Isomerisation of α-pinene oxide on sulfated oxides

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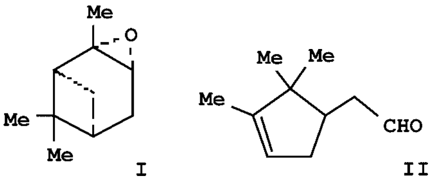
The acid properties of sulfated alumina, titania and zirconia have been characterised, and these solids compared in the isomerisation of α-pinene oxide in the liquid phase at 273 K. This comparison shows that the formation of campholenic aldehyde requires a mild Lewis acid. Only sulfated alumina is a good catalyst giving yields reaching 76% at full conversion in less than 1 h, though with a relatively high catalyst : reactant ratio. The conditions of preparation of this solid show a significant influence on the acid properties and therefore on the catalytic properties of the resulting solid. The best results are obtained with sulfated alumina prepared with a ratio of hydrolysis of 1 and an activation temperature of about 923 K.

KEY WORDS: isomerisation; epoxide; acid properties; sulfated alumina; sulfated zirconia; sulfated titania; α-pinene oxide; preparation of campholenic aldehyde

1. Introduction

The rearrangement of epoxides recently reviewed by Hölderich and Barsnick [1], is commonly used to produce useful intermediates of organic synthesis. This reaction yields aldehydes by acid catalysis, and allylic alcohols by a bifunctional acid–base mechanism [2]. The acid catalyzed isomerisation of α-pinene oxide (I) yields campholenic aldehyde (II) which is a useful intermediate in the manufacture of perfumes.



Scheme 1. Isomerisation of pinene oxide.

This reaction (scheme 1) is homogeneously catalyzed by Lewis acids, and the usual process based on $ZnBr_2$ gives a selectivity of 85% [3]. For a better protection of the environment there is now a trend to heterogenisation of the processes using solid Lewis acids [1,4]. In batch reactors, Hölderich *et al.* reported a 78% yield using USY zeolite dealuminated by a special process [5], and Kunkeler *et al.* a 89% selectivity at a low conversion on Ti-BEA as catalyst [6]. In a flow reactor, 94% selectivity was reached at 95% conversion using $C_2H_4Cl_2$ as solvent. With alkanes as solvents the selectivity reached 89% at full conversion, but the catalyst started to decay after 5–6 h. These results were obtained in diluted conditions: 1% of substrate in the feed diluted in the solvent and with N_2 as carrier. It has been pointed out that very active catalysts can be obtained by impregnation of Zn triflate on silica [7]. The selectivity of this system reaches 80% at 50% conversion and then decreases to 69% at full conversion. Amorphous silica–aluminas have also been employed and yields of 75% have been reported for reaction at room temperature [8]. The main side reaction is usually the polymerization of the epoxide, and the high selectivity of Ti-BEA was attributed to the transition state selectivity induced by the porous structure of the zeolite. If this hypothesis holds, high selectivities should be restricted to zeolites, which is obviously not the case. Sulfated metal oxides are strong Lewis acids which can be obtained with mesoporosity [9–13] and we describe here the properties of these sulfated oxides for the isomerisation of pinene oxide. From previous work it is known that the acid strength increases upon sulfation and that the acidity of the sulfated materials increases in the order $\mathrm{Al} < \mathrm{Ti} < \mathrm{Zr}$ [13]. This gives an opportunity to investigate the influence of the acid strength.

2. Experimental

2.1. Preparation of the catalysts

These solids were obtained by sol–gel using as starting materials: aluminium tri-*sec*-butoxide, $Al(OC_4H_9)_3$ (95%, Merck), zirconium propoxide $Zr(OC_4H_9)_4$ (70% in *n*-propanol, Aldrich) and titanium butoxide $Ti(OC_4H_9)_4$ (98%, Aldrich). Absolute ethanol and 2-propanol (Aldrich) were used as solvents.

For sulfated alumina: a solution A was made under nitrogen atmosphere by mixing under stirring the metal alkoxide with 2-propanol at room temperature. A second solution B including water, sulfuric acid and 2-propanol ($H_2O : H_2SO_4 : \text{2-propanol} = 0.06 : 0.006 : 0.13$). The two

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Table 1
Characteristics of the sulfated oxides after calcination at 923 K.

Sample	S (wt%)	Specific surface area ($m^2\ g^{-1}$)
Al_2O_3 ($h = 1$, $S = 0$)	0	482
Al_2O_3–SO_4 ($h = 1$, $S = 0.05$)	1.9	590
Al_2O_3–SO_4 ($h = 1$, $S = 0.1$)	4.5	522
Al_2O_3–SO_4 ($h = 0.5$, $S = 0.1$)	3.3	608
Al_2O_3–SO_4 ($h = 1.5$, $S = 0.1$)	3.85	611
TiO_2–SO_4[a] ($h = 4$, $S = 0.2$)	1.5	125
ZrO_2–SO_4-7 ($h = 3.8$, $S = 0.2$)	1.5	108

[a] 798 K instead of 923 K.

parameters which define the solid are then the degree of hydrolysis $h = H_2O$/alkoxide and $S = SO_4^{2-}$/alkoxide. Solution B was added dropwise to A under stirring during $2\frac{1}{2}$ h, then the mixture was aged. After 7 days a white opaque gel was obtained, which was dried at 383 K in an oven for 15 h, then ground and calcined at different temperatures. Non-sulfated alumina was obtained omitting sulfuric acid in B.

The preparation of sulfated zirconia has been described in detail before [14,15]: two solutions were made, one by mixing 0.51 cm^3 of sulfuric acid with 20 cm^3 of zirconium alkoxide, and the second mixing water (3.2 cm^3) with 26.6 cm^3 of 2-propanol. The first solution was then slowly added at room temperature under vigorous stirring to the second one. After complete gelation, which roughly corresponds to the time required to add the acid solution, the gel was aged for 1 h at room temperature, then heated at 348 K for 18 h to remove the alcohol, then dried at 393 K for 12 h.

Sulfated titania was also prepared in one step from a 1 M solution of $Ti(OC_4H_9)_4$ in 2-propanol. Gelation was induced by the addition of water in a ratio $h = [H_2O]/[Ti(OR)_4] = 4$; sulfuric acid was added to the isopropoxide solution with a ratio $S = SO_4^{2-}/Ti = 0.2$, then the two solutions were slowly mixed. The activation of sulfated titania was performed in air at 798 K since the earlier work of Hino *et al.* [9,10] demonstrated that the stability of sulfates is lower in the case of TiO_2 and that the higher acidity was reached at this temperature. The sulfur contents and surface areas after calcination at 923 K for sulfated aluminas and zirconias and 798 K for sulfated titania are reported in table 1.

2.2. Characterizations

Nitrogen isotherms at 77 K were obtained on a Micromeritics ASAP 2000 apparatus; the samples were previously outgassed under vacuum at 523 K overnight. The infrared measurements were made on a Victor 22 Bruker instrument equipped with an MCT detector. Self-supporting wafers (about 15 mg) were obtained from the powder, calcined *in situ* in oxygen, then treated in vacuum. In a typical experiment, 60 spectra were accumulated at room temperature for the samples after calcination, then a dose of gaseous benzene (dried on zeolites) was introduced, and the spectra were taken at different intervals of time. The adsorption of pyridine was performed after evacuation of the samples.

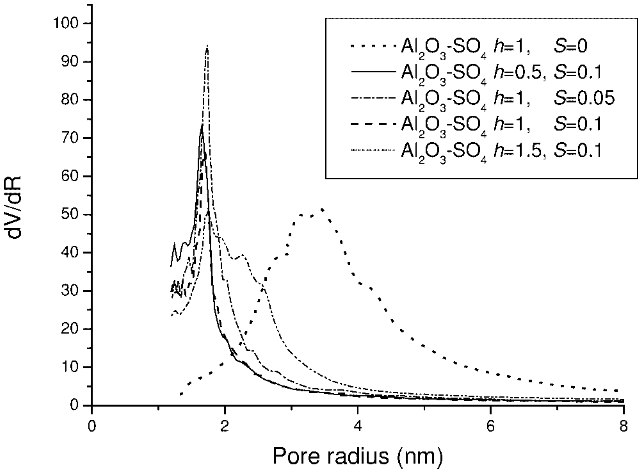


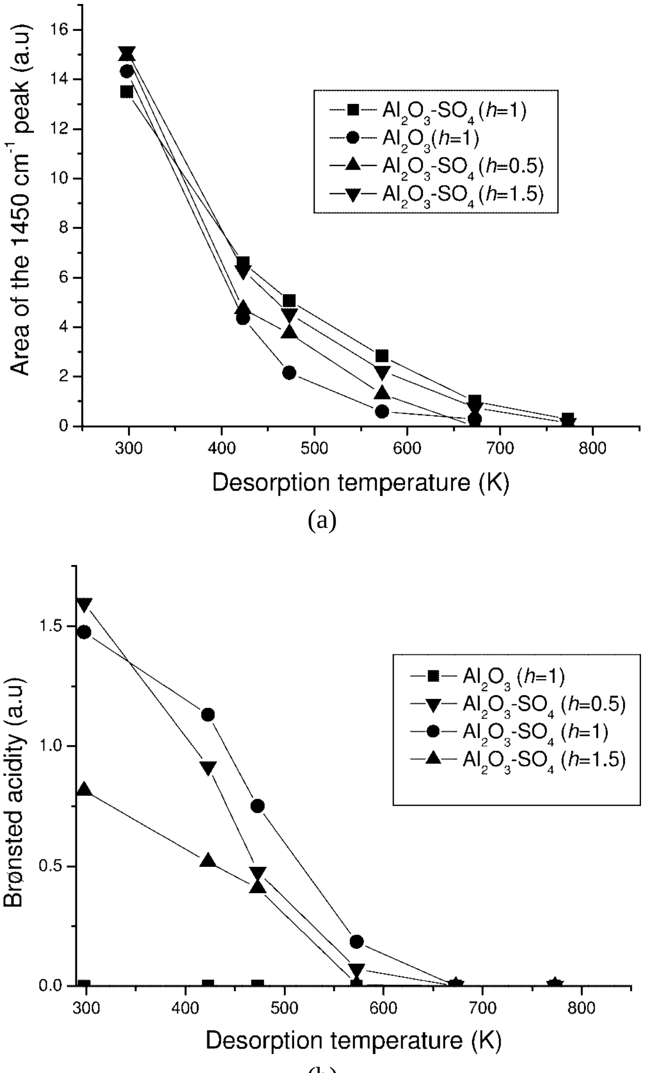
Figure 1. Pore size distributions of alumina and sulfated aluminas.

2.3. Catalytic properties

The catalytic properties of these solid acids were investigated for the isomerisation of the epoxide of α-pinene to campholenic aldehyde, using a round bottom glass flask equipped with a condenser and water trap as reactor. The reactions were performed at ice temperature (273 K): 8 ml of toluene solvent were placed in a 25 ml three-necked glass reactor, 0.2 g of substrate was added, and the catalyst activated at the required temperature in a separate flow reactor was rapidly added. The composition of the reaction medium was analysed by gas chromatography using a Shimadzu instrument equipped with a fused silica capillary column (DB5, 25 m). The products were further identified by GC-MS. The relative response of the chromatograph for α-pinene epoxide and campholenic aldehyde (ratio of surface areas of the chromatographic peaks for the same number of moles: $1:1.055$) permitted to measure the conversion and yield of the reaction. The yield is expressed as usual as the ratio moles of α-pinene epoxide converted into campholenic aldehyde to moles engaged in the reaction.

3. Results and discussion

The catalysts used here show rather large surface areas and pores of about 3–4 nm in size (figure 1). From infrared spectroscopy using pyridine as a probe molecule, sulfated oxides appear as strong Lewis acids, possessing however some Brønsted acidity. The Lewis or Brønsted nature of the sites can be obtained from the integration of the bands at 1450 and 1550 cm^{-1} and their strength from their thermal evolution. Alumina evacuated at 723 K is a pure Lewis acid of moderate strength since pyridine is desorbed above 573 K (figure 2). Upon sulfation the intensity of the bands corresponding to pyridine coordinated to Lewis sites increases, showing a larger number of sites but the acid strength is also higher since pyridine is still detected after desorption at 673 K on samples prepared with $h = 1$ and 1.5.



(a)

(b)

Figure 2. Influence of the ratio of hydrolysis h and of the desorption temperature on the integrated intensity of the pyridine band at (a) 1450 and (b) at 1545 cm^{-1}, for alumina and sulfated aluminas ($S = 0.1$) calcined at 823 K.

Sulfation also promotes Brønsted acidity. This acidity is moderate since pyridinium ions are desorbed at about 573 K. Sulfated zirconia and titanias have also been shown earlier to be strong acids. The acid strength of the protons on the present samples has been estimated by the method of shift of OH bands upon adsorption of benzene previously used for sulfated zirconia [16]. Benzene is a weak base interacting only with the strong acid sites and therefore gives a measure of the higher acid strength present at the surface. The results are reported in table 2. It appears that sulfated alumina is a much weaker Brønsted acid than sulfated titania or sulfated zirconia. The acidity of sulfated alumina is related to the ratio of hydrolysis h (h = water : alkoxide) (figure 2), and the lower acid strength of Brønsted acidity is noticed at $h = 1.5$ (figure 2(b)). The amount of sulfuric acid used in the process has also an influence (figure 3). Since the Lewis acidity was higher on the sample prepared with $S = 0.1$, this ratio was used to prepare the catalysts described hereafter.

Table 2
Shift of the hydroxyl band upon adsorption of benzene for the sulfated oxides.

Sample	Original ν_{OH} (cm^{-1})	Shift (cm^{-1})
Al_2O_3–SO_4 ($h = 0.5$)	3670	60
Al_2O_3–SO_4 ($h = 1.5$, $S = 0.1$)	3653	58
Al_2O_3–SO_4 ($h = 1$, $S = 0.1$)	3700	82
TiO_2–SO_4^{a} ($h = 4$, $S = 0.2$)	3669	201
ZrO_2–SO_4-7 ($h = 3.8$, $S = 0.2$)	3640	244

[a] 798 K instead of 923 K.

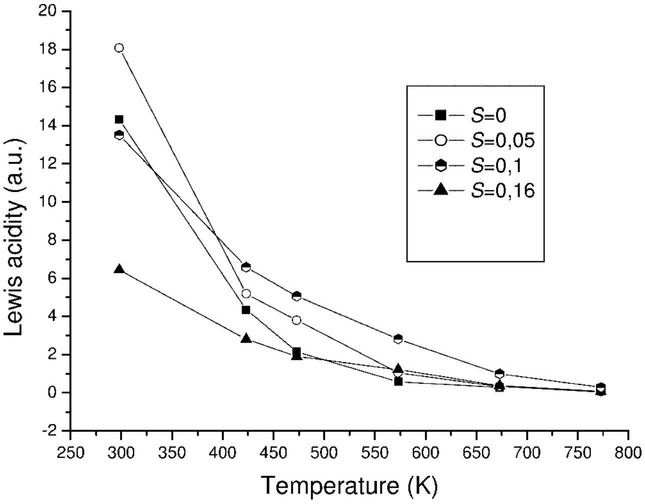


Figure 3. Influence of the amount of acid used for hydrolysis, at constant amount of water ($h = 1$) on the Lewis acidity of the resulting solid.

On sulfated titanias and zironias, α-pinene oxide is isomerized with low yields of campholenic aldehyde at full conversion of the reactant (table 3). Pure alumina also gives moderate yields with low conversion, and the best results are obtained with sulfated aluminas. Both activity and selectivity to campholenic aldehyde are affected as illustrated in figure 4. Controlling the amount of water used in the sol–gel process (h value) allows full conversion to be reached in a short time after activation at moderate temperatures in the range 723–923 K. Here also both activity and selectivity are simultaneously affected and high yields close to 76% can be achieved (figure 5). Calcination above 723 K increases catalytic activity but the impact on the initial rate is relatively small. The changes of the final yield are also marginal. They are also independent of the catalyst weight used in the experiment (table 4) suggesting that deactivation in the course of the reaction is not important and that the formation of the isomeric aldehydes occurs through parallel reactions as reported by Hölderich and Barsnick [1]. The use of a higher concentration of reactants gives lower results as illustrated in table 3. Rehydration of the catalyst or addition of water to the reaction medium results in a loss of selectivity falling to <65% at 40% conversion. The detrimental effect of protons in the process can be partly assigned to the competitive reaction of polymerisation of the epoxide proposed by Kunkeler *et al.* [4]. However, the selectivity decreases with

Table 3
Comparison of the results obtained with sulfated alumina ($h = 1$, $S = 0.1$) with those reported in literature for the isomerisation of α-pinene oxide.

Catalyst	Catalyst weight (g)	Epoxide (g)	Substrate/ catalyst	Solvent (ml)	Reaction temperature (K)	Yield (%)	Ref.
Ti-beta	0.050	4.22	84.4	25	343	25	[6]
Zn triflate	0.050	1	20	100	298	69	[7]
Y zeolite	2	15	7.5	37.5	273	78	[5]
Amorphous SiAl	0.3	0.2	0.66	8	298	75	[8]
Al_2O_3–SO_4 ($h = 1$, $S = 0.1$)	0.15	0.2	1.3	8	273	76	[this work]
Al_2O_3–SO_4 ($h = 1$, $S = 0.1$)	0.4	3	7.5	6.9	273	44	[this work]
Sulfated titania	0.05	0.25	5	4	298	39	[this work]
Sulfated zirconia	0.2	0.2	1	8	273	37	[this work]

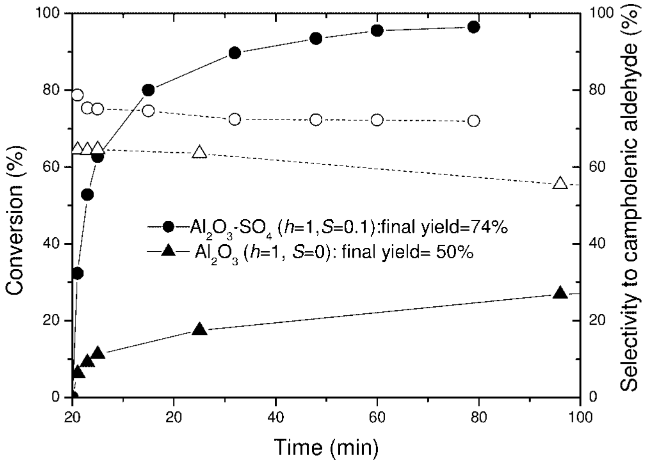


Figure 4. Conversion (•,▲) and selectivity (○,△) as a function of time for the isomerisation of pinene epoxide at 273 K for alumina (▲) and sulfated alumina (•) prepared with an hydrolysis ratio $h = 1$ and previously calcined at 798 K.

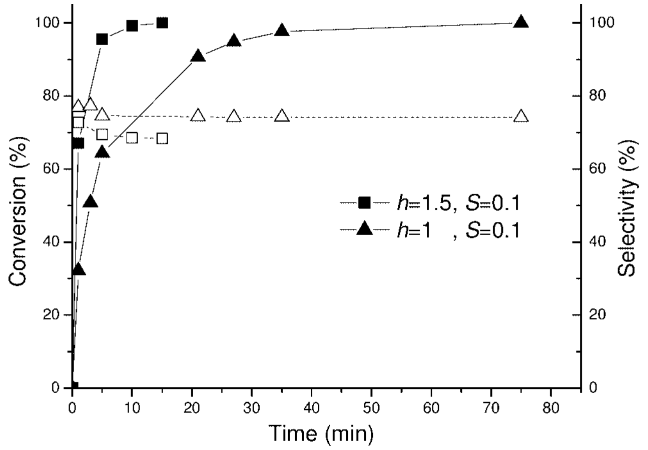


Figure 5. Effect of the degree of hydrolysis h on the conversion (▲,■) and selectivity (△,□) as a function of time of sulfated aluminas calcined at 823 K. Conditions: catalyst = 148 mg, reaction temperature 273 K, toluene as solvent 8 ml, α-pinene epoxide 0.2 g.

Table 4
Effect of the conditions of reaction in the isomerisation of α-pinene oxide on sulfated alumina (sample prepared with $h = 1$, $S = 0.1$, calcined at 798 K). Conversion and selectivity after 30 min.

Catalyst weight (g)	Calcination temp. (K)	Conversion (%)	Selectivity (%)
0.15	723	92.9	76
0.18	723	100	72.8
0.22	723	100[a]	75[a]
0.15	823	97.7	74
0.15	923	100	74

[a] Conversion and selectivity after 5 min.

conversion observed in figures 4 and 5 suggest that a consecutive process also causes a loss of selectivity. Aldolisation of the product catalyzed by H^+ could be a possible side reaction. The use of dioxane instead of toluene decreases both selectivity and final conversion. In that case the yield falls from 76 to 53% probably due to the basic character of dioxane which competes with the substrate for adsorption.

The results obtained here in a batch process can be compared to those reported with Ti-BEA used in a flow process. Sulfated alumina gives lower selectivities than Ti-BEA: 76% against 83–94% at high conversion. The productivity is however much higher: 18.7 mmol/h g at 273 K for sulfated alumina against 3.9 mmol/h g for Ti-BEA. Due to this high activity this catalyst could also be used in a continuous-flow process, which would avoid to transfer the sample in air and therefore possible rehydration.

In conclusion it appears that since high yields can be reached with mesoporous solids, the porous structure has not a determining role in selectivity. The most important factor is the nature and strength of acidity.

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