

Catalytic aerogel-like materials dried at ambient pressure for liquid-phase epoxidation

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Titanium-containing hydrophobic silica with a pore volume and pore sizes in the range of aerogels was prepared by silylation before drying of well-dispersed mixed oxides obtained via a sol-gel method; it showed remarkable properties as a catalyst in the epoxidation of styrene with Bu^tOOH.

Environmental concern surrounding chemical processes for the production of commodity and fine chemicals has led to the development of environmentally-friendly processes based on heterogeneous catalysts. Among them, the epoxidation of olefins is a major target since the epoxide functional group is one of the most useful intermediates in organic synthesis.¹ Heterogeneous catalysts such as silica-supported titania are used on an industrial scale for propylene epoxidation using alkyl hydroperoxides as oxidant.²

The discovery that the Ti-substituted silicalite molecular sieve TS-1 (an isomorphous ZSM-5 zeolite) is a catalyst for selective oxidation reactions with H₂O₂³ has promoted investigation of its use in several oxidation reactions.⁴ To overcome the restriction imposed by the relatively small average diameter (*ca.* 0.55 nm) of the channel system, Ti has been incorporated into materials with larger pore sizes such as zeolite beta,⁵ or hexagonal mesoporous silica (HMS).⁶ Other attempts to obtain suitable epoxidation catalysts have been based on grafting of Ti compounds onto the silica surface⁷ and the use of the sol-gel technique.⁸ The latter has been used to obtain epoxidation catalysts ranging from amorphous microporous⁹ to mesoporous titania-silica mixed oxides,⁸ and even solid precursors with the appropriate properties for Ti-containing zeolite synthesis.¹⁰

The many potential advantages inherent to the use of sol-gel techniques in preparing epoxidation catalysts are strongly dependent on the drying method. Supercritical drying prevents the network collapse induced by capillary forces arising from the liquid-vapour interface, leading to materials with high porosity called aerogels with suitable properties to be used as catalysts,¹¹ although supercritical processing has numerous drawbacks due to the extreme conditions used. Recently a simpler method at ambient pressure for the preparation of aerogel-like films has been reported¹² based on the use of a silylating agent which is reacted with the hydroxy groups on the surface of an inorganic gel, preventing the irreversible shrinkage of the porous structure during drying.

We report here a simple route, based on the above mentioned silylation procedure, for the preparation of titania-silica mixed

oxides with adequate textural properties and highly dispersed Ti atoms, both features leading to active catalysts in epoxidation reactions with *tert*-butyl hydroperoxide (TBHP).

The catalysts were prepared following a two-step sol-gel method. In the first step, a solution of tetraethoxysilane (TEOS) was prehydrolyzed with aqueous HCl (0.05 M) for 45 min at room temperature (samples 1–3). Other catalysts were prepared by diluting TEOS in EtOH (samples 4–6); the solution was prehydrolyzed with aqueous HCl for 90 min, since less water is added to these samples. Then, the Ti precursor [titanium(IV) butoxide, TNBT] diluted in PrⁱOH was added to give gel molar ratios (TEOS : H₂O : HCl : EtOH : PrⁱOH : TNBT) of 1 : 4 : 3.6 × 10⁻³ : 0 : 1 : 0.023 for samples 1–3 and 1 : 1.25 : 9 × 10⁻⁴ : 2 : 1 : 0.023 for samples 4–6, with additional hydrolysis times of 20 and 75 min, respectively. The second step of the synthesis procedure increased the condensation rates by changing the pH to higher values with aqueous NH₃ (1 M) for samples 1–3 and dilute NH₄OH (1 M) in EtOH (1 NH₃ : 5.6 H₂O : 0.7 EtOH) for samples 4–6. Once the gel point of the sol had been reached, the solid gels were aged for 48 h and samples of 1 and 4 were dried at 110 °C overnight, whereas the other catalysts were washed with *n*-hexane and treated with a TMSCl solution in *n*-hexane before drying. For comparison, a silica obtained by an analogous sol-gel procedure was impregnated with a solution of TiCl₄ in EtOH (Si/Ti = 54) and calcined at 550 °C for 5 h. Also, a Ti-containing HMS was provided by Dr Tuel from CNRS¹³ with a Si/Ti molar ratio of 87.3. All the catalyst samples were tested in the oxidation of styrene with TBHP at 60 °C in N₂ atmosphere. Conversions and selectivities were determined by GC, ¹H NMR analysis and iodometric titration.

All samples were characterised by diffuse reflectance UV-VIS spectra (DR UV-VIS) in the range 190 to 500 nm. They presented a maximum absorption band centered at 220 nm, and no absorption around 330 nm was detected. Nitrogen adsorption-desorption isotherms of the samples obtained on an ASAP 2010 from Micromeritics showed a hysteresis loop corresponding to a type IV isotherm, typically assigned to mesopores present in the materials. Samples 1 and 4 present similar textural properties independent of the presence of EtOH as a diluting agent (Table 1), with BET surface areas above 600 m² g⁻¹ pore volumes around 1 cm³ g⁻¹ and average pore sizes in the range of 50 Å as the result of the BJH analysis on the adsorption branch of the isotherm. The silylation procedure leads to a decrease in the final Ti content of the catalysts as a consequence of the reaction of TMSCl with the OH groups at the surface of

Table 1 Textural properties and chemical composition of the different tested samples

Sample	Diluted in EtOH?	Silylated?	Calcined?	Si/Ti	S _{BET} /m ² g ⁻¹	V _P (ADS)/cm ³ g ⁻¹	D _P (ADS)/Å
1	NO	NO	YES	43	682	1.0	50
2	NO	YES	NO	73	871	1.8	71
3	NO	YES	YES	69	849	1.3	68
4	YES	NO	YES	43	604	1.0	57
5	YES	YES	NO	73	723	3.0	132
6	YES	YES	YES	69	688	2.3	125

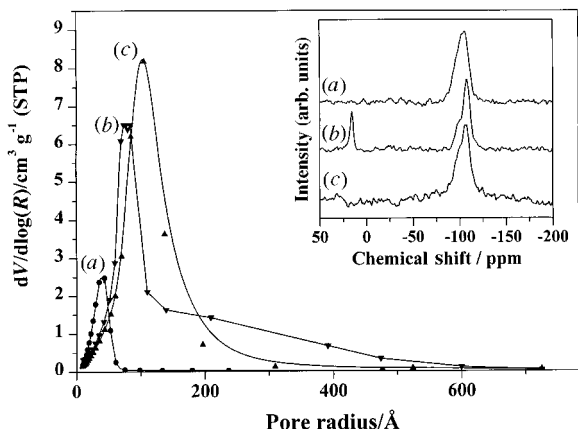


Fig. 1 Pore volume distribution (BJH analysis of the adsorption branch of the isotherm) of (a) **4** (xerogel), (b) **5** (silylated) and (c) **6** (silylated and calcined). Inset: ^{29}Si MAS NMR spectra of these samples are shown.

the gel, which prevents irreversible shrinkage during drying. There is a remarkable increase in the BET surface area, pore volume and mean pore size in the samples prepared with EtOH. It is interesting to note how the silylation procedure is capable of preserving at least partially the different gel structures derived from the use of increasing amounts of EtOH as solvent, something that is not shown in the textural properties of the xerogels when conventional drying is used (samples **1** and **4**). Similarly, after calcination, the differences are clearly shown not only in comparison to the xerogels but also between the materials prepared with different dilution levels, *i.e.* EtOH content. The calcination of the silylated samples leads to a decrease mainly in the pore volume of the samples compared with the uncalcined ones, showing some evidence of pore collapse. In any case, the pore volumes are clearly higher than those corresponding to xerogels and are in accordance with the textural properties of the starting non-calcined silylated samples. The used samples, after reaction, showed similar textural properties to the fresh ones.

Fig. 1 shows the pore size distribution coming from BJH analysis of the N_2 isotherms of samples **4**–**6**. There is a shift in the pore size distribution towards higher values when the silylation procedure is used, with a decrease in the size of the largest pores after calcination. The ^{29}Si MAS NMR spectra of **4**–**6** are shown in Fig. 1 (inset), recorded in a Varian 300 MHz with a spinning rate of 4 kHz. It is clearly shown how the silylation procedure decreases the large Q^3 contribution at -100 ppm in the non-silylated sample, showing up as a peak 15 ppm upfield corresponding to trimethylsilyl groups (TMS) formed in the reaction of TMSCl with the silanol groups of the gel surface.¹⁴ The calcination procedure removes the TMS

Table 2 Activity of the different titanium-containing materials in the epoxidation of styrene^a

Sample	Conversion (%)			Selectivity (%)		
	TBHP	ST	TON ^b	BADH	SO	22ET
Blank	3.9	0.6	—	13.6	86.4	0.0
Impregnated	30.2	9.8	35	1.4	81.5	17.1
Ti-HMS	45.0	16.2	77	1.0	88.3	10.7
1	39.7	15.0	35	1.4	59.9	38.7
2	35.3	12.9	50	1.9	98.1	0.0
3	35.6	13.0	48	1.1	83.9	15.0
4	41.8	15.9	37	1.4	65.7	32.9
5	45.4	16.1	63	1.4	98.6	0.0
6	41.6	17.6	66	1.2	87.8	11.0

^a Reaction conditions: $T = 60^\circ\text{C}$, $t = 3$ h, autogenous pressure, no solvent, stirring speed = 300 rpm, inert atmosphere, catalyst loading = 400 mg, styrene = 100 mmol, TBHP = 40 mmol; ST = styrene; TBHP = *tert*-butyl hydroperoxide; SO = styrene oxide; BADH = benzaldehyde; 22ET = 2-phenyl-2-*tert*-butoxyethanol. ^b In moles of styrene per mole of titanium per hour.

groups, with partial recovery of the surface OHs shown by the increase of the shoulder at -100 ppm. This behaviour is also seen in the IR spectra of the samples, since in the silylated catalysts there is a large decrease in the band corresponding to Si–OH vibrations (3000 – 3750 cm^{-1}), which is partly recovered after calcination.

The catalytic activities of these samples and the materials used as reference were tested in the epoxidation of styrene with TBHP. Besides the conversion of styrene and TBHP, Table 2 shows the turnover numbers (TON), relative to the total amount of Ti in the catalyst, and the selectivity of styrene towards the different products for the different catalysts, including a blank test. Different products were obtained besides the primary product, styrene oxide (SO): benzaldehyde (BADH) formed from oxidative cleavage of styrene by TBHP and 2-phenyl-2-*tert*-butoxyethanol (22ET) formed from nucleophilic attack of Bu^tOH on oxirane ring of the primary product.

The Ti-containing silica xerogels prepared without the use of the silylation procedure (samples **1** and **4**) show similar TON to that of the TiO_2 impregnated silica xerogel, although the selectivity towards SO is higher for the latter. Silylated samples show very high selectivity towards the epoxide with negligible formation of the product coming from the opening of the oxirane ring. The reuse of the silylated sample **5** shows a slight decrease in styrene conversion ($X_{\text{ST}} = 14.2\%$) without any change in selectivity ($S_{\text{SO}} = 98.5\%$). Once the silylated samples are calcined a decrease in SO selectivity is observed due to the regeneration of HO groups on the sample surface, which promotes the catalytic reaction of the epoxide with Bu^tOH formed from TBHP. The pore volume of the Ti-containing silica is an important factor in the preparation of these catalysts, since for comparable BET surface areas (samples **2** and **5**, for example), the higher the pore volume the thinner the pore walls; therefore there is a higher probability of the Ti atoms being located at the surface. Although at first sight the silylation procedure could lead to the complete blocking of Ti atoms at the catalyst surface, hindering their oxidation activity, not all this surface is covered by the silylating agent, as was proved by the catalytic activity of the silylated samples.

The method reported in this work is an easy and reproducible way to obtain a highly hydrophobic Ti-containing material with aerogel properties, oxidation activity comparable to Ti-HMS and higher selectivity towards epoxide formation, without the use of templates or surfactants as in the case of zeolites or micelle structured zeolitic materials.

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