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Platinum on a sulfated zirconia surface: effects and interactions

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The effect of the presence of platinum on the surface of SO_4^{2-}–ZrO_2 was studied. The addition of platinum neither produces significant changes in the textural properties of SO_4^{2-}–ZrO_2 nor interferes in the process of crystalline structure formation. After calcining, the presence of platinum allows the retention of a higher sulfur concentration. When calcination takes place at 600°C, SO_4^{2-}–ZrO_2, with or without platinum, shows S^{6+} species on the surface, but only when platinum is present does a small amount of S^0 species appear. At the same calcination temperature, platinum is found in the metallic state. Therefore, the S^0 species could be associated with platinum by modifying its metallic properties.

Keywords: solid superacids; platinum sulfated-zirconia; surface characterization; superficial species

1. Introduction

The isomerization of linear to branched alkanes plays an important role as an alternative way to improve the octane number in reformulated gasolines. Solid superacids are attracting considerable interest as potential catalysts for that reaction. Among solid superacids, the sulfate-promoted zirconia system is being widely studied. A complete review [1] including different topics related to this material was published last year, and it is an adequate initial point for the following analysis.

It is well known that zirconium precursor and synthesis conditions play an important role in the crystalline structure obtained by calcining [2]. Furthermore, the treatment of zirconium hydroxide with sulfuric acid solution stabilizes the tetragonal structure [3], although some authors [4] have obtained a microcrystalline monoclinic structure by using other synthesis techniques. SO_4^{2-}–ZrO_2 has been widely characterized; data about textural properties and acidity, XPS measurements and, more recently, abundant information using FTIR technique [5] have been published. Parameters reported allow us to consider that minor differences can appear after calcination, the previous history of the material being important. An adequate knowledge of the surface material is essential to understand its behavior.

The catalytic behavior of SO_4^{2-}–ZrO_2 on alkane isomerization shows a sharp deactivation [6], platinum loadings about 0.3–0.5% are added to improve the stability [7,8]. The behavior of the Pt/SO_4^{2-}–ZrO_2 surface in particular, the lack of hydrogen or carbon monoxide chemisorption, raised an interest in studying the platinum state on the surface. Different opinions were initially given considering that platinum was either present as a metal [9] or in a cationic state [10]; more recently, both states were considered to be present on the surface [11,12].

Another issue over which there are several explanations is the effect of platinum on the catalytic behavior. Some authors [13] consider that platinum dissociates hydrogen which spills over the surface forming H^+ and it participates in the reaction sequence, thus affecting activity and selectivity; meanwhile, others [14] postulate that platinum could participate in a bifunctional mechanism. However, it must be mentioned that a complete characterization of the Pt/SO_4^{2-}–ZrO_2 surface, necessary to understand whether the presence of platinum produces changes in the material surface and/or in its properties, is not available in the literature.

The presence of platinum on the surface of SO_4^{2-}–ZrO_2, in a concentration usually used on alkane isomerization catalysts, and its effect on the textural properties and the possible interactions with sulfur species, was studied.

2. Experimental

2.1. Catalyst preparation

Zirconium hydroxide, $Zr(OH)_4$, was prepared by starting from zirconium tetrachloride ($ZrCl_4$, Fluka AG, > 98%) using water as the reaction medium in a weight ratio $ZrCl_4 : H_2O$ of 1 : 6; the technique used has been previously described [6]. The $Zr(OH)_4$ hydrogel was dried at 110°C for 12 h. This material was sulfated by dipping in a 0.5 M sulfuric acid solution without stirring for 1 h and with 15 ml g^{-1} acid solution/solid ratio. Then, the sample was filtered and dried at 110°C for 12 h. This sulfated sample having 0.28 ml g^{-1} pore volume was impregnated by the incipient wetness technique using $H_2PtCl_6 \cdot 6H_2O$ aqueous solutions, and then dried at 110°C for 12 h.

2.2. Catalyst characterization

The catalyst texture was measured using a Micromeritics Accusorb 2100 equipment. From the nitrogen adsorption isothermal data, the BET specific surface area, cumulative pore volume (of pores up to 30 nm diameter) and Wheeler mean pore diameter, were calculated.

Sulfur concentration was measured by combustion in a LECO CS-244 analyzer, and platinum by inductively coupled plasma atomic emission spectrometry (ICPAES) using a Perkin-Elmer ICP/5500 plasma spectrometer.

The crystalline structure of samples calcined at 600°C for 3 h was characterized by X-ray diffraction (XRD) using a Rich-Seifert Iso-Debyeflex 2002 diffractometer. Cu Kα_1 radiation filtered with nickel was used, and the diffraction spectrum range was 25–65°.

The surface species reducibility was determined by temperature-programmed reduction (TPR) using an Ohkura TP 2002S equipped with a thermal conductivity detector. Samples were calcined in situ in an oxygen stream at 600°C during 3 h; then, they were cooled to room temperature under an argon flow. Samples were heated from room temperature up to 800°C, at 10°C min^{-1}, in a gas stream of 1.8% hydrogen in argon, while the signal was being recorded. The calibration was performed with argon pulses.

The superficial electronic state of sulfur and platinum was measured by X-ray photoelectron spectroscopy (XPS) using a Shimadzu ESCA 750 electron spectrometer coupled to a Shimadzu ESCAPAC 760 data system. The C 1s line was taken as an internal standard at 285.0 eV.

3. Results and discussion

Textural properties and the content of sulfur and platinum in samples calcined at 600°C are shown in table 1. The addition of sulfate over zirconium hydroxide allows the retention of a 36.7% higher specific surface area and a 6.3% higher pore volume compared with those corresponding to the ZrO_2 sample. These results can be understood by considering that, during calcination, the sulfate present on the surface preserves the low diameter pores of zirconium hydroxide. This effect of sulfate is increased in the platinum-containing sample; the specific surface area is 47.8% higher and the pore volume 10.0% higher than the ones corresponding to ZrO_2. Nevertheless, the presence of platinum on the surface of zirconia with or without sulfate does not evidently modify textural properties, as previously reported [8]. The previous behavior could be associated with higher sulfur concentrations that occurred in platinum-containing catalysts after calcination, thus resulting in a higher specific surface area and a higher pore volume. Considering the crystalline structure, also shown in table 1, the addition of sulfate stabilizes the tetragonal structure as previously reported [3], whereas the presence of platinum does not interfere in this process as also reported [15].

Table 2 shows the sulfur content of samples with and without platinum calcined at different temperatures. A similar qualitative behavior is observed: at calcination temperatures below 500°C the sulfur concentration remains practically constant, being 2.0 and 3.2% for samples without and with platinum, respectively. At above 500°C, the higher the calcination temperature, the lower the sulfur content on the surface results. Over the entire calcination temperature range, the platinum-containing sample retains a higher sulfur concentration than the one without platinum, as shown in table 1.

Fig. 1 displays TPR profiles of sulfate promoted zirconia with and without platinum calcined at 600°C. The sample without platinum presents only one peak with its maximum at about 740°C, assigned to the reduction of S^{6+} species. The platinum-containing sample shows two peaks: the smallest one centered at about 350°C, and the largest one with its maximum at about 560°C and assigned to the S^{6+} species reduction. The ratio between the total area summing both peaks in the Pt/SO_4^{2-}–ZrO_2 profile and the area of the single peak in the SO_4^{2-}–ZrO_2 profile is 1.807, whereas the ratio between the sulfur content of both Pt/SO_4^{2-}–ZrO_2 and SO_4^{2-}–ZrO_2 is 1.818; both ratios practically showing the same value. The peak assigned to the reduction of S^{6+} species in the platinum-containing sample is 74.7% larger than the one corresponding to SO_4^{2-}–ZrO_2. Considering our results, the presence of platinum on SO_4^{2-}–ZrO_2 catalyzes the reduction of superficial sulfur species promoting the shift of

Table 1
Textural properties, sulfur and platinum content, and crystalline structure of samples calcined at 600°C

Sample	S_g ($m^2 g^{-1}$)	V_g ($cm^3 g^{-1}$)	$r_{Wheeler}$ (nm)	S (wt%)	Pt (wt%)	Crystalline structure [a]
ZrO_2	90	0.160	3.56	–	–	M + T
SO_4^{2-}–ZrO_2	123	0.170	2.76	1.1	–	T
Pt/SO_4^{2-}–ZrO_2	133	0.176	2.65	2.0	0.38	T

[a] M: monoclinic; T: tetragonal.

Table 2
Sulfur content of samples with and without platinum calcined at different temperatures

Sample	Calcination temperature (°C)						
	400	480	500	530	550	600	635
SO_4^{2-}–ZrO_2	1.9	2.0	1.9	1.7	1.2	1.1	0.7
Pt/SO_4^{2-}–ZrO_2	3.2	3.2	3.1	2.6	2.3	2.0	1.2

the S^{6+} reduction peak to lower temperatures, and allows the retention of a higher sulfur content as S^{6+} species on the surface. This last subject is being investigated in order to understand how platinum allows that behavior. The TPR profile of Pt/SO_4^{2-}–ZrO_2 shows another peak which can be attributed to a new sulfur species reduced at a lower temperature than that corresponding to S^{6+} species reduction; the area of the smallest peak being about 3.3% referred to the area of the peak assigned to S^{6+} species. The hydrogen consumption peak corresponding to platinum reduction is not present in the TPR profile of Pt/SO_4^{2-}–ZrO_2 but it appears, centered at about 200°C, in the TPR profile of the non-calcined sample. This behavior is related to the effect of the calcination step on the platinum state, even though there are different opinions [9,10,12] about this subject.

Table 3 shows XPS results for samples with and without platinum calcined at 600°C. In the S 2p region, SO_4^{2-}–ZrO_2 presents only one peak at 169.0 eV assigned to S^{6+} species, in agreement with TPR results. Pt/SO_4^{2-}–ZrO_2 shows the main peak at 169.1 eV corresponding to S^{6+} species, and another peak, the smallest one, centered at about 165.1 eV which could be assigned to S^0 species [16]. The area of S^0 species peak is about 3.9% referred to the one corresponding to S^{6+} species peak, and it can be seen in XPS spectra previously reported [15]. The S^0 species identified by XPS could correspond to the species reduced at a lower temperature than the S^{6+} species reduction, as shown in the TPR profile. Table 3 includes the Pt 4f region. Two peaks can be seen at 71.2 and 74.5 eV, respectively, corresponding to the $4f_{7/2}$ and $4f_{5/2}$ doublet, in agreement with the 3.3 eV reported as the difference between both signals and which may be assigned to Pt^0. These results indicate that metal platinum appears on the material surface after calcination. It could explain previous results where calcined samples, with or without reduction pretreatment, showed the same catalytic behavior [15]. Probably, the presence of Pt^{4+} reported by other authors [11,12] could be associated to the higher platinum loading used in such studies.

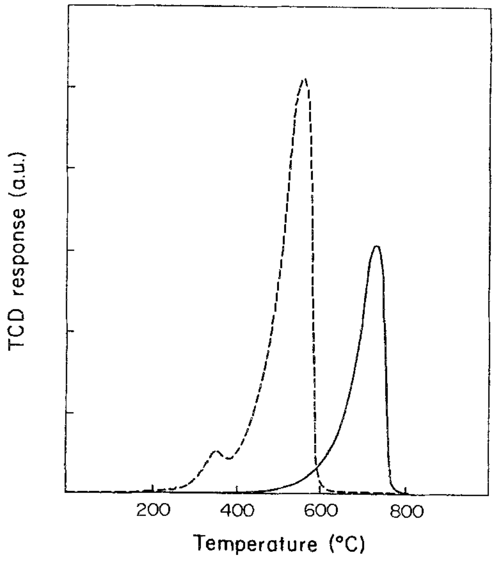

Fig. 1. TPR profile of samples calcined at 600°C. SO_4^{2-}–ZrO_2: solid line; Pt/SO_4^{2-}–ZrO_2: dashed line.

Considering the area of peaks assigned to S^{6+} and S^0 species in both XPS spectrum and TPR profile of Pt/SO_4^{2-}–ZrO_2, the S^0 amount is similar to that of platinum. In this way, we could think that S^0 species are directly related to platinum, and it allows us to explain the no hydrogen chemisorption shown by the metal, as previously reported [15]. A sample of Pt/SO_4^{2-}–ZrO_2 was submitted to TPR conditions up to 450°C at which the small peak assigned to S^0 species disappears; then it does not chemisorb hydrogen. Consequently, another effect, probably an SMSI state favored by a high platinum dispersion, could be present. Nevertheless, reduction at a high temperature is not usually found as a pretreatment in alkane isomerization reactions, S^0 species being present on the surface.

4. Conclusions

The addition of platinum does not significantly modify textural properties of SO_4^{2-}–ZrO_2 and does not interfere in the process of crystalline structure formation. After calcination, the presence of platinum on SO_4^{2-}–ZrO_2 allows the retention of a higher sulfur concentration on the surface, being the behavior with calcination temperature qualitatively similar to the one shown by SO_4^{2-}–ZrO_2. By calcining at 600°C, platinum is found in the metallic state on the SO_4^{2-}–ZrO_2 surface. After that calcination, Pt/SO_4^{2-}–ZrO_2 presents mainly S^{6+} species on the surface (the only one present on SO_4^{2-}–ZrO_2) but a small amount of S^0 species, which could be associated to platinum modifying its metallic properties, also appears.

Table 3
Binding energy in the XPS regions of S 2p and Pt 4f of sulfated samples with and without platinum calcined at 600° C

Sample	S 2p region		Pt 4f region			
	BE (eV)	FWHM (eV)	Pt $4f_{5/2}$ (eV)	FWHM (eV)	Pt $4f_{7/2}$ (eV)	FWHM (eV)
SO_4^{2-}–ZrO_2	169.0	1.9	–		–	
Pt/SO_4^{2-}–ZrO_2	169.1	2.1	74.5	2.0	71.2	1.4
	165.1	1.0				

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