Control of the Texture of Titania−Silica Mixed Oxides Prepared by Nonhydrolytic Sol−Gel

V. Lafond, P. H. Mutin,* and A. Vioux

UMR CNRS 5637, Chimie Moléculaire et Organisation du Solide, Université Montpellier II, Case Courrier 007, F34095 Montpellier Cedex 05, France

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A series of titania−silica xerogels was prepared using nonhydrolytic sol−gel routes. The parameters explored were the nature of the oxygen donors (alkoxides or diisopropyl ether), the amount of liquid phase in the gel, the titanium content, the reaction time, and the reaction temperature. The samples were characterized using FT-Raman, FTIR, and DRUV−Vis spectroscopy, XRD, TGA, and N_2 physisorption. Spectroscopic data indicated a molecular scale dispersion of the Ti atoms. The titania−silica nonhydrolytic xerogels were mesoporous with specific surface areas up to 1040 $m^2\ g^{-1}$ and pore volumes up to 1.53 $cm^3\ g^{-1}$. The mesoporous texture of the xerogels is ascribed to the high degree of condensation of nonhydrolytic gels, which prevents complete pore collapse during the evaporation of solvent. The average pore diameter could be adjusted in the 2−6 nm range by changing the volume fraction of liquid phase, reaction time, or reaction temperature.

Introduction

Titania−silica mixed oxides have attracted considerable attention owing to their applications as advanced materials,[1−3] catalyst supports,[4,5] and catalysts.[6]

In particular, titania−silica solids have been extensively used as catalysts for the epoxidation of alkenes by alkylhydroperoxides. Epoxides are major intermediates in organic synthesis, and the development of heterogeneous epoxidation catalysts is of great industrial and academic importance.[7,8]

The active sites in titania−silica epoxidation catalysts are believed to be isolated or oligomeric Ti^{IV} surface species bonded to the silica network by Si−O−Ti bridges.[9−11] Accordingly, the key points for getting epoxidation catalysts efficient with a large range of organic substrates are (a) molecular scale dispersion of the Ti atoms, (b) high surface area, and (c) pore diameters large enough to accommodate bulky olefins and organic hydroperoxides.

The sol−gel process can offer decisive advantages for the synthesis of heterogeneous catalysts, such as molecular scale homogeneity, high purity, and controlled texture of the final material.[12−15] Indeed, amorphous titania−silica mixed oxides prepared by sol−gel processing have been recognized in the last 10 years as highly efficient epoxidation catalysts.[16−20]

Sol−gel derived titania−silica catalysts are usually prepared by hydrolysis−condensation of alkoxide precursors. Sophisticated procedures have been used to cope with the very different reaction rates of titanium and silicon alkoxides, including strongly acidic hydrolysis,[21] modification of the titanium alkoxides by a chelating ligand,[22−26] controlling the rate of addition of water,[27] prehydrolysis of the silicon alkoxide,[5,24−26,28−31]

* Corresponding author. E-mail mutin@univ-montp2.fr.

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or using single-source precursors with preexisting Si–O–Ti linkages.[32]

In all cases, acidic conditions are required to optimize the dispersion of Ti atoms, but under these conditions the xerogels obtained by routine drying (solvent evaporation) are predominantly microporous,[17,19,21,24,27,33,34] due to the collapse of the relatively loose acidic gel structure under the high capillary forces arising from the liquid–vapor interface.[13] To increase the pore diameter of the materials, elaborate drying procedures are needed. Extraction of the titania–silica gels with supercritical CO_2 suppresses capillary stress and leads to highly porous materials, called aerogels, with excellent performances in olefin epoxidation.[19,24] Alternatively, the collapse of the pore structure of titania–silica gels during solvent evaporation can be effectively minimized either by washing with *n*-hexane and silylation of the gels before drying[5,35] or by aging the wet gels for 10 days then washing them with *n*-heptane, a low-surface-tension solvent, to reduce the capillary stress during drying.[31]

The nonhydrolytic sol–gel process is based on the formation of M–O–M bridges by thermal condensation between metal chlorides and metal alkoxides (eq 1).[36]

$$\text{M–Cl} + \text{M–OR} \rightarrow \text{M–O–M} + \text{R–Cl} \qquad (1)$$

The alkoxy groups may be produced in situ, for instance by etherolysis (eq 2) of chlorides, which offers two routes to oxides, the so-called "alkoxide route" (eq 3) and "ether route" (eq 4).

$$\text{M–Cl} + \text{ROR} \rightarrow \text{M–OR} + \text{RCl} \qquad (2)$$

$$\text{MCl}_n + \text{M(OR)}_n \rightarrow 2\ \text{MO}_{n/2} + n\text{RCl} \qquad (3)$$

$$\text{MCl}_n + {}^{n}/_{2}\text{ROR} \rightarrow \text{MO}_{n/2} + n\text{RCl} \qquad (4)$$

This process, which was developed in Montpellier, offers a very simple and efficient way to synthesize mixed oxides[37–41] starting from mixtures of alkoxides and chlorides (alkoxide route) or from mixture of chlorides and an organic ether (ether route).

The synthesis by nonhydrolytic sol–gel routes of titania–silica xerogels with good homogeneity and high surface area has already been reported,[37] and these materials are promising catalysts for the epoxidation of alkenes by alkylhydroperoxides.[42]

The aim of this work was to identify the parameters that govern the texture of such nonhydrolytic titania–silica xerogels and calcined xerogels. The parameters explored were the nature of the oxygen donor (alkoxides or ether), the amount of solvent, the titanium content, the reaction time, and the reaction temperature. The homogeneity of the samples was examined using X-ray diffraction (XRD) and various spectroscopic techniques (FT-Raman, FTIR, DRUV–Vis). The degree of condensation of the xerogels was inferred from the weight loss during calcination, and the texture of the samples was studied using N_2 physisorption.

Experimental Section

All manipulations were performed under an argon atmosphere using standard Schlenck techniques and an inflatable glovebox; dry, degassed solvents were used. $Si(O^iPr)_4$ was prepared according to the literature procedure.[43] $SiCl_4$ (Acros 99.8%), $TiCl_4$ (Aldrich 99.9%), and $Ti(O^iPr)_4$ (Lancaster 97%) were used as received. $^iPr_2O$ was dried by distillation over sodium wire.

Powder X-ray diffraction (XRD) patterns were obtained on a Siefert MZ IV diffractometer using Cu Kα radiation. The transmission FTIR spectra of the samples in KBr pellets were recorded on a Nicolet Thermo Avatar 320 spectrometer. Fourier transform micro-Raman (FT-Raman) spectra were obtained on a Bruker RFS 100 spectrometer, using a 500 mW YAG laser beam at 1064 nm to avoid fluorescence; 4000 scans were accumulated, at a resolution of 2 cm^{-1}; a background spectrum of silica (550 $m^2\ g^{-1}$) was subtracted in all cases. Diffuse reflectance DRUV–Vis spectra were recorded under ambient conditions on a Perkin-Elmer Lambda 14 spectrometer equipped with a $BaSO_4$ integration sphere; the samples stored under argon were diluted in $BaSO_4$; spectra were plotted using the Kubelka–Munk function. N_2 physisorption experiments were performed at 77 K on a Micromeritics ASAP 2010. The micropore volume was estimated using *t*-plot analysis in the 3.5–5 Å range; the pore size distribution was derived from the desorption using the BJH method; the Harkins and Jura standard isotherm was used for both methods.[44] Thermal analysis was performed in dry air, at a heating rate of 10 K min^{-1}, on a Netzch STA 409 thermobalance.

Preparation of Titania–Silica Samples. In all cases, reactants were used in stoichiometric amount (eqs 3 and 4) as shown in Table 1. The gels were prepared in 5-g quantities in 100-mL sealed glass tubes under autogenous pressure at 110 °C (ca 7 bar) or 150 °C (ca 16 bar), with reaction times ranging from 21 to 188 h. CH_2Cl_2 was added to dissolve the chloroisopropoxide precipitate or to increase the volume of liquid phase in the tube. Under these conditions, liquid ^iPrCl and CH_2Cl_2 are in equilibrium with their vapor. Alternatively, one sample (10SiTiA3) was prepared in a 0.6-g quantity, without CH_2Cl_2; in this case, all the ^iPrCl is in the gas phase.

In a typical preparation, the chloride(s) was first placed in a Schlenck tube equipped with a magnetic stirring bar and connected to an argon line. After addition of the oxygen donor (alkoxide(s) or diisopropyl ether) and CH_2Cl_2 (if any), the mixture was stirred for 1 h (in the ether route a chloroisopropoxide precipitate may form intermediately; this precipitate dissolved on gentle heating or when CH_2Cl_2 was added). The mixture was then transferred into a glass tube, frozen in liquid nitrogen under vacuum, and then the tube was sealed. The sealed tube was heated at 110 °C for 4 days in an oven, leading to a gel surrounded by syneresis liquid. After cooling, the tube was opened and the syneresis liquid was withdrawn by syringe, leading to a yellow, hard, brittle gel. This gel was crushed and washed 3× with 5 mL of CH_2Cl_2. The xerogel was obtained by drying at 120 °C under vacuum (10 Pa) for 12 h. Calcination of the samples was performed in a tube furnace

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Table 1. Synthesis Conditions for the Titania−Silica Gels

xerogel sample	molar ratio of reactants	CH_2Cl_2 (mL)	reaction temp. (°C)	reaction time (h)
10SiTiA1	$Ti(O^iPr)_4$:5.5 $SiCl_4$:4.5 $Si(O^iPr)_4$	20	110	96
10SiTiA2	$Ti(O^iPr)_4$:5.5 $SiCl_4$:4.5 $Si(O^iPr)_4$	0	110	96
10SiTiA3[a]	$Ti(O^iPr)_4$:5.5 $SiCl_4$:4.5 $Si(O^iPr)_4$	0	110	96
7.5SiTiE1	$TiCl_4$:7.5 $SiCl_4$:17 $^iPr_2O$	30	110	96
8.5SiTiE1	$TiCl_4$:8.5 $SiCl_4$:19 $^iPr_2O$	16	150	96
10SiTiE1	$TiCl_4$:10 $SiCl_4$:22 $^iPr_2O$	20	110	96
17SiTiE1	$TiCl_4$:17 $SiCl_4$:35 $^iPr_2O$	20	110	96
17SiTiE2	$TiCl_4$:17 $SiCl_4$:35 $^iPr_2O$	17	150	96
10SiTiE2[b]	$TiCl_4$:10 $SiCl_4$:22 $^iPr_2O$	8	110	21
10SiTiE3[b]	idem	8	110	47
10SiTiE4[b]	idem	8	110	139
10SiTiE5[b]	idem	8	110	188

[a] Prepared in 0.6-g quantity, all ^{i}PrCl in the gas phase. [b] Prepared from the same reaction mixture in 2-g quantity.

Table 2. Weight Loss during Calcination for 5 Hours at 500 °C and Corresponding Estimated Condensation Degree of Titania−Silica Nonhydrolytic Xerogels

sample	parameters varied	weight loss (%)	condensation degree (%)
10SiTiA1	standard (alkoxide route)	14.3	91
7.5SiTiE1	Si/Ti 7.5	15.4	90
10SiTiE1	standard (ether route)	17.7	88
17SiTiE1	Si/Ti 17	31.4	73
17SiTiE2	Si/Ti 17, 150 °C	14.3	91
10SiTiE2	21 h reaction time	24.0	82
10SiTiE5	188 h reaction time	11.4	93

under flowing, dry air (50 mL min^{-1}) for 5 h at 500 °C (heating rate 10 °C min^{-1}).

The samples were labeled according to their nominal Si/Ti ratio, preparation method (alkoxide or ether route), sample number, and heat treatment. For instance, the sample 10SiTiA2 is the second xerogel sample with a Si/Ti ratio of 10 prepared by the alkoxide route; 8.5SiTiE1c is the first sample with a Si/Ti ratio of 8.5, prepared by the ether route, and calcined for 5 h at 500 °C.

Results

Synthesis of the Gels. A series of nonhydrolytic titania−silica xerogels were prepared for this study (Table 1), either by the alkoxide route using $Si(O^iPr)_4$, $SiCl_4$, and $Ti(O^iPr)_4$ precursors, or by the ether route starting from $SiCl_4$ and $TiCl_4$ precursors and $(^iPr)_2O$ as an oxygen donor. The parameters explored were the volume fraction of liquid phase (^{i}PrCl + solvent) in the gel, the titanium content (Si/Ti ratio), the reaction temperature, and the reaction time.

It has already been reported that nonhydrolytic titania−silica xerogels usually exhibit a very high degree of condensation (typically around 90%) as shown by elemental analysis of residual Cl and OR groups.[37] Here, the degree of condensation of the xerogels was estimated from their weight loss during calcinations in air at 500 °C (Table 2), which ideally corresponds to the conversion of residual O^iPr and Cl groups into OH groups, according to

$$Si_RTiO_{[2(R+1)-x]}Cl_x(OiPr)_x \rightarrow Si_RTiO_{[2(R+1)-x]}(OH)_{2x}$$

The estimated degree of condensation of our xerogels thus calculated (Table 2) was very high (about 90%), excepted for the sample 17SiTiE1 (low titanium content) and 10SiTiE2 (short reaction time).

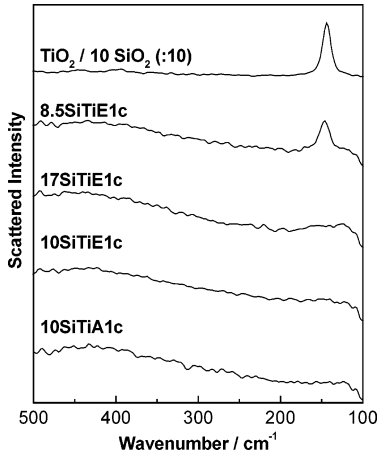

Figure 1. FT-Raman spectra of calcined titania−silica nonhydrolytic xerogels and of a physical mixture of 11.8 wt % anatase in silica (intensities divided by a factor of 10).

Structural Characterization. The homogeneity of selected samples was evaluated using different techniques. All the samples calcined at 500 °C for 5 h were amorphous to X-ray diffraction, indicating the absence of TiO_2 domains larger than about 5 nm. FT-Raman spectroscopy is extremely sensitive to the presence of anatase nanocrystals, that lead to a very strong line at 144 cm^{-1}, with a minimum detectable amount of 0.05 wt % TiO_2.[45] As shown in Figure 1, anatase traces were detected only in sample 8.5SiTiE1c, which was prepared at 150 °C with a relatively high TiO_2 content (13.6 wt %). Comparison with the spectrum of a physical mixture of anatase in silica recorded in the same conditions indicated that the amount of anatase crystallites in 8.5SiTiE1c was very low, around 0.6 wt %.

The FTIR spectra of all of our xerogels and calcined xerogels in the 1400−700 cm^{-1} range (Figure 2) exhibited three broad bands typical of silica at 1200, 1078 cm^{-1} (asymmetric Si−O−Si stretching vibration), and at 800 cm^{-1} (symmetric Si−O−Si stretching vibration).[13] In addition, an intense band was observed at about 950 cm^{-1}. This band has been ascribed to a vibration involving SiO_4 tetrahedra bonded to a titanium atom through Si−O−Ti bonds.[6,11,17,20,24,37,46] The presence in the same region of a band at 970 cm^{-1}

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Table 3. Textural Characteristics of Noncalcined (nc) and Calcined (c) Titania–Silica Xerogels

sample	parameters varied	calcination	S_{BET} (m^2g^{-1})[a]	V_P (cm^3g^{-1})[b]	D_P (nm)[c]	V_{micro} (cm^3g^{-1})[d]	S_{meso} (m^2g^{-1})[e]
10SiTiA1	standard[f] (alkoxide route)	nc	1026	1.28	5.0	0	860
		c	858	0.96	4.5	0.02	710
10SiTiA2	no solvent	nc	1043	0.82	3.2	0	710
		c	781	0.52	2.7	0.01	440
10SiTiA3	no liquid phase	nc	450	0.24	2.1	0.18	20
7.5SiTiE1	Si/Ti 7.5	nc	1000	1.25	5.0	0	830
		c	870	0.97	4.5	0.01	720
10SiTiE1	standard[f] (ether route)	nc	1000	1.14	4.6	0	820
		c	800	0.80	4.0	0.01	650
17SiTiE1	Si/Ti 17	nc	550	0.33	2.4	0.06	160
17SiTiE2	Si/Ti 17, 150 °C	nc	1030	1.54	6.1	0	870
10SiTiE2	21 h reaction time	c	590	0.34	2.3	0.13	140
10SiTiE3	47 h reaction time	c	840	0.70	3.3	0.05	610
10SiTiE4	139 h reaction time	c	960	1.23	5.1	0.02	780
10SiTiE5	188 h reaction time	c	980	1.45	6.0	0.02	790

[a] BET specific surface area. [b] Total pore volume at P/P_0 0.99. [c] Average pore diameter (4 V_p/S_{BET}). [d] t-Plot micropore volume. [e] BJH desorption cumulative surface area of pores between 2 and 300 nm in diameter. [f] Standard conditions: 74 mmol Si, 7.4 mmol Ti, 20 cm^3 CH_2Cl_2, 4 days reaction at 110 °C.

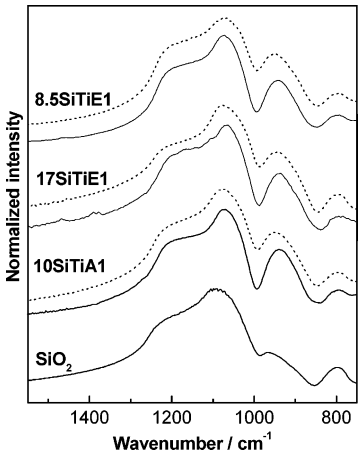

Figure 2. FTIR spectra of silica (bottom), selected xerogels (full lines), and calcined xerogels (dotted lines).

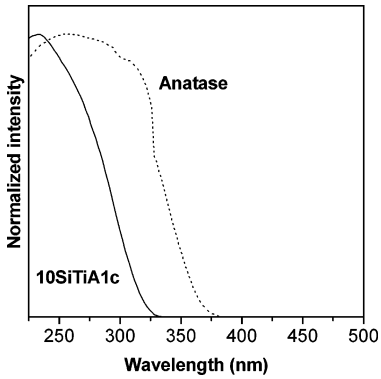

Figure 3. Normalized DRUV–Vis spectra of anatase (dotted line) and 10SiTiA1c (full line).

arising from Si–OH groups prevents quantitative analysis; however, the high intensity of the 950 cm^{-1} band in our materials points to the presence of a large amount of Si–O–Ti linkages. The spectra of the calcined xerogels were very similar, indicating that the majority of Si–O–Ti linkages were retained during calcination.

The DRUV–Vis spectra of calcined xerogel samples (10SiTiA2c, 10SiTiE1c, 17SiTiE1c, and 8.5SiTiE1c) were recorded under ambient conditions. All spectra were similar, with an absorption onset around 320 nm, blue-shifted by about 50 nm from the absorption of anatase (Figure 3). In titania–silica materials, a blue shift of the absorption onset may indicate the presence of TiO_2 nanodomains (quantum size effect) or the presence of Ti species with different first and/or second coordination spheres (matrix or support effect).[6] Our FT-Raman results suggested that very few (if any) anatase nanodomains are present in our samples, which points to a matrix effect. Isolated tetrahedral $Ti(OSi)_3OH$ sites in titanium silicalite[47] or in titania–silica catalysts prepared by grafting[46,48] give rise to charge transfer (LMCT) bands with very low absorption onsets, around 250–270 nm. Isolated $Ti(OSi)_4$ sites in titanium silicalite or in a titania–silica xerogel with a very low Ti content (1.5%) led to LMCT bands with absorption onsets at about 285 nm for dehydrated samples, and about 295 nm for hydrated samples.[47] The higher absorption onset (320 nm) of our calcined xerogels is consistent with a distribution of isolated and oligomeric Ti sites bonded to the silica matrix by Si–O–Ti bridges, as reported for other sol–gel titania–silica catalysts with relatively high Ti contents.[11]

Texture of the Xerogels. The xerogels obtained using "standard" conditions (Si/Ti = 10, 20 cm^3 of CH_2Cl_2, 4 days reaction at 110 °C) either by the alkoxide route (10SiTiA1) or the ether route (10SiTiE1) showed extremely high surface areas (around 1000 $m^2\ g^{-1}$) and pore volumes (1.14 and 1.28 $cm^3\ g^{-1}$) (Table 3). Their N_2 adsorption–desorption isotherm (Figure 4a) was of type IV, according to the BDDT classification.[49] *t*-Plot analysis indicated the absence of micropores, and the pore size distribution (Figure 4b) showed that most of the pore volume was located in mesopores of diameters ranging from 3 to 10 nm. Calcination of the xerogels at 500 °C for 5 h led to a decrease (ca 20–30%) of the surface area and pore volume of the samples (Table 3), as exemplified in Figure 4 for the 10SiTiE1c sample.

In the synthesis of the 10SiTiA1 gel, the volume of liquid phase (CH_2Cl_2 + ^iPrCl) at 110 °C is about 31 cm^3,

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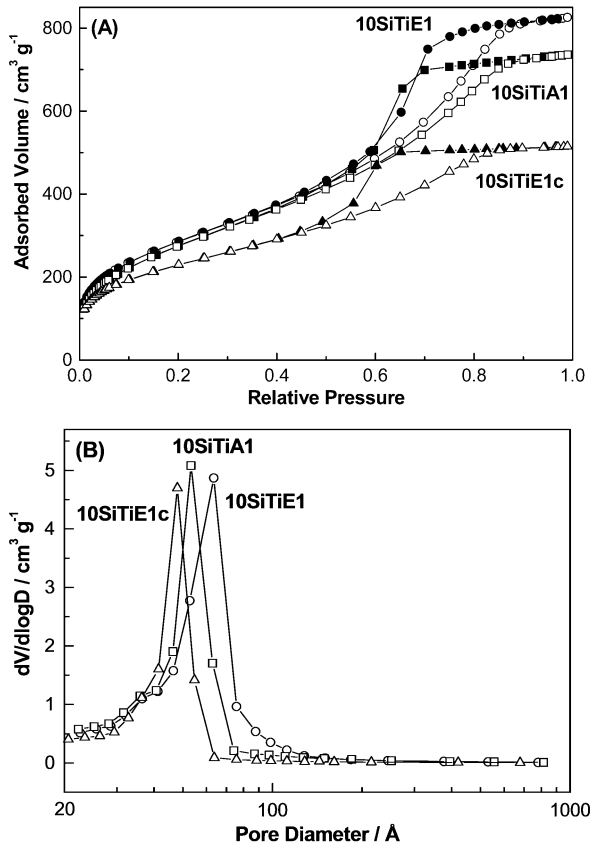

Figure 4. N_2 physisorption results at 77 K of "standard" xerogels prepared by the alkoxide route (10SiTiA1) or by the ether route (10SiTiE1), and of 10SiTiE1 calcined in air at 500 °C for 5 h (10SiTiE1c). (A) Adsorption−desorption isotherms (open and filled symbols correspond to the adsorption and desorption branches, respectively); (B) pore size distributions derived from the desorption branches, using the BJH method.

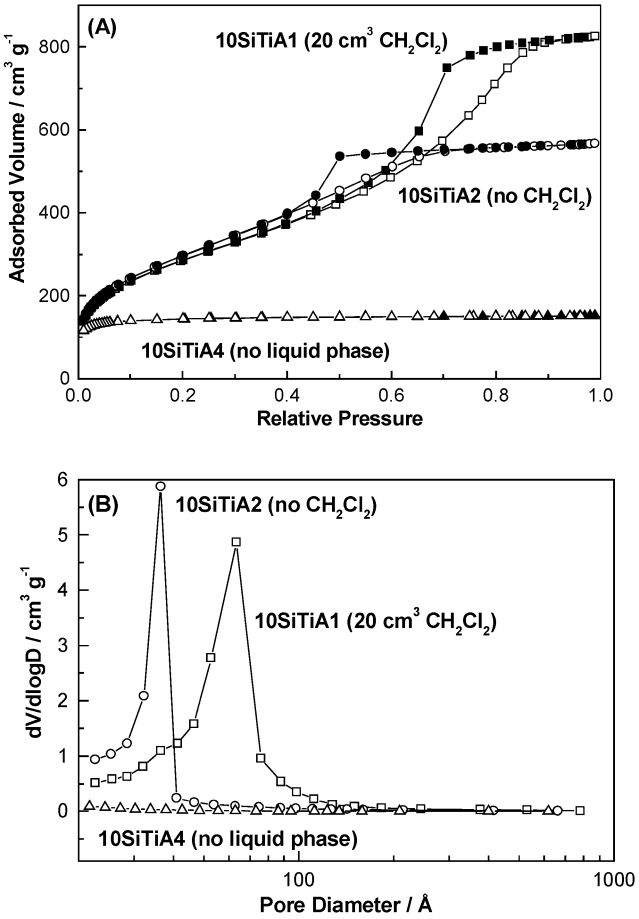

Figure 5. N_2 physisorption results at 77 K of xerogels prepared by the alkoxide route with different volume fractions of liquid phase. (A) Adsorption−desorption isotherms (open and filled symbols correspond to the adsorption and desorption branches, respectively); (B) pore size distributions derived from the desorption branches, using the BJH method.

assuming a degree of condensation of 80%. In the case of 10SiTiA2, prepared without CH_2Cl_2, the volume of liquid ^{i}PrCl at 110 °C is about 11 cm^3. The 10SiTiA3 sample was prepared in 0.6-g quantity, so that there was no liquid phase, all the ^{i}PrCl being in the gas phase. As shown in Figure 5 and Table 3, the texture of the xerogels depended strongly on the volume of liquid phase. The xerogel 10SiTiA2 is still purely mesoporous, but 10SiTiA2 is mostly microporous, as shown by its type I isotherm.

Comparison of physisorption data for xerogels 17SiTiE1 (7.3 wt % TiO_2), 10SiTiE1 (11.8 wt % TiO_2), and 7.5SiTiE1 (15.1 wt % TiO_2) (Figures 4 and 6) shows that the texture of nonhydrolytic xerogels also depended on the titanium content of the gel: the lower the titanium content, the lower the pore volume and average pore diameter. Thus, xerogel 17SiTiE1 is predominantly microporous, with a small pore volume (0.33 cm^3 g^{-1}). However, increasing the synthesis temperature to 150 °C led to an impressive increase in the pore volume, up to 1.54 cm^3 g^{-1} (Figure 6).

To evidence the influence of the reaction time, four samples prepared from the same reaction mixture were reacted at 110 °C for 21, 47, 139, and 188 h. The gel time was approximately 10 h, which means that the gels were aged for about 10 to 180 h at the reaction temperature. This aging had a remarkable influence on the texture of the calcined xerogels: pore volume and average pore diameter increased continuously with the aging time (Figure 7). Although the pore size distribution of the 188 h sample was bimodal, these results showed that the reaction time also allows a very simple and direct control on the texture of nonhydrolytic titania−silica.

Discussion

The nonhydrolytic sol−gel process provides very simple routes to homogeneous titania−silica materials with an excellent control on the texture. Both alkoxide and ether routes offer efficient one-step syntheses, whereas hydrolytic sol−gel syntheses often require complicated procedures to cope with the very different reactivities of titanium and silicon alkoxides. XRD and IR, Raman, and UV spectroscopies point to a molecular scale dispersion of the Ti atoms in nonhydrolytic samples prepared at 110 °C. This good homogeneity has been previously ascribed[37] to a catalysis by titanium Lewis acidic species[50] of the condensation around silicon, which is otherwise quite slow.[51]

(50) Arnal, P.; Corriu, R. J. P.; Leclercq, D.; Mutin, P. H.; Vioux, A. *Chem. Mater.* **1997**, *9*, 694.
(51) Bourget, L.; Corriu, R. J. P.; Leclercq, D.; Mutin, P. H.; Vioux, A. *J. Non-Cryst. Solids* **1998**, *242*, 81.

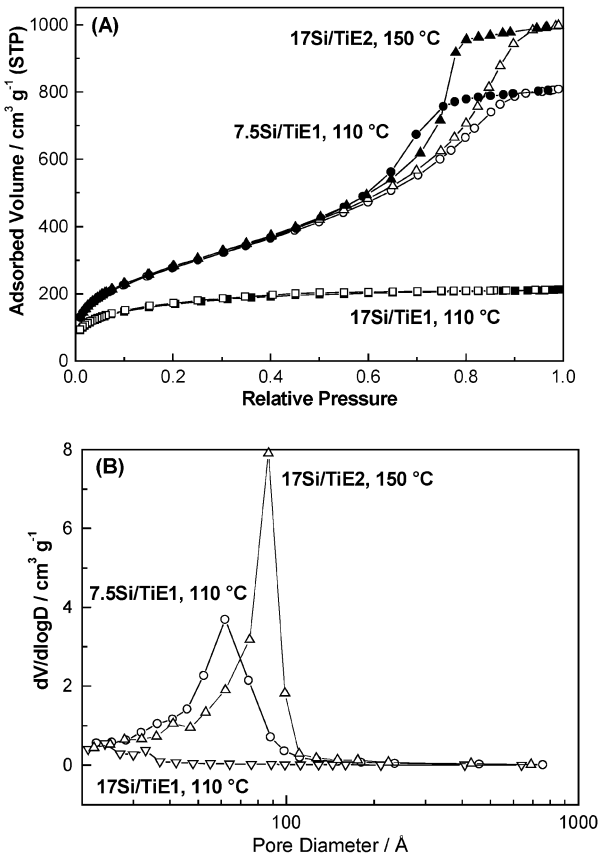

Figure 6. N_2 physisorption results at 77 K of xerogels prepared by the ether route with different Si/Ti ratios or at different temperatures. (A) Adsorption–desorption isotherms (open and filled symbols correspond to the adsorption and desorption branches, respectively); (B) pore size distributions derived from the desorption branches, using the BJH method.

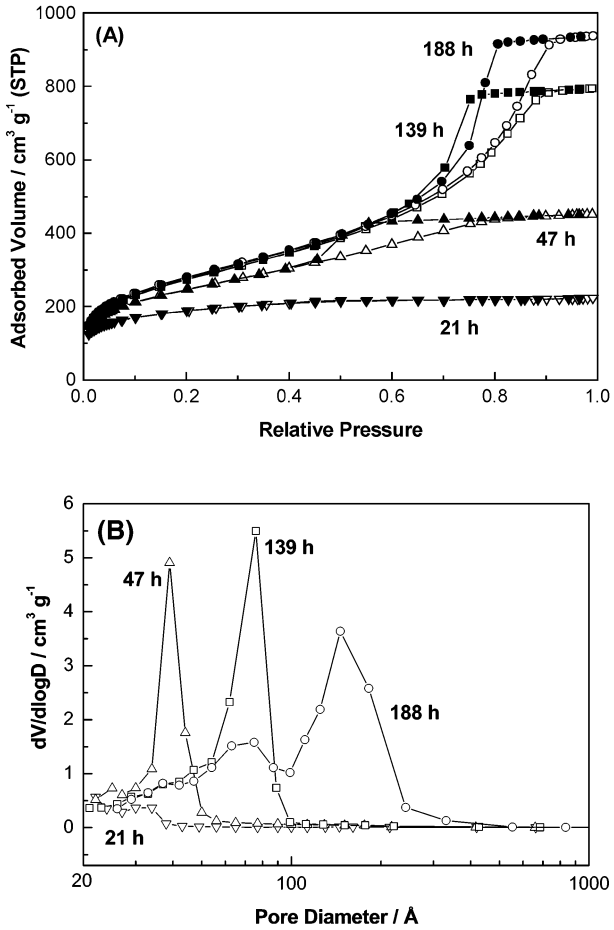

Figure 7. N_2 physisorption results at 77 K of calcined xerogels 10SiTiE2–5c prepared by the ether route at 110 °C with different reaction times. (A) Adsorption–desorption isotherms (open and filled symbols correspond to the adsorption and desorption branches, respectively); (B) pore size distributions derived from the desorption branches, using the BJH method.

Contrary to hydrolytic titania–silica xerogels that are usually microporous, "standard" nonhydrolytic xerogels are mesoporous, with pore diameters ranging from 3 to 10 nm (Figure 5), and have very high surface area and pore volumes. Hence, sophisticated drying procedures such as silylation, solvent exchange, and/or supercritical drying are not necessary. In addition, calcination of the xerogels at 500 °C for 5 h leads to a decrease of only 20 to 30% of the surface area and pore volume. The mesoporous texture of our xerogels indicates that they do not dramatically collapse under the capillary stresses resulting from solvent evaporation. The main reason for this is probably the very high degree of condensation of nonhydrolytic gels (around 90%), which leads to a very rigid oxide network. In addition, the interactions between the pore surface and the liquid phase are probably much weaker than those in hydrolytic xerogels: the surface of nonhydrolytic gels is covered by chloride and alkoxide groups instead of hydroxyl groups, and the liquid phase is constituted of ^{i}PrCl and CH_2Cl_2 instead of alcohol and water.

Our results show that the texture of nonhydrolytic xerogels strongly depends on several parameters such as the volume of liquid phase, reaction time and temperature, and the titanium content of the gel.

The nonhydrolytic sol–gel process offers the possibility to prepare gels not only without solvent but also in the absence of any liquid phase, which permits to evidence the importance of the liquid phase in the creation of the pores. Actually, porosity in a xerogel (or aerogel) mostly arises from the volume of liquid trapped in the wet gel; thus, the higher the volume fraction of liquid, the higher the porosity, provided that the gel does not completely collapse during drying. In our case, varying the volume of liquid-phase allows direct control of the texture of titania–silica xerogels, from microporous to mesoporous.

The influence of titanium content, reaction temperature, and reaction time is similar and may be understood in terms of condensation kinetics, keeping in mind that in our process the titanium species catalyze the condensation around the silicon atoms.[50] Indeed, the samples prepared with the lowest titanium content (17SiTiE1) or the shortest reaction time (10SiTiE2) exhibit the highest TGA weight loss (31.4 and 24.0%), hence the lowest degree of condensation (73 and 82%). Their low pore volume and pore size may thus be ascribed to the collapse of the oxide network during drying. Conversely, high reaction temperature, high titanium content, or long reaction times lead to mesoporous, well-condensed samples with high pore volumes and pore sizes.

Aging hydrolytic silica gels at high temperature may lead to an increase of pore size and a decrease of surface area, due to a dissolution–precipitation process.[13] A

similar process cannot be discarded in nonhydrolytic sol−gel process where redistribution of M−OM, M−O^{i}-Pr and M−Cl bonds (M = Si, Ti) could lead to soluble silicon and titanium oxo-chloroisopropoxide species. However, in our case the surface area increased during aging, indicating that such dissolution−precipitation remains marginal. Nevertheless, the traces of anatase detected in the 8.5SiTiE1 sample prepared at 150 °C suggests the occurrence of structural rearrangements at high temperature.

Conclusion

Nonhydrolytic sol−gel processing provides very simple syntheses of titania−silica xerogels and mixed oxides with both a high dispersion of Ti atoms and a controlled texture. The possibility to obtain highly condensed nonhydrolytic gels that withstand well the capillary stresses generated by solvent evaporation permits the synthesis of mesoporous xerogels with high pore volumes originating from the liquid phase trapped in the gel. Thus, the porosity of nonhydrolytic titania−silica gels is governed by the volume fraction of liquid phase and by the degree of condensation of the gel, which permits adjustment of the average pore diameter simply by changing the volume of solvent, the reaction time, or the reaction temperature. This should also be true for other metal oxide−silica systems, such as alumina−silica or zirconia−silica, which have many applications as catalysts and catalyst supports.

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