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CHARACTERIZATION OF SULFATED ZIRCONIAS BY DTA-TG AND DRIFT SPECTROSCOPY

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Abstract

Sulfated zirconias were prepared either by impregnation of zirconia with sulfuric acid or by a one step sol gel process by using different solvents. Solids prepared under closely similar conditions in different solvents show different amounts of sulfur and surface areas, thus demonstrating that the crystallization is different. Clear differences occur in the DTA-DTG curves with the appearance of a composite peak for the sol-gel catalysts, whereas the solid obtained by the classical two-step technique shows only one peak. The number of acid sites of these samples is changed by a factor of 3 depending on the preparation. Two types of hydroxyls are observed by infrared spectroscopy: one with bands at 3640 and 3585 cm^{-1}, associated with protons of moderate acidity, and a second at about 3300 cm^{-1} able to exchange D with C_6D_6. Moreover, the infrared band of sulfates also contains two components: one at 1405 cm^{-1} more intense for the most acidic solids and a second one at 1380 cm^{-1}. After activation, these solids are as active as zeolite beta for the acylation of anisole with acetic anhydride.

Keywords: acidity, isotopic exchange, sol-gel, sulfated zirconia, thermal analysis

Introduction

Sulfated zirconia is attractive for the substitution of liquid acids since it is believed to be a strong solid acid, active for the isomerisation of paraffins [1–5] and naphtenes [6] at low temperature, acylation of aromatics [7], as well as for the elimination of NO_x in an oxidizing atmosphere [8]. There are now several reports showing that its acid properties can be modified by changing the preparation conditions, in particular by using a one-step sol-gel method [9–12]. Sol-gel techniques are expected to be sensitive to the type of solvent, and we attempted to investigate the solvent effect in the synthesis of sulfated zirconias. The identification of the acid sites is still a matter of debate. Sulfated zirconia exhibits both Lewis and Brönsted acidity, and synergy between both centers has been postulated. The description of the sulfated species at the surface is also controversial: many authors relate the strong acid

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sites to disulfates, but adsorbed sulfuric acid has also been proposed. Another problem is the discrepancies concerning the determination of the acid strength with different probes: weak bases such as CO or benzene interact only with the stronger acid sites, whereas acetonitrile, ammonia or pyridine, being stronger bases, probe weaker sites as well. From infrared studies of the adsorption of different bases, the acidity of sulfated zirconia can be found comparable to that of CsHX or of HY zeolites. It is usually believed that catalytic activity is related to the stronger acids, and benzene was used as probe of acidity in order to magnify the contribution of strong acidity.

Experimental

Catalysts preparation

The alkoxide precursor for the sol-gel preparations was zirconium *n*-propoxide ($Zr(OC_3H_7)_4$, 70 wt% in *n*-propanol, Aldrich) and the solvent was *n*-propanol (99% purity, EDS). When the hydrolysis is performed in acid medium, the addition of sulfuric acid leads in one step to sulfate alcogel, which, after drying, gives the sulfated zirconia sample. Following this procedure two methods are available. On the one hand sulfuric acid is added to the solution of zirconium alkoxide in *n*-propanol (nP) and stirred for a given pre-hydrolysis period; water is then added drop-wise to complete hydrolysis. On the other hand an aqueous solution of sulfuric acid is added dropwise into the mixture of zirconium alkoxide and *n*-propanol. These two types of samples are respectively denominated ZR7 and ZR5. When the hydrolysis is performed in neutral medium by slow addition of water alone, a zirconia aerogel is obtained. After drying it is sulfated by impregnation with sulfuric acid. This sample will later be denominated ZR2. The detailed procedures for preparing ZR2, ZR5 and ZR7 are given below.

ZR2: in one beaker, 20 cm^3 of zirconium *n*-propoxide (0.045 mol) was mixed with 26.6 cm^3 of *n*-propanol (0.348 mol) and stirred with a magnetic stir bar. Then, 3.2 cm^3 of water were added dropwise in order to carry out the hydrolysis and gelation of zirconium *n*-propoxide. Under our reaction conditions, the time of water addition corresponds to the gelation time (the addition of hydrolysis water takes about 5 min, after that it was impossible to continue the stirring). The gel is aged for one hour at room temperature, it was then placed into an oil-bath, at 80°C, to remove the alcohol. The solid was then dried at 120°C for 12 h. For the sulfation, the $Zr(OH)_4$ precursor was suspended into a 0.5 M H_2SO_4 solution (15 cm^3 of solution per 1 g of dried solid). The mixture was stirred for 1 h, then filtered and dried overnight at 120°C. Finally, the solid was calcined at 650°C for 4 h under flowing air (8 $dm^3\,h^{-1}$) in a quartz tube inside a tubular furnace.

ZR5(nP): 0.51 cm^3 of sulfuric acid (94–96% purity, EDS) is mixed with the hydrolysis water (3.2 cm^3) and then slowly added at room temperature under vigorous stirring to the mixture of 20 cm^3 of zirconium *n*-propoxide and 26.6 cm^3 (0.35 mol) of *n*-propanol. After gelation is complete, which corresponds to the time required to add the acid solution, the gel is aged for one hour at room temperature. Then it is heated at 80°C for 18 h to remove the alcohol. The solid is then dried at 120°C for

12 h. Finally, the solid was calcined at 625°C for 4 h under flowing air (8 $dm^3 h^{-1}$) in a quartz tube inside a tubular furnace.

ZR7(nP): in one beaker, 0.51 cm^3 of sulfuric acid is added to the mixture of 20 cm^3 of $Zr(OC_3H_7)_4$ and 26.6 cm^3 of *n*-propanol and stirred for 30 min at room temperature. The hydrolysis and gelation were obtained by adding dropwise 3.2 cm^3 of water. The gel is then treated as described above for the ZR5 sample.

ZR5(iP and CH) and ZR7(iP and CH) type catalysts were synthesized by dissolving the 0.045 mol zirconium *n*-propoxide in the same 0.348 mol of *i*-propanol (iP) or cyclohexane (CH).

Thermal analysis

The solids were charged in a Setaram TG.DTA 92-12 analyzer and heated up to 1000°C with a temperature ramp of 5°C min^{-1}, under flowing air (1.2 $dm^3 h^{-1}$). DTA, TG and DTG traces were obtained and compared to previous work in this field [13].

Thermal desorption of ammonia

The number of acid sites was determined by thermal desorption of NH_3. After saturation of the samples at 80°C and desorption under N_2 for 2.5 h, the temperature was increased up to 550°C using a ramp of 5°C min^{-1}. The amount of ammonia desorbed from the sample was determined by thermal conductivity.

Infrared spectroscopy

The measurements were made using a Nicolet 550 instrument equipped with a MCT detector, and a DRIFT cell (Spectratech) used in flow mode. The sample (about 40 mg) was used in powder form after sieving to 60–80 mesh, dried in situ in a He flow at 500°C, then kept in a flow of helium dried by a nitrogen trap. In a typical experiment, 60 spectra were accumulated at room temperature for the samples after drying, then a dose of 1 µl of liquid benzene (dried on zeolites) was introduced, and the spectra were taken. After that several doses of deuterated benzene were injected at different intervals of time and the spectra were recorded.

Catalytic properties

They were determined for the reaction of acylation of anisole by acetic anhydride in the liquid phase at 90°C. The reaction was performed in a glass spherical reactor equipped with a condenser. 92 mmol of anisole and 18.4 mmol of acetic anhydride were introduced in the reactor, and heated to the reaction temperature. The time zero was taken when the catalyst activated in a flow of air at 625°C then rehydrated at room temperature was introduced into the reactor. The concentrations were determined as a function of time by gas chromatographic analysis using a carbowax capillary column.

Chemical analysis

Elemental analysis of the solids for sulfur was performed at the Service Central d'Analyse CNRS (Solaize, France), by decomposition of the sample above 1000°C and potentiometric titration of SO_2 trapped in a solution.

Results and discussion

Changing the synthesis conditions and the solvent changes the composition of the solid as illustrated in Table 1. The higher sulfur content is observed for the sample ZR2 prepared in two steps. The surface area is also significantly modified and can vary by a factor of 2 by using either cyclohexane or *n*-propanol as solvent. This indicates different sizes of crystallites and, therefore, different rates of formation of the solid.

Table 1 Characteristics of the different samples

Sample	%S after treatment at		BET surface area (m^2/g) after treatment at	
	120°C	625°C	120°C	625°C
ZR2(nP)	7.4		150	70 (650°C)
ZR5(nP)	3.7	2.0	165	80
ZR5(CH)	3.3	2.1	213	103
ZR7(nP)	4.1	2.1	217	122
ZR7(CH)	3.6	1.8	347	131
ZR7(iP)	3.5	1.9	308	131

Since strong acidity appears only after high temperature treatment, thermal analysis was used in order to get some information on the evolution of the solids (not yet calcined) in this treatments. The DTA-DTG curves reported in Fig. 1 show common characteristics with those recently reported [13], but exhibit clear differences in the shape of the DTG peak at 600–700°C attributed to the decomposition of sulfates: a single peak appears with ZR2 and two peaks with ZR5 and ZR7, the separation of which is altered by the use of a different solvent. It can be concluded from this behaviour that different types of sulfate species exist on the solid.

At 200–250°C another decomposition peak can be observed, much less intensive for ZR2 than with the samples prepared in one step synthesis. The decomposition, probably dehydration, is somewhat endothermic except for ZR5 where it is very exothermic, independently of the solvent used for preparation. This exothermic behaviour could be a sign of some organic material, result of an incomplete hydrolysis during preparation.

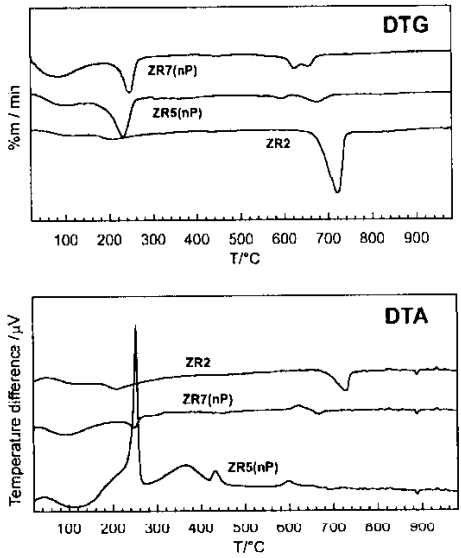

Fig. 1 Thermoanalytical traces of three representative samples of sulfated zirconias

The ammonia thermal desorption results are reported in Table 2 which shows that the different preparations result in quite different number of sites, and also in significant differences in the temperature at which ammonia desorbs from the samples.

Table 2 Acidities of some characteristic samples

Sample	Maximum desorption temperature/°C	Number of acid sites/ meq/g	Shift of OH band/ cm^{-1}
ZR7(iP) calc. 575°C	130	0.96	244
ZR7(iP) calc. 625°C	160	0.55	219
ZR7(nP) calc. 625°C	150	0.57	237
ZR7(CH) calc. 625°C	120	0.36	218
ZR5(nP) calc. 625°C	240	0.38	210

Infrared spectroscopy affords a measurement of the acid strength from the shift of OH bands upon formation of hydrogen bonds with benzene and a further identification of the sulfate species. The spectra of the dried sulfated zirconia samples show two main bands in the region of OH stretching (Fig. 2): a narrow band at 3640 cm^{-1} and a broad one centered at about 3300 cm^{-1}. Also, weak bands at 3740 and 3585 cm^{-1} (shoulder) are observed. According to Kustov *et al.* [14], the 3300 cm^{-1} band is assigned to hydroxyl groups associated to sulfate species, while the other bands are as-

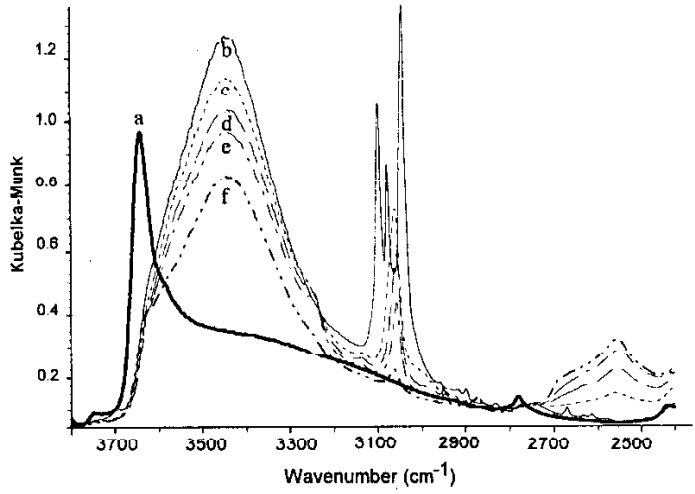

Fig. 2 IR spectra of ZR7(nP)-625 in the region of hydroxyls: (a) after drying at 500°C, (b) after injection of 1 μl of C_6H_6, (c), (d) and (e) after injection of 1–1 μl of C_6D_6, (f) 10 min after the last injection

signed to isolated (3740 and 3640 cm^{-1}) and bridging (3585 cm^{-1}) OH groups on zirconia. By adsorption of C_6H_6 the band at 3640 cm^{-1} is shifted to about 3420 cm^{-1}. By desorption of benzene the original band is restored. The shift is attributed to the formation of a hydrogen bond and is a measure of the acid strength of the protons associated to these hydroxyls. The shifts measured for different sulfated zirconias are reported in Table 2. They correspond to mild acidities that can be observed on HX zeolites for instance.

It appears in Table 2 that changing the solvent in the sol-gel process results in modifications in the acid strength, and also that ammonia and benzene do not give parallel results. The differences between these two probes can stem from their very different acidity: benzene is a weak base and reacts preferentially with the stronger acid sites whereas ammonia is a real base which neutralizes all the sites without discrimination.

The broad band at about 3300 cm^{-1} is relative to an OH that can be exchanged by D from C_6D_6 [15] as observed in Fig. 2, in which a band with maximum at 2520–2530 cm^{-1} appears after introduction of perdeuterated benzene. The intensity of this band increases with a concomitant decrease of the intensity of the OH band if more C_6D_6 is introduced, and the OH band can be restored with a concomitant decrease of the OD band if the solid is further contacted with C_6H_6. This exchange results from a protonation of benzene which requires stronger acidity than simple hydrogen bonding. The effect of the solvent on the acidity of the resulting solid also appears here since ZR7(nP) shows a higher degree of exchange of the OH than the similar solid ZR7(CH).

The DRIFT spectra also contain a band at about 1400 cm^{-1} attributed to sulfates. This band is clearly asymmetric, indicating that it is composed of several bands. We have performed its deconvolution using PeakFit of Jandel Scientific. In order to limit the number of parameters the deconvolution was done with only two peaks, centered at 1390–1400 cm^{-1} and 1370–1380 cm^{-1}, respectively. Two facts appear then rather clearly:

1. The relative intensity of the bands is related to the acidity of the sample, and strong acidity increases with the intensity of the first one. For instance, the solids prepared by the sol-gel method, such as ZR7 and ZR5, show a band at 1398–1409 cm^{-1} more intense than the band at 1370–1385 cm^{-1}, whereas the reverse is true for solids of lower acidity (Fig. 3).

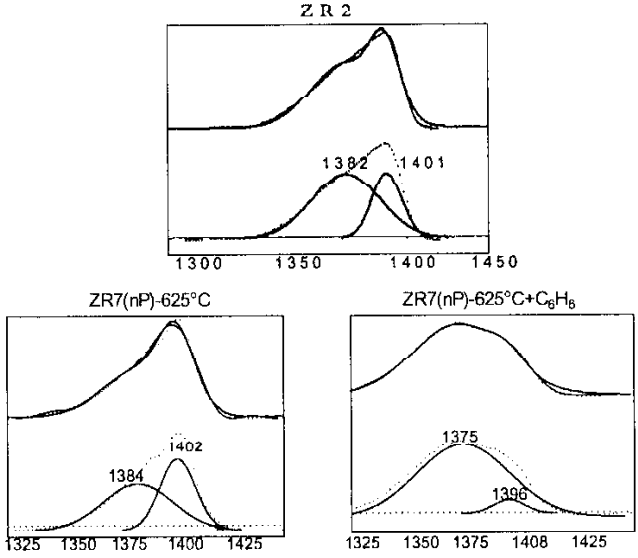

Fig. 3 Decomposition of the IR spectra in the region of sulfates and illustration of the modification of the band of sulfates by interaction with benzene

2. The intensity of the bands is affected by the adsorption of benzene, which induces a shift of the band, first reported by Valyon *et al.* [16]. It appears here from the deconvolution that the component at 1400 cm^{-1} is preferentially decreased by the adsorption of benzene. The same conclusion can be drawn by subtracting the spectrum of the original solid from that of the solid in the presence of benzene (Fig. 4): it appears then that a band at 1407 cm^{-1} has been lost and that the band at 1360 cm^{-1} has been created by the adsorption of benzene. Since benzene is a weak base, it adsorbs at the stronger acid sites, and it can be concluded that the stronger acid sites are associated with this infrared band at 1407 cm^{-1}.

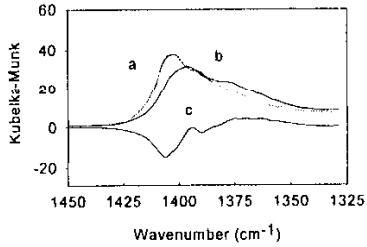

Fig. 4 IR spectra in the region of sulfates (a) of ZR7(nP) calcined at 625°C, (b) of the same sample in the presence of benzene and (c) difference spectrum (a)–(b)

It can then be deduced from this study that two different types of protons exist at the surface, and it is tempting to associate them with the different sulfate species detected by DTA and IR measurements. In agreement with Escalona Platero *et al.* [17] it could be proposed that the strong acid sites are related to the sulfate band at 1407 cm^{-1}, assigned to disulfate species, and the weaker acid sites to monosulfate species at 1380 cm^{-1}.

The catalytic properties of these sulfated zirconias have been measured for the acylation of anisole, and compared to those of a zeolite beta in Fig. 5. It has to be pointed out that, when using acetic anhydride as acylating agent, the catalytic activity of sulfated zirconias highly depends on the degree of rehydration of the solid, which shows only very low activity if it has been just calcined above 500°C. This clearly suggests that this reaction requires protons of high acidity. A second clear point is that a properly activated sulfated zirconia is as good for this reaction as a zeolite beta, since the final yield is 75% with the zeolite and 72% with ZR7(nP) after activation at 625°C in air and rehydration. The conditions of preparation do have a great influence on the catalytic properties since both ZR5(nP) with only 41% conversion and ZR2(nP) with 33% appear as much less active.

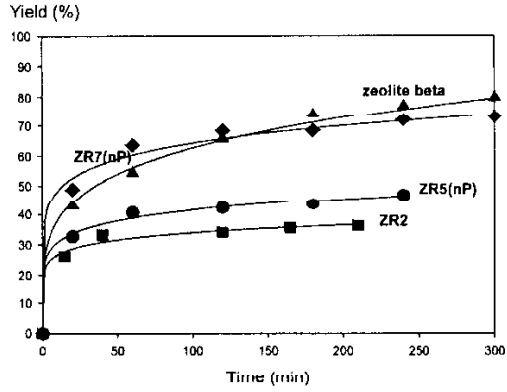

Fig. 5 Catalytic activity of different types of zirconia and of zeolite beta in acylation of anisole

Conclusions

Small changes of the method of preparation of sulfated zirconias alter the number of acid sites, their strength and, consequently, the catalytic properties. The study of the solid by TG-DTA and infrared spectroscopy suggests that this is due to the heterogeneity of the surface with the presence of different sulfated species, which can be discriminated by the adsorption of benzene. The influence of the solvent observed on the formation of the solid suggests that a key factor could be the differences in the kinetics of crystallization, which would influence the number of defects in the final solid. A suitable activation procedure yields a catalyst that can be compared to zeolites beta for the reaction of acylation of anisole with acetic anhydride.

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References

1 V. C. F. Holm and G. C. Bailey, US Patent 3,032,599 (1962).
2 K. Arata, Advances in Catal., 37 (1990) 165.
3 H. Hino, S. Kobayashi and K. Arata, J. Amer. Chem. Soc., 101 (1979) 6439.
4 T. Yamaguchi and K. Tanabe, J. Phys. Chem., 90 (1986) 4794.
5 F. Garin, D. Andriamasinoro, A. Abdulsamad and J. Sommer, J. Catal., 131 (1991) 199.
6 F. R. Chen, G. Coudurier, J-F. Joly and J. C. Vedrine, J. Catal., 143 (1993) 616.
7 A. Corma, V. Fornés, M. I. Juan Rajadell and J. M. Lopez Nieto, Appl. Catal., 116 (1994) 151.
8 F. Figueras, B. Coq, C. Walter and J-Y. Carriat, J. Catal., 169 (1997) 103.
9 P. R. Kurek, US Patent 5,126,489 (1992).
10 F. Figueras, B. Coq, E. Ensuque, D. Tachon and G. Delahay, Catal. Today, 42 (1998) 117.
11 D. A. Ward and E. I. Ko, J. Catal., 150 (1994) 18.
12 D. Tichit, B. Coq, H. Armendariz and F. Figueras, Catal. Lett., 38 (1996) 109.
13 H. Armendariz, B. Coq, D. Tichit, R. Dutartre and F. Figueras, J. Catal., 173 (1998) 345.
14 L. M. Kustov, V. B. Kazansky, F. Figueras and D. Tichit, J. Catal., 150 (1994) 143.
15 H. Armendariz, C. Sanchez Sierra, F. Figueras, B. Coq, C. Mirodatos, F. Lefebvre and D. Tichit, J. Catal., 171 (1997) 85.
16 F. Lónyi, J. Valyon, J. Engelhardt and F. Mizukami, J. Catal., 160 (1996) 279.
17 E. Escalona Platero, M. Peñarroya Mentruit, C. Otero Arean and A. Zecchina, J. Catal., 162 (1996) 268.