelation step. The AP33 sample was even the most active in the series. Note that sulfates with higher decomposition temperatures were still present in these samples in amounts comparable with AP23 (see insert to Fig. 17).

To sum it up, the most active catalysts prepared by different methods have been shown to have a close to monolayer (4–5 wt%) coverage with covalent sulfates, and these important sulfates decompose in the TGA instrument at 820–830°C.

CONCLUSION

Sulfated zirconia aerogels were prepared by a one-step sol-gel method followed by high temperature supercritical drying. Textural properties of the aerogels containing 20 or less mol% of sulfuric acid were shown to be analogous to those of pure zirconia aerogels. Guidelines worked out for the latter (20) can be used to fine-tune the desired textural properties. Sulfated zirconia aerogels had surface areas and pore volumes higher than pure zirconia aerogels and conventional sulfated zirconia.

A method for preparation of active superacid catalysts by incipient wetness impregnation of zirconia aerogels with $(NH_4)_2SO_4$ has been worked out. The samples had surface areas and particle sizes close to those of sulfated zirconia aerogels.

Both methods were shown to give catalysts active in butane isomerization. Maximum activity of the samples prepared by this method was slightly higher than that of conventional precipitated samples. The IAP method was shown to require substantially smaller nominal sulfur loading than conventional samples to obtain maximum activity. The highest loading was required for sulfated aerogels.

TGA was shown to give valuable information on the properties of surface sulfates. Small sulfur loading resulted in more ionic sulfates with lower isomerization activity. Close to monolayer surface coverage with the decomposition peak at 820–830°C was observed on the most active samples irrespective of the preparation method. Presence of the overmonolayer surface sulfates was shown to hinder the isomerization activity, whereas bulk sulfates on AP samples had little effect on it. IAP samples were shown to retain most of their sulfates after the 600°C calcination, thus having higher surface areas, catalytic activity, and smaller particle sizes at low sulfur loadings.

REFERENCES

1. Arata, K., *Adv. Catal.* **37**, 165 (1990).
2. Yamaguchi, T., *Appl. Catal.* **61**, 1 (1990).
3. Yaluris, G., Larson, R. B., Kobe, J. M., Gonzalez, M. R., Fogash, K. B., and Dumesic, J. A., *J. Catal.* **158**, 336 (1996).
4. Chen, F. R., Coudurier, G., Joly, J.-F., and Vedrine, J. C., *J. Catal.* **143**, 616 (1993).
5. Ward, D. A., and Ko, E. I., *J. Catal.* **150**, 18 (1994).
6. Nascimento, P., Akratopoulou, C., Oszgyan, M., Coudurier, G., Travers, C., Joly, J.-F., and Vedrine, J. C., *in* "Proceedings of the 10th International Congress on Catalysis, Budapest, 1992" (L. Guzsi *et al.*, Eds.), Vol. B, p. 1185. Akademiai Kiado, Budapest, 1993.
7. Morterra, C., Cerrato, G., Pinna, F., Signoretto, M., and Strukul, G., *J. Catal.* **149**, 181 (1994).
8. Kustov, L. M., Kazansky, V. B., Figueras, F., and Tichit, D., *J. Catal.* **150**, 143 (1994).
9. Lunsford, J. H., Sang, H., Campbell, S. M., Liang, C.-H., and Anthony, R. G., *Catal. Lett.* **27**, 305 (1994).
10. Morterra, C., Cerrato, G., Pinna, F., Signoretto, M., and Strukul, G., *J. Catal.* **157**, 109 (1995).
11. Fogash, K. B., Yaluris, G., Gonzales, M. R., Ouraipryvan, P., Ward, D. A., Ko, E. I., and Dumesic, J. A., *Catal. Lett.* **32**, 241 (1995).
12. Jin, T., Yamaguchi, T., and Tanabe, K., *J. Phys. Chem.* **90**, 4794 (1986).
13. Farcasiu, D., Ghenciu, A., and Li, J. Q., *J. Catal.* **158**, 116 (1996).
14. Hino, M., and Arata, K., *J. Chem. Soc. Chem. Commun.*, 851 (1980).
15. Ward, D. A., and Ko, E. I., *J. Catal.* **159**, 321 (1995).
16. Teichner, S. J., *Chemtech,* 372 (1991).
17. Schwarz, J. A., Contescu, C., and Contescu, A., *Chem. Rev.* **95**, 477 (1995).
18. Pajonk, G. M., *Appl. Catal.* **72**, 217 (1991).
19. Schneider, M., and Baiker, A., *Catal. Rev.-Sci. Eng.* **37**, 515 (1995).
20. Bedilo, A. F., and Klabunde, K. J., *NanoStructured Materials* **8**, 2, 119 (1997).
21. Ward, D., and Ko, E., *Chem. Mater.* **5**, 956 (1993).
22. Suh, D. J., and Park, T. J., *Chem. Mater.* **8**, 509 (1996).
23. Srinivasan, R., Watkins, T. R., Hubbard, C. R., and Davis, B. H., *Chem. Mater.* **7**, 725 (1995).
24. Jin, T., Yamaguchi, T., and Tanabe, K., *J. Phys. Chem.* **90**, 4794 (1986).
25. Morterra, C., Cerrato, G., Emanuel, C., and Bolis, V., *J. Catal.* **142**, 349 (1993).