Sulfated zirconia catalysts: Are Brønsted acid sites the source of the activity?

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The thermal decomposition products of pyridinium sulfate differ from those of pyridinium sulfate supported on zirconia which in turn differs from that of pyridine adsorbed on a sulfated zirconia. Unsupported pyridinium sulfate decomposes to produce pyridine and sulfuric acid, and these subsequently react to produce oxides of carbon and sulfur. Zirconia that is sulfated and then exposed to pyridine does not release detectable amount of pyridine during heating in an inert gas; rather the pyridine undergoes oxidation reduction reactions simultaneously to release CO_2 and sulfur compounds. Pyridinium sulfate supported on zirconia decomposes upon heating to release pyridine and sulfuric acid, which reacts with the zirconia. The desorption of pyridine in one case and only CO_2/SO_x in the other case suggests that sulfated zirconia does not contain Brønsted acidity that can form pyridinium sulfate.

Keywords: sulfated metal oxides; sulfated zirconia catalyst; Brønsted acidity; catalytic activity

1. Introduction

The recognition that sulfated metal oxides, particularly sulfated zirconia, possess an activity for hydrocarbon conversion that exceeds most, or all, acidic zeolite catalysts elicited great interest in these materials [1–6]. A similar hydrocarbon conversion may be obtained at 100–200°C lower temperatures using the sulfated zirconia catalyst compared to the most active acidic zeolite catalyst. To make effective use of the acidity of the sulfated zirconia catalyst, the incorporation of a metallic function provides for significant improvements in both activity and stability (e.g., ref. [7]). Many investigators incorporate platinum as the metallic function [1]; however, some reports indicate that other combinations, such as iron and manganese, may be superior to platinum [7,8]. While the state of the added metal has been debated, it is the type of acidity that is responsible for the superactivity of this catalyst which has attracted much attention. Most authors refer to the sulfated zirconia as having superacid properties [1–6]. Thus, much of the debate concerns the acid function and whether the superacidity is a result of Brønsted or Lewis acid sites as well as the dynamic nature of these sites in the presence of reactants and/or hydrogen [9–14].

The nature of the acidity of sulfated zirconia is still controversial [1]. There are claims that the catalytic activity derives mainly, or completely, from protonic (Brønsted) acid sites. Other authors are equally convinced that the acid sites are aprotic (Lewis sites). Various techniques employing IR spectroscopic techniques provide data to distinguish between these two general acid types. Arata [4] summarized earlier results for the adsorption of pyridine on sulfated zirconia and indicated that there was an increase in Lewis sites relative to the Brønsted sites. Results reported more recently by Morterra et al. [15,16] likewise emphasize that the fractions of Brønsted and Lewis sites depend not only upon the initial calcination temperature but also the temperature that the sample is outgassed in situ in the infrared cell. Thus, these latter authors find that the Brønsted sites are the most liable to heating, and that the Lewis sites therefore assume an increasingly larger fraction as the outgassing temperature increases. Zhang et al. [17] found that about equal amounts of Brønsted and Lewis acid sites were present when the sample was outgassed at 400°C in situ, the upper temperature limit for the cell utilized in the study. Presumably, this distribution of sites would change as the outgassing temperature was increased above the 400°C used in the study by Zhang et al. [17]. Ebitani et al. [18] conducted a study in which the in situ pretreatment was not given but is presumed to be 600°C for 3 h. They obtained IR spectra of adsorbed pyridine that indicated that the surface acid sites of Pt–ZrO_2 and Pt–SO_4^{2-}–ZrO_2 were mostly Lewis sites but that SO_4^{2-}–ZrO_2 possessed Brønsted acid sites. Furthermore, temperature desorption profiles led the authors to conclude that the Lewis acid sites on Pt–SO_4^{2-}–ZrO_2 were stronger than those of either Pt–ZrO_2 or SO_4^{2-}–ZrO_2.

Yamaguchi et al. [19,20] reported infrared spectra of adsorbed pyridine to show that the catalysts evacuated at 500°C possess only Lewis acidity; no Brønsted acid sites were observed. Beňsitel et al. [21] and Tret'Yakov et al. [22] never observed the IR bands characteristic of the pyridinium ion. However, Nakano et al. [23] reported evidence for Brønsted acidity. Babou [24] utilized IR to obtain results they reported to provide evidence for two Lewis and one Brønsted acid sites. These latter authors concluded that their IR results, combined with their previous theoretical calculations, indicated that the sulfated zirconia can be visualized as a H_2SO_4 compound grafted onto the surface of zirconia in a way which makes it very sensitive to water in a reversible way. They claim that its acidity is similar to that of sulfuric acid, and that it is not really superacidic.

Adeeva et al. [25] utilized the adsorption of CO and acetonitrile and found that their FTIR results revealed the presence of Lewis and Brønsted acid sites on both sulfated zirconia and sulfated zirconia promoted with iron and manganese ions; these precalcined samples were apparently heated for 2 h at 450°C.

Escalona Platero and Peñarroya Mentruit [26] utilized CO adsorption to reveal several types of sulfate groups that are resistant to heating up to 700°C; two kinds of Lewis acid sites were identified. Pinna et al. [27] provide convincing data to support the view that the sites that are active for *n*-butane isomerization are poisoned by the adsorption of CO and provide IR data to show that the CO is adsorbed σ-coordinatively to unsaturated surface Zr^{4+} cations in the 25–200°C temperature range.

Considering the above reports of IR data, it appears that the dominant theme is that a sulfated zirconia sample that has been heated to high (>600°C) temperature has a predominance of Lewis sites and few, if any, Brønsted sites. The current results show that the sites present when the sample is prepared from sulfuric acid are different from those of sulfuric acid in interacting with pyridine to form, at least in the latter instance, pyridinium sulfate, the product of the base reacting with a Brønsted acid.

The purpose of this communication is to compare the nature of the reactions that occur during thermal treatments of zirconia which contains the preformed pyridinium sulfate to a material that results from adsorbing pyridine on a sulfated zirconia sample. The results support the view that the majority of the sulfur atoms in the sulfated zirconia system are not part of Brønsted acid sites.

2. Experimental

The hydrous zirconia was prepared by rapid precipitation from a 0.3 M aqueous solution prepared from anhydrous $ZrCl_4$ by the very rapid addition of a 4–5 molar excess of concentrated ammonium hydroxide [10]. The precipitate was washed with deionized, distilled water until the wash water gave a negative test for chloride ion (silver nitrate test). The washed precipitate was dried at 100–120°C for 18 h. A portion of the dried material was stirred in an aqueous H_2SO_4 solution (0.5 M; 15 ml/gram hydrous zirconia) for 2 h [11].

Pyridinium sulfate was prepared by the addition of 1 ml of concentrated H_2SO_4 to a solution containing 3 ml of pyridine in benzene or in *n*-pentane. The mixture was vigorously agitated for one hour and then most of the *n*-pentane (or benzene) was removed by passing a flow of dry nitrogen over the sample. The remaining *n*-pentane (or benzene) was removed under vacuum (ca. 25 mm Hg) at room temperature. The salt was stored until use in a desiccator containing anhydrous desiccant.

Pyridinium sulfate was generated to impregnate the dried zirconia in an amount to provide about 10.4 wt% SO_4^{2-} in the final material. This was accomplished by placing the dried zirconia powder in 100 ml of *n*-pentane, adding an excess (1.3 times stoichiometry) of pyridine, and then slowly dropping the required amount of concentrated H_2SO_4 into the vigorously stirred suspension. The removal of *n*-pentane and other steps followed the procedure used to prepare pyridinium sulfate.

Differential thermal analysis (DTA), thermogravimetric analysis (TGA) and mass spectrometric (MS) analysis of the gases that evolved from the samples were conducted simultaneously using a Seiko TG/DTA/ 320 instrument coupled to a VG Micromass quadrupole mass spectrometer. The sample was heated at 20°C/min in a helium purge gas (200 ml/min).

Pyridine was adsorbed on all zirconia samples except the one prepared using pyridinium sulfate. The sample of sulfated hydrous or calcined zirconia was placed in a desiccator and exposed to pyridine vapors in equilibrium with liquid pyridine during a 24 h period. A small portion of the sample with adsorbed pyridine was transferred, quickly in air, to the sample holder of the TGA/ DTA/MS instrument, and then sealed in a helium flow. The sample was held in a flow of helium at room temperature for a 30 min period. Pyridine desorbed during this period at room temperature, rapidly at first and then asymptotically approaching a constant weight. The sample was then heated at 20°C/min to 800°C, and held at this temperature for 10 min. The sample temperature may vary slightly from the temperature shown by the indicating thermocouple; in addition, the highest desired temperature may be exceeded because of overshooting the upper temperature set-point.

3. Results and discussion

The data obtained for a sample of pyridinium sulfate during heating are shown in fig. 1. A small amount of benzene evolved at 80 and 120°C and this is due to the retention of the solvent used for the preparation of this sample. Pyridinium sulfate is very hygroscopic and adsorbs moisture very readily. Presumably the water (mass 18) that desorbs below about 200°C is due to the moisture that is picked up during the transfer of the sample from the desiccator to the instrument. Pyridine (mass 79) beings to desorb to the gas phase at about

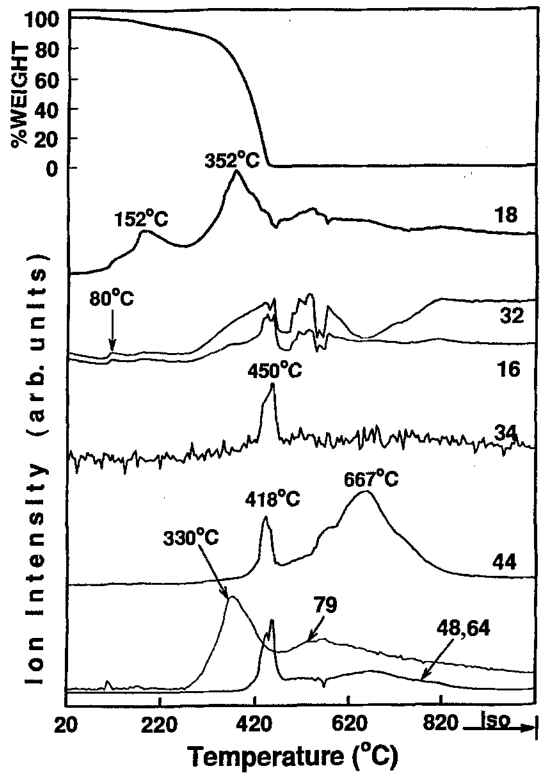

Fig. 1. Weight loss, temperature profile, and mass spectroscopic traces for masses of 16 (O), 18 (H_2O), 32 (O_2), 34 (H_2S), 44 (CO_2), 48 (SO), 64 (SO_2, same curve as SO), and 79 (pyridine) during heating of pyridinium sulfate.

280°C and then desorbs at an increasing rate with increasing temperature to attain a maximum rate centered at 330°C; as the temperature continues to increase the amount of pyridine declines to a minimum after which its evolution increases to attain a second maximum centered at about 550°C. The temperature for the second maximum corresponds roughly to the temperature where oxides of sulfur begin to evolve for a second time. However, the total weight was lost at temperatures below 400°C. The evolution of gases beyond 400°C is considered to be due to hold-up in the transfer tube, due to the large sample size employed, and the large amount of pyridine evolved.

A broad peak of mass 18, corresponding to loss of water, is centered at 352°C; this broad peak is similar in both shape and intensity to that of pyridine but is displaced to about 20°C higher temperature. This broad water peak is not accompanied by the release of sulfur or carbon containing compounds; thus, it is presumed that the water is formed resulting from the dehydration reactions of sulfuric acid, formed concurrently with the evolution of pyridine, such as:

$$2H_2SO_4 \rightarrow HO(SO_2)O(SO_2)OH + H_2O \qquad (1)$$

$$HO(SO_2)O(SO_2)OH \rightarrow H_2O + SO_2 + SO + O_2 \qquad (2)$$

Following the release of water corresponding to the broad mass 18 peak (about 275–450°C), water is slowly and continuously evolved as the sample is heated to and held at 800°C.

During the temperature range of about 400–470°C, a series of complex oxidation–reduction reactions must occur. Thus, carbon originally present in pyridine is evolved as CO_2 and, during the same period, oxides of sulfur (SO_2 and SO) evolved. Thus, the evolved products show that pyridinium sulfate decomposes to produce pyridine as expected for the decomposition of the salt of a Brønsted acid; however, sulfuric acid also participates in an oxidation/reduction reaction at the same time. In this temperature range, a peak of mass 34 (H_2S) is also observed. In this study, as well as in our other studies, we have not been able to observe a peak that corresponds to the evolution of nitrogen present in pyridine in either the oxidized (NO or NO_2) or the reduced form (e.g., NH_3). The reaction of ammonia with a metal oxide in the 500–700°C temperature range has been used to prepare metal nitrides [28]. Zirconium nitride is a stable compound so that it is possible that some zirconium oxynitride is formed, and a nitrogen compound would not be evolved.

The weight loss is complete at a temperature of about 430°C. However, peaks corresponding to pyridine, oxides of sulfur, carbon dioxide and hydrogen sulfide are observed at higher temperatures; this is most certainly due to the condensation of the volatile materials in the capillary transfer line followed by slow decomposition reactions for the deposits in the transfer line. In this instance, the complete volatility of the sample means that a much larger amount of volatiles will be formed than in the analysis of a similar size sample of a sulfated zirconia. Even so, it is clear that pyridine bonded to Brønsted sites of sulfuric acid will desorb as pyridine.

Data obtained during the heating of the zirconia samples containing sulfate and pyridine are presented in fig. 2. In one instance the sulfate was added to zirconia as aqueous H_2SO_4, the resulting solid was calcined at 725°C for 2 h; in the other the zirconia dried at 110°C was "impregnated" with pyridinium sulfate. A comparison of the DTA curves reveals major differences. When dried unsulfated zirconia is heated at 20°C in helium, an exothermic event is observed at about 450°C [12]. The exothermic event shifts to a higher temperature when sulfate is added to the zirconia [13], and the shift in temperature is directly related to the amount of sulfate present [11]. The DTA curve for the zirconia sample prepared by impregnation with pyridinium sulfate exhibits an exotherm at 450°C -the same temperature where the event would occur if the sample did not contain sulfate. For the other sample, where the sulfate was added by reaction with sulfuric acid, the exothermic event is not observed because of the prior calcination of the sample.

One model of the sulfated zirconia is that it is supported sulfuric acid [24]. However, the differences in the thermal conversion and the desorbed products for these two samples (fig. 2) appear to eliminate protonic acidity

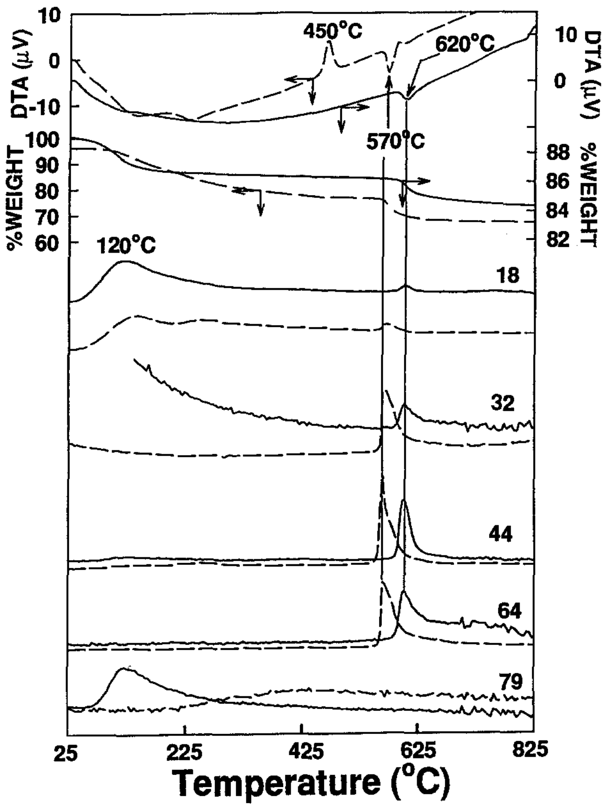

Fig. 2. DTA, TGA and mass spectroscopic traces for mass 18 (H_2O), 32 (O_2), 44 (CO_2), and 64 (SO_2) for a sample of calcined SO_4^{2-}/ZrO_2 with adsorbed pyridine (—) and an uncalcined ZrO_2 impregnated with pyridinium sulfate (– – –).

associated with sulfuric acid. The calcined sample exhibited the desorption of pyridine below 250°C and this was presumably physically adsorbed pyridine; however, significant quantities of pyridine were not desorbed that would correspond to either pyridinium sulfate (fig. 1) or to pyridinium sulfate adsorbed on zirconia. The adsorbed pyridinium sulfate, on the other hand, exhibits the evolution of pyridine in the temperature range of about 225–550°C and the indication of a small, continuous weight loss during this period. Oxides of sulfur are not observed during the temperature ramp from 225 to 550°C. Thus, it is concluded that the adsorption of pyridinium sulfate alters the nature of the decomposition during heating but that pyridine was liberated by thermal decomposition of the salt of the Brønsted acid.

A reviewer has suggested that sulfated zirconia could promote pyridine oligomerization, and then decompose to either coke or a coke-precursor. This possibility cannot be eliminated but if it does occur would also eliminate the desorption of pyridine as a measure of acid strength as reported [29–31] and this agrees with the observation that "desorption" of organics adsorbed on sulfated zirconia involves oxidation/reduction reactions [32].

Another sample that would resemble the zirconia that was impregnated with pyridinium sulfate, which had not been calcined, was also utilized. Thus, sulfate was added to zirconia using sulfuric acid and then dried at 120°C; this sample contained about 3.5 wt% S. The dried sample was placed in the desiccator containing pyridine. During 24 h the sample gained about 30 wt%. The sample lost more than 20 wt% during the 30 min period at room temperature in the TGA/MS instrument. The amount of pyridine evolved plugged the transfer line so that MS data could not be obtained. Thus, a portion of the sample containing pyridine was evacuated at room temperature in a vacuum desiccator for about 18 h. When this sample was heated the exothermic event occurred at about 610°C (table 1; fig. 3). A portion of the sulfated zirconia that had not been exposed to pyridine exhibited an exotherm at about 614°C. Thus, the sulfate present in the 120°C dried sulfated zirconia is present in a form that prohibits it from forming significant amounts of pyridinium sulfate. Pyridine was retained by the sample that had been dried at 120°C. This is documented by the simultaneous evolution of CO_2 and SO_2/SO resulting from complex oxidation/reduction reactions (fig. 3).

The implication of the exotherm temperatures is obvious: for the pyridinium sulfate impregnated sample, the sulfate was prevented from interacting strongly with the zirconia surface, whereas the hydrous zirconia impregnated with sulfuric acid indicated that the sulfate reacted with the zirconia prior to the adsorption of the pyridine. This requires pyridine to be a significantly stronger base than zirconia. During the impregnation with pyridine present, the added sulfuric acid preferentially reacts with pyridine to form pyridinium sulfate rather than reacting with zirconia to form sulfated zirconia. If this conclusion is valid, it is anticipated that the addition of sulfate to a dried zirconia sample using ammonium sulfate will produce a material that resembles supported pyridinium sulfate. The TGA/DTA data in fig. 4 show that this expectation agrees with the experimental data; the exothermic event occurs at 540°C, a temperature that falls between that of an unsulfated zirconia sample (450°C) and one that contains the same amount of sulfate added as sulfuric acid (610°C). The data show that the nitrogen base, either NH_4^+ or pyridinium ion, diminishes the interaction of sulfate with zirconia, and that pyridine is more effective than ammonia in decreasing this interaction. This result is anticipated on the basis of the relative pK_a values for the nitrogen bases.

Table 1
Temperature for the exothermic event during heating zirconia and sulfated zirconia prepared using different salts as the source of the sulfate

Sulfate source	Exotherm temperature (°C)
none	450
pyridinium sulfate	450
$(NH_4)_2SO_4$	540
H_2SO_4, then pyridine	610
H_2SO_4	614

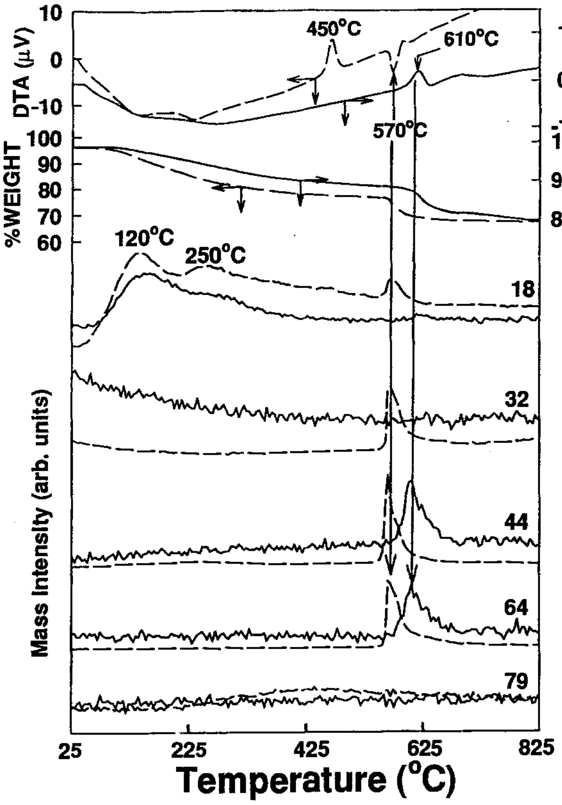

Fig. 3. DTA, TGA and mass spectroscopic traces for mass 18 (H_2O), 32 (O_2), 44 (CO_2), and 64 (SO_2) and 79 (pyridine) for a sample of uncalcined ZrO_2 impregnated with pyridinium sulfate (– – –) and uncalcined SO_4^{2-}/ZrO_2 with adsorbed pyridine (—).

It was speculated that impregnation with sulfuric acid "catalyzed" the partial dehydration of the dried zirconia since all samples, with a sulfate loading varying from 1 to 10 wt%, lost about 4 wt% less water during the thermal analysis than the sulfate free precursor sample did when it was heated using the same conditions [11]. The data in fig. 2 are consistent with this view. Thus, the sample prepared by impregnation with pyridinium sulfate lost more weight as low-temperature water than the sample prepared using sulfuric acid.

The decomposition of the pyridinium sulfate occurred at a much higher temperature when it was impregnated on zirconia than when the pure compound was heated under similar conditions. In addition, the supported pyridinium sulfate did not decompose to desorb significant quantities of pyridine to the gas phase as unsupported pyridinium sulfate did. Instead, the supported pyridinium sulfate undergoes decomposition that begins at about 570°C and corresponds to an oxidation/reduction reaction rather than a decomposition to form pyridine and sulfuric acid. The differences between the decomposition of the supported pyridinium sulfate and the pure compound clearly show that the supported pyridinium sulfate interacts with zirconia; however, the interaction differs from that of the pyridine/sulfated zirconia complex formed when pyridine is adsorbed on a sulfated zirconia. Another significant difference between the samples is shown in fig. 5. During the oxidation/reduction reactions for the zirconia containing pyridinium sulfate, significant amounts of water evolved at 540°C but this is less evident for the other samples pre-

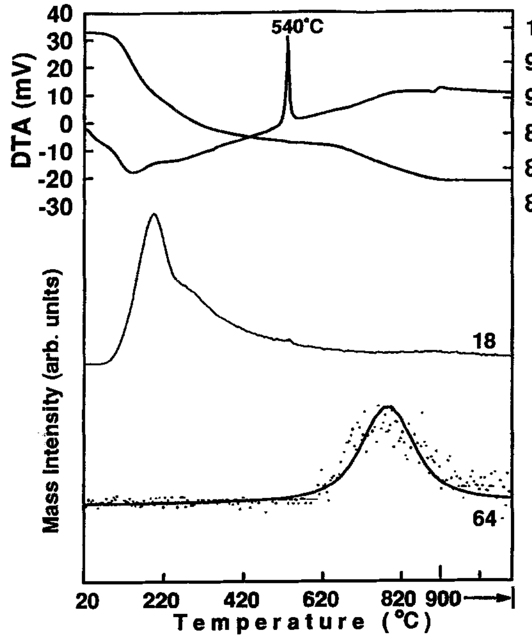

Fig. 4. DTA, TGA and mass spectroscopic traces for mass 18 (H_2O), 48 (SO) and 64 (SO_2) for a sample prepared by impregnating zirconia with ammonium sulfate.

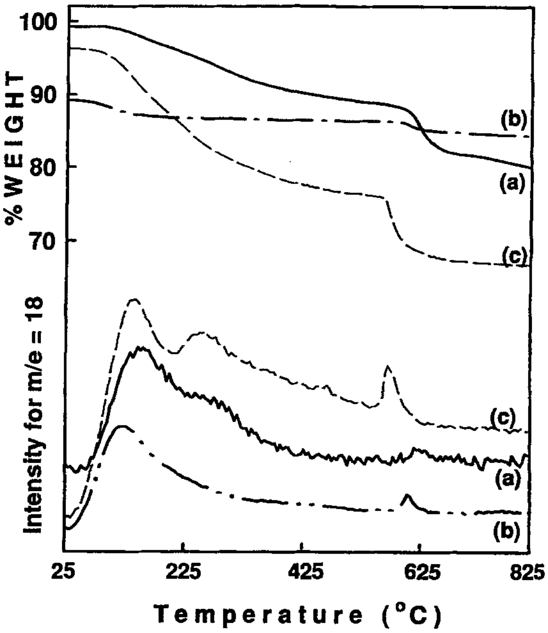

Fig. 5. TGA weight loss curves and mass spectroscopic traces for mass 18 (H_2O) for catalyst precursor samples: (a) SO_4^{2-}/ZrO_2, prepared using H_2SO_4, uncalcined with adsorbed pyridine; (b) SO_4^{2-}/ZrO_2, prepared using H_2SO_4, calcined at 725°C for 2 h, pyridine adsorbed; (c) SO_4^{2-}/ZrO_2, prepared with pyridinium sulfate, uncalcined.

pared by reacting sulfuric acid and zirconia. In this sense, the pyridinium sulfate supported on zirconia resembles the decomposition of pure pyridinium sulfate. In addition, the supported pyridinium sulfate decomposes very sharply over a narrow temperature range, indicative of the decomposition of a common structure. On the other hand, the oxidation/reduction reactions for the material prepared by adsorbing pyridine on sulfated zirconia decomposes over a wider temperature range, indicative of a wide range of chemical structures, each with their own activation energy and reaction rate.

The data suggest the following sequences of reactions for the preparation and activation of the two samples (chemical structures are for illustration purposes; the actual structures may vary from those shown):

(1) Sulfated zirconia with adsorbed pyridine

$$ZrO(OH)_2 \cdot xH_2O + H_2SO_4 \rightarrow ZrOSO_4 \cdot xH_2O + 2H_2O \tag{3}$$

$$ZrOSO_4 \cdot xH_2O + \text{pyridine} \rightarrow ZrOSO_4 \cdot \text{pyridine} \cdot xH_2O \tag{4}$$

$$ZrOSO_4 \cdot \text{pyridine} \cdot xH_2O \xrightarrow[25\text{–}400^\circ C]{\Delta} ZrOSO_4 \cdot \text{pyridine} + xH_2O \tag{5}$$

$$ZrOSO_4 \cdot \text{pyridine} \xrightarrow[\sim 600^\circ C]{} [ZrO(O)_x] + SO + SO_2 + CO_2 + [N] + H_2S \tag{6}$$

$$ZrO(O)_x \xrightarrow[\sim 600^\circ C]{} ZrO_2 + heat + \tfrac{1}{2}(x - 1)O_2 \tag{7}$$

(2) Zirconia with adsorbed pyridinium sulfate

$$ZrO(OH)_2 \cdot xH_2O \cdot (PyH)_2SO_4 \xrightarrow[25\text{–}400^\circ C]{} ZrO_2 \cdot (PyH)_2SO_4 + H_2O \tag{8}$$

$$ZrO_2 \cdot (PyH)_2SO_4 \xrightarrow[450^\circ C]{} ZrO_2 \cdot (PyH)_2SO_4 + \text{heat} \tag{9}$$

$$ZrO_2 \cdot (PyH)_2SO_4 \xrightarrow[540^\circ C]{} ZrO_2 + H_2O + CO_2 + O_2 + SO + SO_2 + [N] \tag{10}$$

Eqs. (4) and (8) are written to indicate possible products of the decomposition, and are not balanced equations (for more details see ref. [11]).

In the "impregnation" with aqueous sulfuric acid, the acid causes dehydration so that, during the 25–400°C heating, the water loss is about 4 wt% less than for a similar unsulfated sample [11], and this is the basis for eq. (3). Following adsorption, and subsequent desorption of pyridine at room temperature, heating to 400°C results in the continuous evolution of water, and not the stepwise evolution expected for decomposition of a specific compound. Thus, the structure $ZrO(OH)_2$ is considered to be an idealized representation of the actual range of structures. Pyridine is not detected in significant quantities during the heating period. Rather, complex oxidation/reduction reactions occur so that the carbon in pyridine evolved as CO_2 and the sulfur evolved both in oxidized (SO, SO_2) and reduced (H_2S) forms. Nitrogen oxides (NO, NO_2) have not been detected nor have significant peaks corresponding to NH_3 derived ions been observed. Thus, the evolved nitrogen, if in fact nitrogen is evolved rather than forming a surface $ZrON_x$ species, has been written as [N] in eqs. (6) and (10). The base strength of pyridine is sufficiently strong to prevent the added H_2SO_4 from reacting with $ZrO(OH)_2 \cdot H_2O$, as in eq. (3); thus, upon heating, the normal exotherm due to loss of surface area and/or crystallization, is observed at 450°C (eq. (9)). The adsorbed pyridinium sulfate interacts with the zirconia so that the decomposition temperature is higher than for unsupported pyridinium sulfate; however, the decomposition occurs with evolution of water just as was observed for the unsupported pyridinium sulfate. In summary, the pyridinium sulfate behaves upon heating as would be expected if it was the salt of a Brønsted acid; however, both the adsorbed pyridinium sulfate and the pyridine on sulfated zirconia do not follow the decomposition pathway expected for the salt of a Brønsted acid.

The properties of the materials obtained by activating the zirconia sulfated using sulfuric acid and pyridinium sulfate are given in table 2. The two samples were prepared to have a similar sulfate content and, following calcination at 650°C, this was found to be the case. Likewise, the crystal phase and the surface areas are similar for the two samples. The two materials were utilized for the conversion of *n*-hexadecane using a microreactor as described earlier [14]. The catalytic activity of the two catalysts were evaluated using *n*-hexadecane as the feedstock in batch microautoclave reactors under the same conditions (150°C for 15 min, 2 g catalyst/4 g feed, and 500 psig H_2). The catalyst made using the sulfuric acid achieved a slightly higher conversion (93 wt%) than that of the catalyst made using the pyridinium sulfate

Table 2
The properties and catalytic activity [a] of samples prepared using sulfuric acid or pyridinium sulfate

	H_2SO_4	Pyridinium sulfate
as-prepared hydrous zirconia		
XRD crystal phase	amorphous	amorphous
surface area (m^2/g)	275	275
sulfur (wt%)	3.05	3.61
activated, 625°C, 2 h in air		
XRD crystal phase	tetragonal	tetragonal
surface area (m^2/g)	121	97
sulfur (wt%)	1.22	1.10
catalytic activity [a]		
total conversion (wt%)	93	76

[a] Conditions as in ref. [14] (microautoclave, 150°C, 15 min, 500 psig hydrogen pressure, hydrocarbon : catalyst = 4 g/2 g).

(76 wt%). In order to evaluate the selectivity differences (i.e., isomerization and cracking yields, which are a function of the total conversion of *n*-hexadecane), the catalyst prepared using sulfuric acid was run using the same conditions except a lower pressure was used (300 psig) to obtain a lower conversion comparable to the catalyst prepared with pyridinium sulfate. At these comparable conversions (H_2SO_4 78 wt%; Py-sulfate 76 wt%), no significant difference was noted for the isomerization yields (H_2SO_4 19 wt%; Py-sulfate 22 wt%) and cracking yields (H_2SO_4 60 wt%; Py-sulfate 54 wt%). The data make it clear that adding sulfate as pyridinium sulfate deposits sulfur on the solid following activation in about the same amount as when sulfuric acid is used. Both methods produce an active catalyst.

4. Conclusions

The present data demonstrate that sulfate, added to zirconia using various salts, interacts with zirconia to different extents. This is clearly shown by the different temperatures for the exothermic event that accompanies loss of surface area. This difference is also indicated by the differences in the temperature at which the oxidation/reduction reactions occur to liberate oxides of sulfur and carbon. Finally, the differences in the behavior of the two catalysts – one prepared by precipitating pyridinium sulfate and the other by adsorbing pyridine on sulfated zirconia – make it difficult to consider the latter catalyst to possess Brønsted acid sites. The data clearly show that the desorption of pyridine during TPD represents oxidation/reduction reactions, and not the decomposition of a salt of a Brønsted acid. Both catalysts have similar catalytic activity and this suggests, but does not prove, that Brønsted sites are not responsible for the catalytic activity.

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