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TiO_2 with a high sulfate content—thermogravimetric analysis, determination of acid sites by infrared spectroscopy and catalytic activity

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Abstract

Sulfated metal oxides have a very high acidity, being considered by some as superacids, although it is still a controversial matter. There has been considerable investigation into sulfated ZrO_2 in recent years, but sulfated TiO_2 has been relatively neglected. There is evidence that the Brönsted acid sites would be responsible for the high levels of acidity and catalytic activity in sulfated ZrO_2, since these sites would be present in samples with higher sulfate content. In order to verify whether for sulfated TiO_2, a high level of acidity also occurs in samples with a higher sulfate content, samples were prepared with elevated levels of sulfate. Characterization was carried out through thermogravimetric analysis, determination of acid sites by infrared spectroscopy, through adsorption of pyridine and measurement of the catalytic activity in the isomerization reaction of *n*-hexane. It was verified that samples with elevated sulfate content were actually those which had Brönsted acid sites and a higher catalytic activity in the isomerization reation of *n*-hexane. It was also verified that the sulfate loss in the thermogravimetric analysis occurred at different temperatures, depending on the sulfate content of the sample.

Keywords: TiO_2; Acid sites; Infrared spectroscopy

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1. Introduction

Superacids are an important class of catalyst, since they allow many reactions to occur at temperatures lower than those with conventional catalysts [1]. The majority of superacids utilized as catalysts are liquids, and this presents many problems, such as the difficulty in separating the reaction mixture, its corrosiveness and the fact that it is a material whose disposal causes environmental damage. A solid superacid catalyst could solve many of these problems [2].

Sulfated metal oxides, classified by some as superacids, were reported around 20 years ago by Hino and Arata [3], and Hino et al. [4], who studied sulfated ZrO_2 and TiO_2, with which it was possible to carry out isomerization of *n*-butane at ambient temperature. The isomerization of alkanes at ambient temperature is of interest to the petroleum industry, since branched alkanes are important in the generation of products which increase the octane number of gasoline. Reaction at ambient temperature represents not only a saving of energy, as it also favors, thermodynamically,

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branched products [5]. Along with sulfated TiO_2 and ZrO_2, other sulfated metal oxides have also been investigated, such as Fe_2O_3, HfO_2, etc. [6].

In the sulfated metal oxides there are as many Lewis acid sites present as there are Brönsted acid sites. The superacidity of these materials is attributed to the Brönsted acid sites, created or already existing, whose acidity is increased by the presence of neighboring, strong Lewis acid sites. The strength of these Lewis acid sites is, in turn, due to the inductive effect exerted by the sulfate on the metal cation, which becomes more electron deficient. The presence of the Lewis and Brönsted acid sites in the sulfated metal oxides is defended by some authors, such as Komarov and Sinilo [7] and Nascimento et al. [8], while other authors, such as Jin et al. [9] and Bensitel et al. [10], report the existence of very strong Lewis acid sites only, in sulfated ZrO_2.

Many studies demonstrate that Brönsted acidity is important for the catalytic activity of sulfated ZrO_2 [11,12]. The formation of Brönsted acid sites would be favored in samples with a higher sulfate content [11–14], but other factors such as the degree of hydration, the preparation method and the activation temperature are also important.

The structure of the sulfate bound to the metal oxide is also a subject of investigation in the literature. Jin et al. [9] propose that the sulfate would be coordinated to the metal in a chelated form (two of the oxygen atoms of the sulfate would be bound to one metal atom). On the other hand, Bensitel et al. [10] and Waqif et al. [13] propose a structure in which the sulfate would be bound to the metal through three oxygen atoms, for samples with lower sulfate contents (I). For higher sulfate contents, the formation would be, according to the authors, a species with polynuclear sulfates (II) (polysulfates, S_2O_7, etc.). The two structures are shown below. Morterra et al. [12], who agree with the structures of Bensitel et al. and Waqif et al. verified that samples with polynuclear sulfates are the origin of the higher proportion of Brönsted acid sites in relation to Lewis acid sites (Fig. 1).

In order to verify whether for sulfated TiO_2, an elevated acidity also occurs in samples with a higher sulfate content, samples with high and low sulfate contents were prepared in this study. The samples were characterized by thermogravimetric analysis and the acid sites characterized by infrared spectroscopy, by adsorption of pyridine.

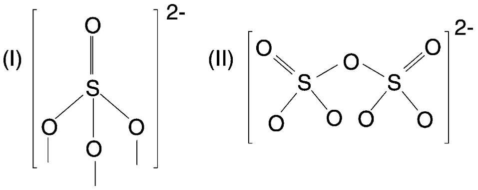

Fig. 1. Structures of sulfate bound to metal oxide. (I) Samples of lower sulfate content and (II) samples with higher sulfate content.

2. Experimental

2.1. Preparation of sulfated TiO_2

The TiO_2 was prepared by the sol–gel method, starting with the hydrolysis of titanium isopropoxide (Ti(*i*PrO)$_4$), based on the work by Rodriguez et al. [15]. The hydrolysis was carried out in an acid medium with a proportion of HNO_3 to Ti(*i*PrO)$_4$ of 0.2/1 mol/mol. The Ti(*i*PrO)$_4$ in anhydrous ethanol, contained in an addition funnel, was added slowly to a round bottom flask with deionized water, maintained in a bath at around 70 °C. After the addition of Ti(*i*PrO)$_4$, the resulting mixture was left under reflux for 1 h. A solution of 10% HNO_3 (v/v) was added to the flask, leaving it to reflux for 1 h. The alcohols (ethanol and isopropanol) were eliminated, by heating the flask. The mixture was left under reflux for 18 h. Afterwards, the excess water was removed by heating. The resulting gel was transferred to a Petri dish, in a desiccator, under vacuum, to eliminate the residual water. The resulting material was heated in an oven at 150 °C. The sulfation was carried out with H_2SO_4, leaving the recently prepared TiO_2 in a solution of H_2SO_4, under agitation, varying the concentration of the H_2SO_4 solution between 1 and 7 mol/l. After filtration, the resulting solid was heated to 200 °C.

2.2. Thermogravimetric analysis

The thermogravimetric analyses were carried out on a Shimadzu TGA-50 instrument, under a nitrogen atmosphere, within a temperature range of 25–900 °C, with a heating velocity of 10 °C/min.

2.3. Infrared spectroscopy of pyridine adsorbed onto sulfated TiO_2

The diffuse reflection spectra of pyridine adsorbed onto sulfated TiO_2 were obtained with a FTIR Bomem DA3 spectrometer, in a Spectra-Tech catalytic cell, which allows heating, creation of a vacuum and the introduction of the vapor of the desired substance.

The TiO_2, in the form of a powder, slightly compacted, was previously heated to 400 °C in the catalytic cell with a nitrogen flow for 2 h then cooled to 150 °C; creating a vacuum, and again cooled to 30 °C. The pyridine vapor was introduced into the cell at 30 °C, leaving the entrance valve open for around 3 m, later a vacuum was created to remove the excess pyridine. The temperature was increased from 30 to 150 and 250 °C (or 300 °C), with spectra being registered at each temperature under vacuum.

2.4. Catalytic tests: isomerization of n-hexane

The isomerization of *n*-hexane was chosen to test the catalytic activity of sulfated TiO_2, since such a reaction occurs only with catalysts of high acidity. The reactions were studied with the reagent in the gaseous phase, in a continuous flow reactor, utilizing nitrogen as the diluent gas, the reactor being attached to a chromatograph (Shimadzu GC-14B), with a CBP1 column and a flame ionization detector. The tubular reactor was made of glass and had a sinterized glass disc, on which the solid catalyst was placed. The mass of catalyst utilized was 200 mg and the relation w/F relation (where w is the mass of the catalyst in grams and F is the flow of *n*-hexane in moles per minute) was 2.3×10^4 g min/mol. The catalyst activation was regulated: the catalyst was activated in the reactor at 400 °C, in air, for 3 h, and then cooled in nitrogen until the reaction temperature was reached.

3. Results and discussion

3.1. Thermogravimetric analysis

In Figs. 2 and 3 the thermograms and first derivative curves can be seen for two samples of TiO_2, (I) and (II) with sulfate contents of 2.8 and 17.5%, respectively. Below 200 °C a loss of mass can be seen due

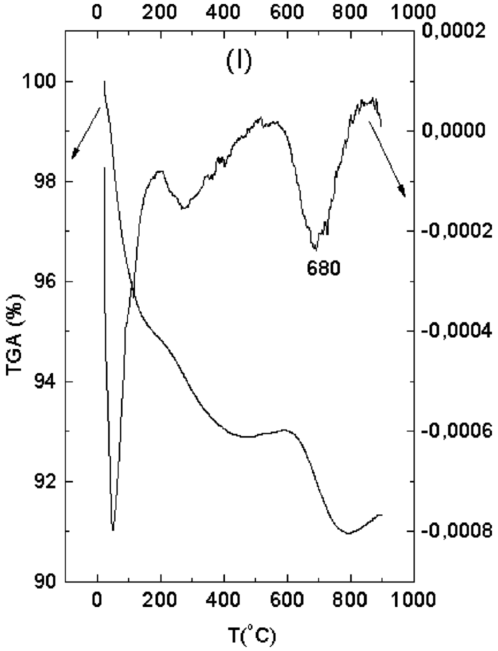

Fig. 2. Thermogram and first derivative curve of sulfated TiO_2 (sample I), with a sulfate content of 2.8%.

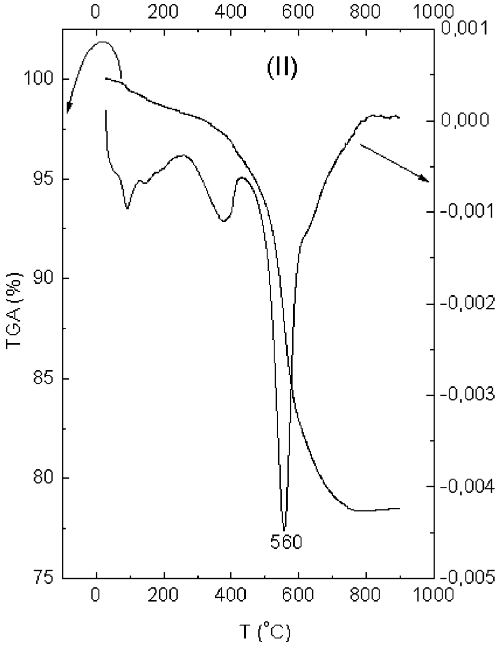

Fig. 3. Thermogram and first derivative curve of sulfated TiO_2 (sample II), with a sulfate content of 17.5%.

to the removal of water (in hydration or structural), at 250–300 °C a loss of mass ascribed to nitrate (used in the synthesis of titanium dioxide) was observed, while in the region of 450–750 °C there is a loss of mass due to the sulfate bound to the oxide. The loss of sulfate in sample I occurred at a higher temperature (a peak in the first derivative curve at 680 °C) than in sample II (peak at 560 °C). Looking more closely at the first derivative curve of sample II, a shoulder can be seen at around 630 °C. The presence of distinct regions of sulfate loss have already been reported in studies by Ward and Ko [16], who prepared sulfated ZrO_2 with high and low sulfate contents.

3.2. Infrared spectra of pyridine adsorbed onto sulfated TiO_2

Pyridine adsorbed onto acid sites has infrared frequencies characteristic of the Lewis or the Brönsted acid sites [17], whose values reported in the literature, along with the values for liquid pyridine, are given in Table 1.

In Figs. 4 and 5 the infrared spectra of pyridine adsorbed onto sulfated TiO_2 (samples I and II, respectively) at the temperatures indicated, along with the spectrum of sulfated TiO_2 before the introduction of pyridine, obtained in the catalytic cell, are shown.

Table 1
Infrared frequencies (cm^{-1}) of liquid pyridine and pyridine adsorbed at Lewis and Brönsted acid sites [17]

Neat pyridine	Coordinated pyridine (Lewis acid site)	Pyridinium ion (Brönsted acid site)
1439	1447–1460	
1482	1488–1503	1485–1500
		1540
1572	1580 (ca.)	
1583	1600–1633	1640 (ca.)

For sample I, the frequencies at 1445, 1490 and 1607 cm^{-1} are characteristic of a Lewis acid site, while the frequencies at 1439, 1482, 1580 and 1597 cm^{-1} which appear only at lower temperatures are close to the frequencies for liquid pyridine, these being attributed to physically adsorbed pyridine. The bands at 1490 and 1540 cm^{-1} are assigned to Brönsted acid sites.

For sample II, the frequencies at 1489, 1536–1538 and 1634–1636 cm^{-1} are characteristic of a Brönsted acid site, while the frequencies at 1447, 1489 and 1608–1611 cm^{-1} are characteristic of a Lewis acid site. It can be verified that the frequencies for pyridine at Lewis and Brönsted acid sites appear at all temperatures, only changing in relative intensity between the bands. The acidity of these sites is very high, since the pyridine is not desorbed even at high temperatures.

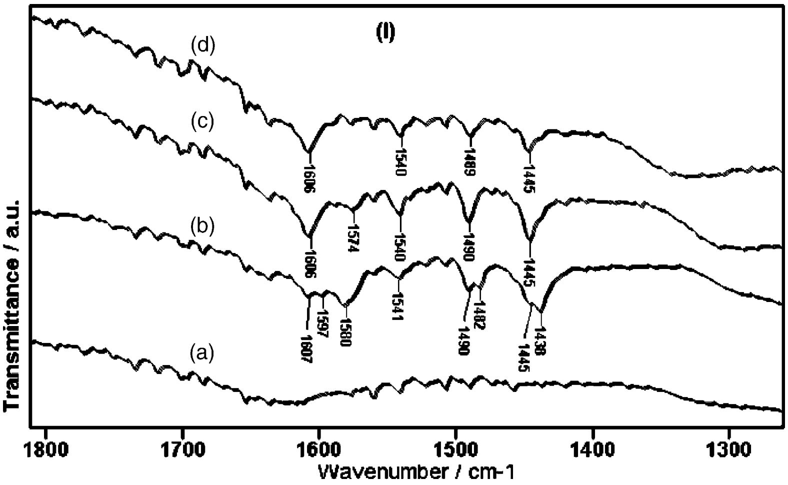

Fig. 4. Infrared spectra of sulfated TiO_2 (sample I): (a) under a nitrogen atmosphere; and after the introduction of pyridine at: (b) 20 °C, (c) 150 °C and (d) 250 °C in the catalytic cell.

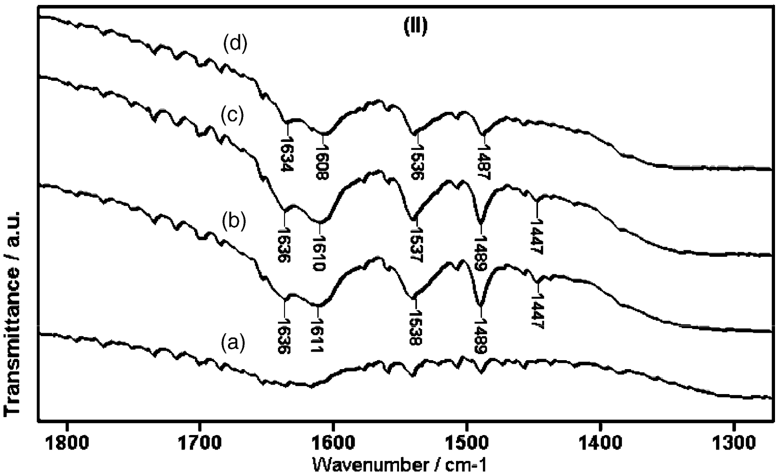

Fig. 5. Infrared spectra of sulfated TiO_2 (sample II): (a) under a nitrogen atmosphere; and after the introduction of pyridine at: (b) 30 °C, (c) 150 °C and (d) 300 °C in the catalytic cell.

On comparing samples I and II, sample II has a proportion of Brönsted acid sites/Lewis acid sites, measured by 1490/1445 cm^{-1} relative intensities, much higher than sample I, which can be explained by its higher sulfate content (17.5%) in relation to sample I (2.8%). Both samples have Lewis acid sites. In the catalytic tests (described above) sample II showed very high catalytic activity in the isomerization reaction of *n*-hexane, indicating that the higher concentration of Brönsted acid sites could be responsible for the activity of the reactions which require high acidity, and not the Lewis acid sites (Table 2).

3.3. Catalytic tests: isomerization reaction of *n*-hexane

The catalytic test was carried out at 100 °C with a w/F relation (where w is the mass of the catalyst in grams and F is the flow of *n*-hexane in moles per minute) of 2.3×10^4 g min/mol. Sample I showed a very low conversion (2% for a reaction time of 20 min), while sample II showed an extremely high conversion (86.6% in 25 min). Even after a relatively long time (180 min) the catalytic activity of sample II was still considerably high (around 30%, as can be seen in the figure below (Fig. 6)). Although reaction products are due to isomerization and cracking, conversion due to isomerization was about 25%, a value that is considerably high.

Therefore, sample II, with a higher sulfate content and which had higher proportion of Brönsted acid sites was the most active in the isomerization reaction of *n*-hexane. Sample I, which had less Brönsted acid sites, compared to sample II, showed almost no catalytic activity.

Table 2
Infrared frequencies for pyridine adsorbed onto sulfated TiO_2 (samples I and II) at the temperatures indicated

Sample	T (°C)	Wavenumber (cm^{-1})								
I	20	1439	1443	1482	1490	1540	1580	1597	1607	
	150		1445		1490	1540	1574		1606	
	250		1445		1490	1540			1606	
II	30		1447		1489	1538			1611	1636
	150		1447		1489	1537			1610	1636
	300				1487	1535			1608	1634

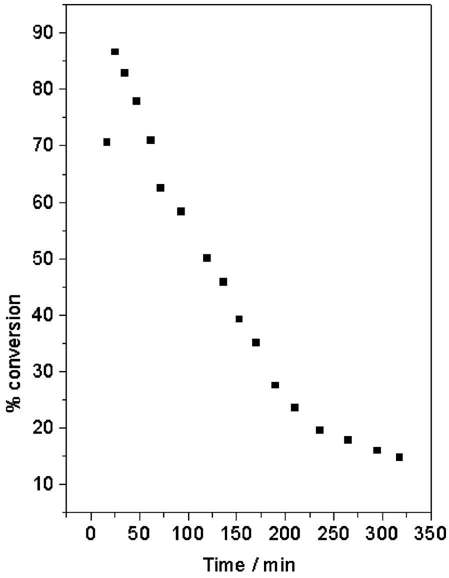

Fig. 6. Graph showing percentage of conversion of *n*-hexane in the presence of sulfated TiO_2 (sample II). $w/F = 2.3 \times 10^4$ g min/mol.

4. Conclusions

Through the thermogravimetric analysis it was verified that sulfated TiO_2 with a higher sulfate content (sample II) showed a peak in the loss of sulfate at a lower temperature than the sample with a lower sulfate content (sample I).

Through the infrared spectra of pyridine adsorbed onto sulfated TiO_2, it was determined that sample II has a relation of Brönsted acid sites/Lewis acid sites higher than sample I.

Sample II showed a very high catalytic activity in the isomerization reaction of *n*-hexane, which was not observed in the case of sample I. Analysis of these results indicates that the higher proportion of Brönsted acid sites in samples with higher sulfate contents is the factor which determines the catalytic activity of sulfated TiO_2, for the reactions which require sites with high acidity. These results agree with those observed by other authors investigating sulfated ZrO_2 [12,16].

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