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Surface modified amorphous titanosilicate catalysts for liquid phase epoxidation

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Abstract

Titanium-containing mesoporous silica has been prepared by silylation of mixed oxides obtained via sol–gel method. These samples displayed enhanced activity in the epoxidation of styrene with $\mathrm{Bu}^t\mathrm{OOH}$ in comparison to normal xerogels or other titanium-containing catalytic systems. The influence of the extension of the silylation reaction, as well as the use of different silylating agents, have been investigated. Samples were characterised by FTIR, XRF, ^{29}Si-MAS NMR, diffuse reflectance UV–Vis and N_2 adsorption–desorption isotherms, X-ray photoelectron spectroscopy (XPS) and FTIR of adsorbed deuteroacetonitrile. The improvement in the catalytic activity achieved has been related to the removal of OH groups by means of calcination or silylation treatments. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Amorphous titanosilicate; Epoxidation; Sol–gel method; Silylation reaction

1. Introduction

Epoxidation of olefins is a widely used process in the chemical industry, since the epoxide functional group is one of the most useful intermediates in organic synthesis. Traditionally percarboxylic acids have been employed in these processes. However, this alternative presents several drawbacks such as the use of corrosive conditions and the production of pollutants with a considerable environmental impact. To overcome these problems heterogeneous catalysis is proposed as alternative. Among these systems, zeolitic materials have been extensively studied, the oxidation activity being provided by the incorporation of transition metals with redox properties into the solid framework (such as Ti-silicalite-1 [1] and Ti-β zetolite [2]) or grafting metal containing compounds on the silica surface [3]. However, they present some problems for the oxidation of bulk molecules with organic peroxides due to the relatively small average diameter of the channel system in the case of zeolites and the possible leaching of the metal during the reaction for grafted compounds.

Very promising catalytic systems are based on amorphous materials obtained through the sol–gel route [4] in which many variables could be manipulated to obtain the desired properties in the solid. Recently we have reported a simple method to obtain selective catalysts for epoxidation with *tert*-butyl hydroperoxide (TBHP) by chemical modification of the surface of a titania–silica gel by trimethylsilylation [5]. This treatment not only allows the synthesis of

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materials with large BET area, pore sizes and pore volumes in the range of aerogels, but also the modification of their surface from hydrophilic to hydrophobic, which seems to have a significant role in the epoxidation of olefins [6]. In this work, we describe the influence of the different preparation conditions on the catalyst activity and selectivity, and the correlation with the different physico-chemical properties derived from the chemical modification of the surface properties by this silylation treatment.

2. Experimental

Catalysts were prepared by a two-step sol–gel method (acid hydrolysis and basic condensation), by prehydrolysis of the less reactive precursor (the silica precursor: tetraethyl orthosilicate, TEOS) with aqueous hydrochloric acid (0.05 N, 90 min) at room temperature (molar ratios: TEOS:H_2O:HCl of $1:1.25:9\times10^{-4}$). Then, the titanium source (titanium (IV) butoxide) was added and the hydrolysis was stopped after 45 min through addition of ammonia solution (1 N). Once the gel point is reached, the gels were dried if a normal xerogel is required or aged for 48 h and washed with ethanol and *n*-hexane before the silylation treatment. The resultant solid is then mixed with the silylating agent using *n*-hexane as solvent and heated up to the boiling point of the solution in N_2 atmosphere for 1 h. The resultant powder is washed with *n*-hexane again and dried at 110°C overnight. Two different silylating agents were used: trimethylchlorosilane (TMCS) and 1,1,1,2,2,2-hexamethyldisilazane (HMDSZ). Three samples with different TMCS loading were prepared for their study, being the TMCS/SiO_2 molar ratios: 0.09, 0.23 and 0.46. If needed, the samples were calcined at 550°C for 5 h.

All catalysts were tested in the oxidation of styrene with TBHP at 60°C in N_2 atmosphere for 3 h run carried out in an autoclave laboratory batch reactor. Substrate to oxidant molar ratio was 2.6 and the catalyst loading 0.036 g g^{-1} of styrene. Anhydrous conditions were used by mixing TBHP solution (30 wt.% H_2O) with $MgSO_4$ and styrene overnight and removing the solid prior to use in the reaction. Conversions and selectivities were determined by GC, ^{1}H-NMR, MS and iodometric titration. Samples were characterised by FTIR, XRF, ^{29}Si-MAS NMR, diffuse reflectance UV–Vis and nitrogen adsorption–desorption isotherms (pore volume and size distribution are calculated by BJH analysis of the adsorption branch of the isotherm). In addition, X-ray photoelectron spectroscopy (XPS) and FTIR of adsorbed deuteroacetonitrile were also used to determine titanium sites on the catalyst surface.

3. Results and discussion

The influence of the silylation procedure has been studied not only from the point of view of the catalytic properties of the samples but also through the changes induced in their physico-chemical properties. Table 1 shows the composition, textural properties and reaction parameters for normal Ti-containing xerogels (calcined and non-calcined) and silylated xerogels (with and without thermal treatment). For

Table 1
Textural properties and catalytic activity for: (a) Ti impregnated silica, (b) normal Ti-containing xerogel, (c) sample b calcined, (d) silylated xerogel (TMCS/SiO_2=0.46), (e) sample d calcined (ST=styrene; SO=styrene oxide; BDH=benzaldehyde; 2EET=2-phenyl-2-*tert*-butoxyethanol; TON=mole of ST converted per mole of Ti and hour)

Sample	Catalyst activity							Textural properties		
	Si/Ti (XRF)	X_{TBHP} (%)	X_{ST} (%)	TON (h^{-1})	S_{SO} (%)	S_{BDH} (%)	S_{2EET} (%)	$^{B.E.T}$area ($m^2\,g^{-1}$)	V_P^{ADS} ($cm^3\,g^{-1}$)	R_P^{ADS} (Å)
Blank	–	3.9	0.6	–	86.4	13.6	0.0	–	–	–
a	54	30.2	9.8	35	81.5	1.4	17.1	553	0.3	15
b	43	12.7	2.9	7	72.1	15.1	12.8	637	1.0	28
c	43	41.8	15.9	37	65.7	1.4	32.9	608	0.9	28
d	73	41.5	15.9	63	98.6	1.4	0.0	723	3.0	66
e	73	41.6	17.6	66	87.7	1.2	11.1	711	2.3	62

comparison a blank reaction without catalyst has been included as well as the result obtained with a $TiCl_4$ impregnated silica. Silylated samples (calcined and non-calcined) presented a higher activity than their non-silylated counterparts, mainly if activity per Ti atom is compared. This difference is noteworthy for the non-calcined pair, where the silylated xerogel shows fivefold oxidation activity than the non-silylated one. In all cases selectivity towards styrene oxide (SO) is above 60% with a remarkable value (98.6%) for the silylated sample. Two by-products are detected: benzaldehyde (BDH) coming from the oxidative cleavage of styrene oxide and 2-phenyl-2-*tert*-butoxyethanol (2EET) formed through the nucleophilic attack of Bu^tOH to the oxirane ring of the primary product. From the textural properties summarised in Table 1, the silylation procedure leads to a sharp increase in the pore volume and pore sizes of the solid samples that should expose more Ti atoms for comparable BET surface areas, although the reaction of TMCS with the hydroxyl groups of the gel also decreases the Ti/Si atomic ratio. It is noteworthy how the silylated samples show the highest styrene and TBHP conversion, although the SiO_2 content is almost twice corresponding to the non-silylated ones.

Since no clear differences were found among the samples regarding the Ti coordination by means of UV–Vis spectroscopy, XPS analysis were carried out to explain the catalytic results obtained. As it will be published elsewhere [7], the binding energies of Ti $2p_{3/2}$ and O 1s core levels confirm the absence of TiO_2 segregated phases and the presence of highly dispersed Ti atoms in tetrahedral coordination.

Fig. 1 presents the ^{29}Si-MAS NMR and FTIR spectra between 2775 and 4000 cm^{-1} for these samples. Both techniques reveal that calcination or silylation of a normal xerogel remove hydroxyl groups from the solid surface. Thus, ^{29}Si-MAS NMR spectra exhibit two broad features associated with Q^3 (-95 to -104 ppm) and Q^4 (-104 to -115 ppm) Si connectivities. Peaks in the Q^3 region are due to silanol groups, while those in the Q^4 region are attributed to Si connected to four Si atoms through O bridges. An extra peak, located at 15 ppm upfield is observed for the silylated sample and assigned to trimethylsilyl groups coming from the reaction of TMCS with the silanol groups of the gel surface [8]. The ^{29}Si-MAS NMR spectrum corresponding to a normal non-calcined xerogel shows an additional peak located at ca. -90 ppm associated with geminal $Si(OH)_2$ groups (Q^2). This spectrum shows clear differences compared to silylated or calcined samples, in which a large decrease in the Q^2 and Q^3 contributions are observed. In a similar way, the broad band (centred ca. 3500 cm^{-1}) shown in the IR spectra of these samples is attributed to different Si–OH groups and trapped water, although in this case it is not possible to assign single features to each type of SiOH groups. In any case, this broad band clearly drops when the IR spectrum of the silylated sample is observed. From the analysis of all these data, the oxidation activity seems to be related with the presence of non-saturated silanol groups (Q^2 and Q^3) since the sample with the largest contribution of both features shows the lowest styrene conversion. The Q^3 groups still present in the calcined xerogel or in the silylated and calcined sample seems to be related to the formation of 2EET. The silylation procedure leads to a sharp decrease in the Q^3 contribution and therefore the removal of the secondary reaction.

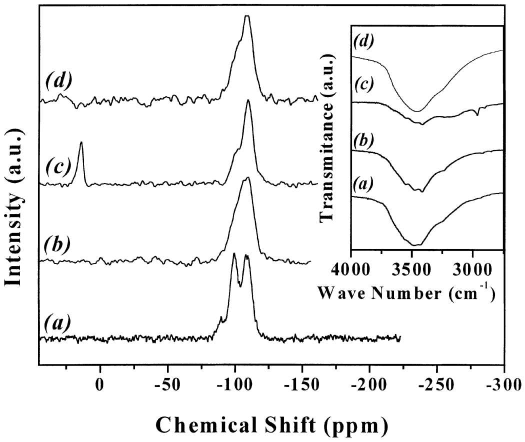

Fig. 1. ^{29}Si MAS NMR spectra: (a) normal Ti-containing xerogel; (b) sample b calcined; (c) silylated xerogel ($TMCS/SiO_2=0.46$); (d) sample d calcined. Inset: FTIR spectra for these samples in the region 2775–4000 cm^{-1}.

In recent literature different catalytic system such as Ti-MCM41 [6] and Ti-MCM48 [9] have been modified by means of silylation treatment, reaching better oxidation activities and selectivities due to the hydrophobicity of the catalysts. This increase in the epoxidation activity with H_2O_2 [9] has been related to the presence of the catalyst in the organic phase preventing the oxidation inhibition caused by water.

Table 2
Influence of TMCS loading on Ti exposed and catalyst activity

$TMCS/SiO_2$ (^{29}Si NMR)	Si/Ti XFR (XPS)	X_{TBHP} (%)	X_{ST} (%)	S_{SO} (%)	S_{2EET} (%)	TON (mol ST/mol Ti h)
0.00 (0.00)	43 (56)	12.7	2.9	72.1	12.8	7.0
0.09 (0.05)	54 (58)	32.1	11.2	93.5	5.4	32.8
0.23 (0.18)	64 (87)	42.1	18.5	99.1	0.0	62.1
0.46 (0.20)	73 (92)	41.5	15.9	98.7	0.0	63.1

On the other hand, Corma et al. [6] have attributed the better performance of the silylated catalysts to the absence of diol formation that deactivates the Ti centres rather than intrinsic changes in the oxidation active sites.

Since hydrophobicity affects so thoroughly the catalytic activity, a deeper study of the silylation procedure has been made. With this aim, samples with different TMCS loading were prepared (Table 2). It is worth mentioning that, even for the smaller $TMCS/SiO_2$ ratio, there is a sharp increase in the styrene conversion as well as in the epoxide selectivity or the TBHP efficiency. As the $TMCS/SiO_2$ molar ratio in the solution is increased, the $TMCS/SiO_2$ ratio measured in the solid increases up to a certain limit regardless the amount of TMCS used for the silylation treatment. Thus, for a molar ratio above 0.23, there is not significant TMCS incorporation which is also shown in the trend observed for styrene and TBHP conversions or the selectivity. With the highest TMCS loadings the formation of 2EET is totally avoided. Although the silylation reaction increases the Si/Ti molar ratio of the samples, not only the bulk but also that on the surface, it is remarkable, the improvement in the turnover number achieved through this treatment probably due to changes induced in the Ti sites since water or diol are absent in this reaction system.

Fig. 2 shows the nitrogen adsorption–desorption isotherms and the pore size distribution of the samples described above. All isotherms correspond to Type IV isotherm with the hysteresis loop that indicates the presence of mesopores in the solids. However, there is a strong change for high partial pressures when the sample is treated with TMCS. In this case, the last part of the isotherm rises sharply and no plateau is found like in the non-silylated sample. This may indicate the presence of slit-shape pores, large pores in the range of mesopores or even non-rigid structures capable to swallow once capillary condensation takes place. The changes introduced in the textural properties of the samples with different silylation level are clearly displayed in the pore size distribution with a shift for the maximum of each distribution towards higher pore sizes as the $TMCS/SiO_2$ ratio is increased. The limit for the TMCS loading above mentioned is also confirmed by means of this technique, since there are not significant changes in the isotherm or in the pore size distribution for the samples with TMCS/silica ratios above 0.23.

Again ^{29}Si-MAS NMR and FTIR spectra reveal clear changes to explain the different reactivity of these samples. There has been already mentioned the possible relationship between the OH population on the catalyst surface and its activity in the epoxidation reaction. Therefore, it should be reasonable, attending to the results summarised in Table 2, to find a decrease in the amount of the silanol groups present on the samples as the TMCS loading increases. Fig. 3 displays the ^{29}Si-MAS NMR and FTIR spectra for the samples studied in this section. The deconvolution of the global

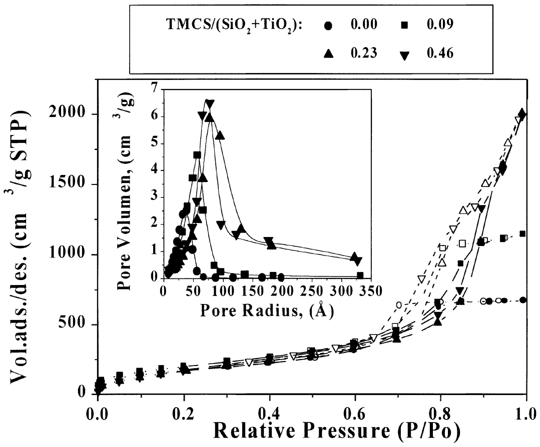

Fig. 2. N_2 adsorption–desorption isotherms and pore size distributions for samples with different TMCS loading.

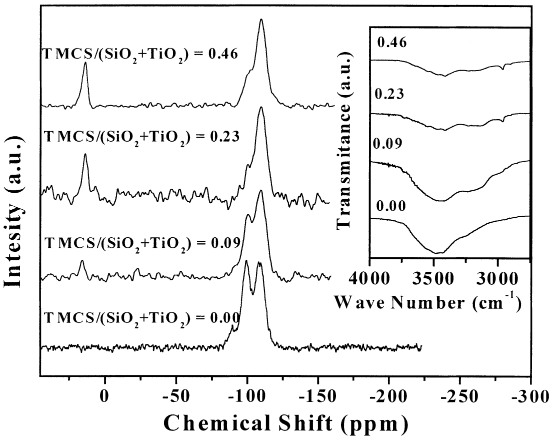

Fig. 3. ^{29}Si-MAS NMR and FTIR (2775–4000 cm^{-1}) for samples with different TMCS loading.

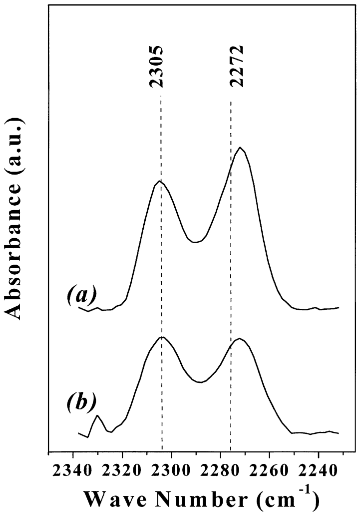

Fig. 4. FTIR of adsorbed CDCN$_3$: (a) normal xerogel and (b) silylated xerogel.

signal into Q^2, Q^3 and Q^4 peaks for all the samples shows a clear decrease of the silanols groups as the TMCS loadings are increased. Thus (Q^2+Q^3)/Q^4 ratio values varies from 0.9 for the normal non-calcined xerogel to 0.4 for the sample prepared with the lowest TMCS/SiO$_2$ ratio (0.09). The other two samples have similar values for the (Q^2+Q^3)/Q^4, ca. 0.3. It is noteworthy the limit found again in the silylation treatment for TMCS/SiO$_2$ ratios above 0.23 and the existence of a barrier for the total silylation of SiOH groups. Similarly the FTIR spectra of these samples show a decrease in the intensity of the broad band centred at 3500 cm^{-1}, associated to silanol groups and adsorbed water, indicating also the hydrophobicity of the more silylated samples.

The comparison between the bulk chemical composition of these samples obtained by XRF and that on the surface determined by XPS (Table 2) do not show large differences indicating that the silylation takes place not only on the outer surface of the catalyst particles but also within the pore system. A more surface sensitive technique for the titration of titanium sites is based on the FTIR analyses of adsorbed deuteroacetonitrile [10]. The IR spectra for the normal (a) and silylated (b) xerogel (Fig. 4) show two bands present also in all the other samples: one located at 2272 cm^{-1} assigned to CD$_3$CN adsorbed on hydroxyl groups [10], and another located at 2305 cm^{-1} attributed to Lewis acidity associated to coordinatively unsaturated tetrahedral Ti ions incorporated into the silica matrix. Although the Si/Ti molar ratios determined by this technique have higher values than those measured by XRF and XPS, there are no large differences in the amount of Ti atoms titrated between both samples to justify the sharp increase in the oxidation activity when the silylated xerogel is used.

For comparison, a silylating agent of different nature was used. Table 3 shows the reaction results obtained for two titanium-containing xerogels treated with the same silylant agent/SiO$_2$ molar ratio in the solution, TMCS and HMDSZ. XRF analysis shows a lower Si/Ti molar ratio for the sample treated with HMDSZ (0.23), as well as lower oxidation activity and

Table 3
Influence of the nature of silylating agent on the catalyst activity

Silylating agent	Si/Ti (XRF)	X_{TBHP} (%)	X_{ST} (%)	S_{SO} (%)	S_{2EET} (%)	TON (mol ST/mol Ti h)
TMCS	64	42.1	18.5	99.1	0.0	62.1
HMDSZ	65	31.5	11.2	86.0	12.7	39.7

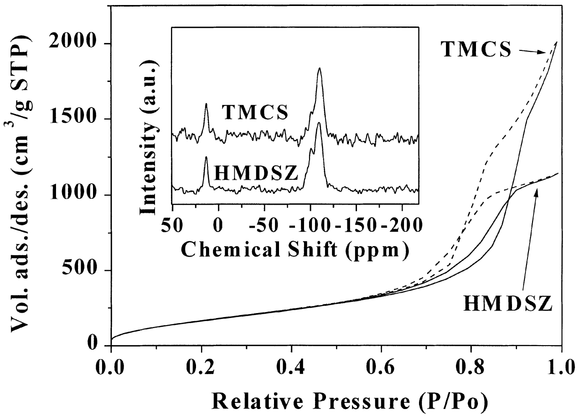

Fig. 5. N_2 adsorption–desorption isotherms and ^{29}Si-MAS NMR for samples with different silylating agent.

styrene oxide selectivity, suggesting the presence of non-reacted SiOH groups in the surface of this sample.

Fig. 5 shows the N_2 adsorption–desorption isotherms and the ^{29}Si-MAS NMR spectra for these two silylated xerogels. By analogy with Fig. 2, the silylation reaction with HMDSZ has a lower extension than that corresponding to TMCS since the isotherms with the latter reach higher N_2 uptake values for P/P_0 above 0.6. In the same way, ^{29}Si-MAS NMR shows a higher Q^3/Q^4 ratio for the sample silylated with disilazane (0.4 vs 0.3) as well as a lower TMS/(Q^3+Q^4) ratio. These results indicate that the efficiency of the HMDSZ silylation of the gel surface is lower probably due to a lower reactivity of this compound with hydroxyl groups, at least for the conditions used for such treatment in this work.

4. Conclusions

The removal of the OH groups present in TiO_2–SiO_2 mixed oxides leads to an improvement of the performance of this type of catalyst in the epoxidation of styrene with TBHP. This enhancement of the oxidation activity is related with changes in the catalytic site environment induced by calcination or reaction of silanol groups with silylating agents. The latter procedure also has influence on the styrene oxide selectivity, preventing the formation of secondary products coming from the oxirane ring opening. The extension of the silylation reaction has a limit as it has been detected through the use of different techniques. The efficiency of the silylation treatment depends on the nature of the agent used in similar reaction conditions.

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