One-step sol–gel synthesis of sulfated-zirconia catalysts

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Sulfated-zirconia catalysts were prepared by a one-step sol–gel method. Two different protocols were studied in which sulfuric acid is introduced either with the hydrolysis water, or in the zirconium alkoxide solution in *n*-propanol. After calcination at 923 K these two materials were compared with sulfated-zirconia prepared in two steps by post-sulfation of zirconium hydroxide obtained either by the sol–gel method or by precipitation of inorganic salts. The sulfated-zirconias prepared by the one-step protocol are the most active catalysts for the hydroconversion of *n*-hexane. Moreover, the sample prepared by adding sulfuric acid through the hydrolysis water exhibits different textural properties and enhanced activity for *n*-hexane conversion. These different behaviours cannot be explained by the sulfur content.

Keywords: sulfated-zirconia catalysts; one-step sol–gel method; *n*-hexane hydroconversion; activity

1. Introduction

Since the first report on the superacid properties of the sulfate promoted zirconium oxides [1] several synthesis routes have been investigated. The stability and the surface acidity of the sulfated-zirconia is indeed directly dependent on the textural properties of the parent zirconium hydroxide and on the sulfation process. The doping effect of sulfur on specific areas, crystallographic phase transitions and sintering of the zirconia is now well established [2]. By contrast, the sulfur influence on the strength and type of acid sites is not straightforward. Careful tuning of preparation parameters should improve thermal stability, specific surface areas, amount and dispersion of the sulfate species and therefore the catalytic properties of the samples.

The classical preparation of sulfated-zirconia proceeds by precipitation of an aqueous zirconium salt solution with a base; the zirconium hydroxide ($Zr(OH)_4$) thus obtained is sulfated by immersion in sulfuric acid or by impregnation with ammonium sulfate [2]. An alternative preparation proceeds through a sol–gel method, where the type of zirconium alkoxide, alcohol and drying procedure determine the properties of ZrO_2. The sulfation of $Zr(OH)_4$ then occurs as for the classical aforementioned preparation. Beside these preparations of ZrO_2–SO_4^{2-} by a two-step process, a one-step preparation of sulfated-zirconia has been described recently [3]. This procedure yields a zirconium sulfate alcogel by addition of dilute sulfuric acid to the alkoxide precursor followed by supercritical drying in order to obtain a zirconium-sulfate aerogel. The sulfated-zirconia thus obtained has a high specific area and thermal stability and its Brønsted acidity is shown to depend on the sulfur content.

The sol–gel method thus appears very useful to prepare in a simple way sulfated-zirconia catalysts and led us to investigating the influence of the protocol for introducing concentrated sulfuric acid, either with the hydrolysis water, or with the zirconium alkoxide solution in alcohol as done by Ward et al. [3]. Zirconia samples sulfated by immersion in sulfuric acid of a zirconia support obtained either by the sol–gel method or by precipitation of inorganic salts, were also prepared for comparison. The catalysts were tested in the conversion of *n*-hexane.

2. Experimental

2.1. 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 and stirred for a given prehydrolysis period; water is then added dropwise 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

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SGZR-7 and SGZR-5. 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 be later denominated SGZR-2. The detailed procedures for preparing SGZR-2, 5 and 7 are given below.

SGZR-2: In one beaker, 20 cm^3 of zirconium *n*-propoxide was mixed with 26.6 cm^3 of *n*-propanol and stirred with a magnetic stir bar. Then, 3.7 cm^3 of water is 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 1 h at room temperature and then placed into an oil-bath, at 348 K, to remove alcohol. The solid was then dried at 393 K 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 393 K. Finally, the solid was calcined at 923 K for 4 h under flowing air (4 dm^3 h^{-1}) in a quartz tube inside a tubular furnace.

SGZR-5: 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 vigourous stirring with a magnetic stir bar to the mixture of 20 cm^3 of zirconium *n*-propoxide and 26.6 cm^3 of *n*-propanol. After gelation is complete, which corresponds to the time required to add the acid solution, the gel is aged for 1 h at room temperature. Then it is heated at 348 K for 18 h to remove the alcohol. The solid is then dried at 393 K for 12 h.

SGZR-7: 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 SGZR-5 sample.

Sulfated-zirconia prepared by precipitation of inorganic salts according to classical procedures was obtained as a gift from Magnesium Electron Limited (UK). It was designated ZrO_2–SO_4^{2-} (MEL).

The samples were tested in the hydroconversion of *n*-hexane as mechanical mixtures of ZrO_2–SO_4^{2-} (100 mg) with Pt/Al_2O_3 (300 mg), and designated Pt + ZrO_2–SO_4^{2-}. Pt/Al_2O_3 was prepared by ion exchange between H_2PtCl_6 and γ-Al_2O_3; it contains 0.37 wt% Pt with an accessibility of H/Pt = 0.90. This sample does not exhibit any activity for *n*-hexane conversion in the temperature range investigated. A ZrO_2–SO_4^{2-} supported Pt catalyst was prepared for comparison. This catalyst, designated Pt/ZrO_2–SO_4^{2-} (MEL), was obtained by dry impregnation of ZrO_2–SO_4^{2-} with an aqueous solution of H_2PtCl_6. The filtered solid was dried at 393 K, calcined at 773 K and reduced at 473 K; it contains 1 wt% Pt.

The zirconia samples were characterized by X-ray diffraction and N_2 physisorption. Chemical analyses of the samples were performed at the Service Central d'Analyse du CNRS (Solaise, France). X-ray diffraction patterns were recorded on a CGR theta 60 instrument with Cu Kα radiation. Nitrogen isotherms at 77 K were obtained by using a Micromeritics ASAP 2000 apparatus.

2.2. *n-hexane conversion*

The reaction of *n*-hexane (*n*H, Carlo Erba > 99%) with hydrogen (AGA, high purity grade > 99.99%) was carried out at atmospheric pressure in a dynamic glass reactor. The partial pressure of *n*H was maintained at 6.04 kPa. The effluents were analysed by sampling online to a FID gas chromatograph equipped with a J&W capillary column (60 m × 0.5 mm i.d., DB1 apolar bonded phase).

The catalyst was reactivated in situ by reduction in flowing hydrogen (20 cm^3 min^{-1}) up to 623 K (ramp: 2 K min^{-1}), kept at this temperature for 2 h before being cooled down to reaction temperature (403 K). The typical range of reaction temperatures studied was 403–650 K, depending on the activity of the sample. The following parameters were evaluated:

$$\text{conversion (mol\%)} = \frac{\sum_1^6 (i/6) C_i}{C_6^0 + \sum_1^6 (i/6) C_i} \times 100\,,$$

selectivity S_i to compound i:

$$S_i\ \text{(mol\%)} = \frac{C_i}{\sum_1^6 C_i} \times 100\,,$$

where C_i is the mole percent in the feed of product with i carbon atoms and C_6^0 is the mole percent in the feed of *n*H.

3. Results and discussion

Table 1 presents some characteristics of the zirconia samples. X ray diffraction patterns show that after drying at 393 K, SGZR-2, SGZR-5 and SGZR-7 are in the amorphous state. All samples crystallized after calcination at 923 K (fig. 1). Tetragonal and a very small amount of monoclinic phases are found in all the samples. A similar sulfur content results from the two different one-step sulfation processes. The highest specific surface area is obtained for SGZR-7 either at room temperature or after calcination at 923 K, where a similar surface area decrease, higher than 50%, occurs for each sample. It must also be emphasized after calcination at 923 K the different textural properties between SGZR-7, showing a broad pore size distribution between 30 and 200 Å, and SGZR-2 or SGZR-5 showing narrower mesopore distributions between 15 and 35 Å in size (fig. 2). This is in line with the isotherm shapes of type II for the latter samples, and of type IV for the former,

Table 1
Main characteristics of the sulfated-zirconia

Sample	Sulfur content (wt%)		Surface area ($m^2 g^{-1}$)		Pore volume ($cm^3 g^{-1}$)	
	393 K	923 K	393 K	923 K	393 K	923 K
ZrO_2–SO_4^{2-} MEL	n.d.	3.8	n.d.	125[a]	n.d.	0.12[a]
SGZR-2	5.90	1.0	191	81	0.110	0.070
SGZR-5	3.15	1.35	186	88	0.110	0.075
SGZR-7	3.15	1.50	233	108	0.230	0.160

[a] At 873 K.

according to the classification of Brunauer. Moreover, one can remark that after calcination at 923 K, the SGZR-7 sample exhibits textural properties close to that of zirconia obtained by precipitation of zirconyl chloride in alkaline medium [4]. The sharp peak at 35 Å in the pore size distribution of SGZR-7 does not reflect the presence of specific mesopores; it corresponds to the limit of stability of the nitrogen capillary condensate ($P/P_0 \approx 0.45$) [5]. By using a one-step preparation similar to that for the SGZR-7 sample, Ward et al. [3] obtained a sulfated-zirconia which, after calcination at 773–873 K, exhibits a surface area of 110 $m^2 g^{-1}$ and pore size distribution centered around 45 to 80 Å. The surface area decreased to 90 $m^2 g^{-1}$ after calcination at 973 K.

This peculiar textural property of SGZR-7 may be related to the pre-hydrolysis step included in the synthesis, as previously reported for pure zirconia aerogels [6] or zirconia silica aerogels [7]. This pre-hydrolysis step could be induced by the trace amounts of water present in concentrated H_2SO_4. Indeed, the in situ sulfation appears different between the two one-step sol–gel procedures. Actually, when H_2SO_4 is previously mixed with $Zr(OC_3H_7)_4$ in *n*-propanol solution, there is an occurrence of a sharp gradient in sulfate concentration at the interface between the micro-domains of alkoxide solution and the first drops of added water. This phenomenon could modify the surface properties of the final sulfated-zirconia. Anyway, SGZR-5 and SGZR-7 samples exhibit the same sulfur content before and after calcination.

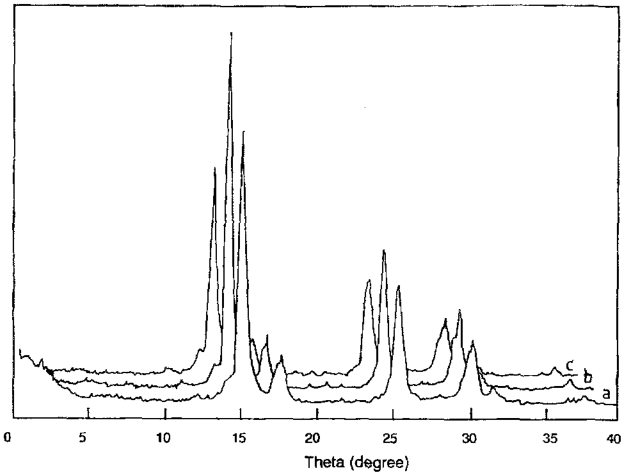

Fig. 1. X-ray diffraction patterns of sulfated-zirconia prepared by the sol–gel method and calcined at 923 K; (a) SGZR-2, (b) SGZR-5, (c) SGZR-7.

From the literature [8–10] emerges that the hydroconversion of alkanes over Pt/ZrO_2–SO_4^{2-} shows a positive order for hydrogen; thus does not proceed through the conventional bi-functional mechanism which occurs on zeolite-supported metal catalysts with a negative order for hydrogen. According to these authors, the isomerization of alkanes could occur by direct reaction of alkanes on acid sites assisted by the presence of metal sites and/or hydride transfer agents, which can form and terminate carbenium ions. Moreover, it has been claimed that hydrogen spillover, initiated at the metal sites, occurs to a great extent [11] and increases the Brønsted acidity. In particular, Ebitani et al. [11] have clearly shown the changes in Brønsted and Lewis acid sites according to the amount of Pt introduced, or with the use of a mechanical mixture of ZrO_2–SO_4^{2-} with Pt black. However, Garin et al. [12] have shown that Pt is not necessary for a high activity when the partial pressure of hydrogen is high enough. In that case, a negative order is observed for hydrogen in the isomerisation of butane, and similar activities are reported at 523 K for a mixture $H_2/nC_4 = 75$ in presence or absence of Pt. Under our conditions, close to those of Garin et al. [12], the location of Pt has an importance on activity. This is shown in table 2 where the results for activity and selectivities in the hydroconversion of *n*-hexane over different sulfated-zirconia catalysts with platinum are presented. The respective behaviours of Pt/ZrO_2–SO_4^{2-} (MEL) and Pt + ZrO_2–SO_4^{2-} (MEL) show that sulfated-zirconias in a mechanical mixture with platinum are much less active than sulfated-zirconia supported Pt. Furthermore, the mechanical mixtures suffer deactivation, likely due to the longer distance between Pt and acid sites in these catalysts with respect to Pt/ZrO_2–SO_4^{2-}. This behaviour emphasizes dramatically the importance of the metal–acid interface. The use of mechanical mixtures of ZrO_2–SO_4^{2-} with Pt/Al_2O_3 for comparing the catalytic properties of different sulfated-zirconias are then far from the

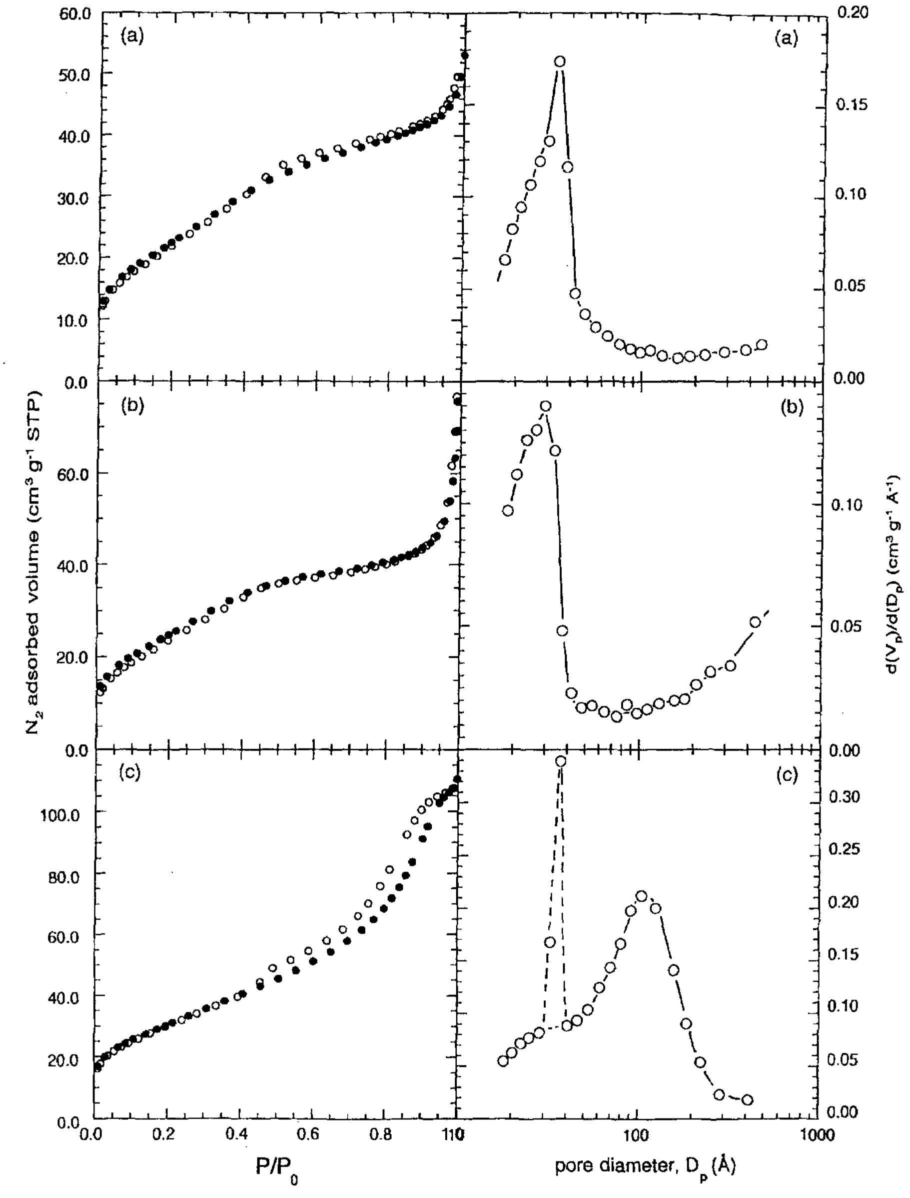

Fig. 2. Nitrogen isotherm adsorption at 77 K (left side) and pore size distribution (right side) of sulfated-zirconia prepared by the sol–gel method and cacined at 923 K; (J) adsorption ramp, (E) desorption ramp; (a) SGZR-2, (b) SGZR-5, (c) SGZR-7.

Table 2
Conversion of *n*-hexane on sulfated-zirconia catalysts with platinum, in the presence of hydrogen

Sample	Temp. (K)	Conv. (mol%)	TOF (h^{-1})	Selectivity[a] (mol%)								
				$C_{1,2}$	C_3	iC_4	iC_5	$nC_{4,5}$	2,2dMB	2,3dMB	2MP	3MP
Pt/ZrO_2–SO_4^{2-} (MEL)	473	28.8	2.2	–	–	–	–	–	0.8	11.5	53.5	34.1
Pt + ZrO_2–SO_4^{2-} (MEL)	473	0.57	0.05	–	–	–	–	–	–	–	55.1	44.8
Pt + SGZR-2	473	2.2	0.67	1.7	2.3	–	–	–	–	9.8	53.7	32.5
Pt + SGZR-5	409	13.6	3.12	–	1.0	1.9	1.1	–	6.1	14.5	49.3	26.1
	423	24.1	5.5	–	0.2	0.5	0.3	–	8.6	14.6	49.0	26.8
	473	46.6	10.6	0.3	2.4	2.8	1.8	0.7	6.4	13.2	45.3	27.0
Pt + SGZR-7	473	24.9	5.3	0.3	2.8	3.7	2.0	0.6	4.0	13.5	45.8	27.2

[a] $C_{1,2}$: $CH_4 + C_2H_6$; C_3:C_3H_8; iC_4: i-C_4H_{10}; iC_5: i-C_5H_{12}; $nC_{4,5}$: n-C_4H_{10} + n-C_5H: 2,2dMB: 2,2-dimethylbutane; 2,3dMB: 2,3-dimethylbutane; 2MP: 2-methylpentane; 3MP: 3-methylpentane.

optimum which could be reached by preparing Pt/ ZrO_2–SO_4^{2-} by impregnation of ZrO_2–SO_4^{2-} with H_2PtCl_6.

It appears from table 2 that ZrO_2–SO_4^{2-} catalysts obtained by sulfation of $Zr(OH)_4$ prepared either by classical precipitation of zirconium salts (MEL samples) or by hydrolysis of $Zr(OC_3H_7)_4$ in neutral medium (SGZR-2), exhibit very similar catalytic properties. However, if the rates are expressed as the moles of *n*-hexane converted per moles of sulfur in the sample per unit time (equivalent to a turnover frequency, TOF), it seems that ZrO_2–SO_4^{2-} based on the $Zr(OH)_4$ prepared by the sol–gel method is slightly more active. By contrast, a large difference of reactivity for *n*-hexane conversion exists between the ZrO_2–SO_4^{2-} prepared either by post-sulfation of $Zr(OH)_4$ material, or by the one-step sulfation during the hydrolysis of $Zr(OC_3H_7)_4$. This difference cannot be easily explained either by the respective sulfur contents which are very close, or by the textural properties of the solids since the SGZR-2 and SGZR-5 samples look very similar with respect to N_2 isotherms and pore size distribution. It is worth noting that the SGZR-2 sample only retains 15% of the sulfur initially deposited by post-sulfation; by contrast, the SGZR-5 and SGZR-7 samples almost retain 50% of the sulfur introduced during the hydrolysis of $Zr(OC_3H_7)_4$. However, in this last procedure, sulfate is introduced throughout the bulk of zirconium hydroxide [3], and the exact amount which migrates toward the active surface after calcination at 923 K is difficult to evaluate. Nevertheless, the stronger retention of sulfate by zirconia in SGZR-5 and SGZR-7 could be the reflection of stronger acid sites. Studies are in progress to elucidate this point. On the other hand, the differences observed in the textural properties, mesoporosity in the 15–35 Å range for SGZR-5, wide mesoporosity ranging from 30 to 200 Å for SGZR-7, could be considered as an explanation for the enhanced activity of the SGZR-5 sample.

In conclusion, the one-step sulfation during the sol–gel preparation of $Zr(OH)_4$ yields, after calcination at 923 K, ZrO_2–SO_4^{2-} catalysts which are much more active for the hydroconversion of *n*-hexane than the sample prepared by post-sulfation of $Zr(OH)_4$ obtained from sol–gel preparation. This behaviour could be tentatively assigned to SO_4^{2-} species strongly bonded on zirconyl sites. On the other hand, the protocol followed for in situ sulfation has an influence on the catalytic properties of the final ZrO_2–SO_4^{2-} sample. ZrO_2–SO_4^{2-} exhibits wide mesoporosity ranging from 30 to 200 Å when H_2SO_4 is mixed with $Zr(OC_3H_7)_4$ in propanol solution, whereas a narrow mesopore distribution between 15 and 35 Å is obtained when H_2SO_4 is added by means of the hydrolysis water. Moreover, the latter sample is more active for *n*-hexane conversion.

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