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Communications

One-Step Synthesis of Mesoporous Hybrid Titania−Silica Xerogels for the Epoxidation of Alkenes

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Owing to the industrial importance of epoxides as intermediates in organic synthesis, the sol−gel synthesis of titania−silica epoxidation catalysts has attracted considerable attention in the past 10 years.[1−4] Indeed, the sol−gel process offers the possibility to prepare homogeneous mixed oxides with high specific surface areas.[5] In addition, the low temperatures involved in this process allow the direct synthesis of hybrid gels containing covalently bound organic groups, using organosilicon precursors. Hybrid titania−silica catalysts containing $RSiO_{1.5}$ units (R = Me, Ph, acetoxypropyl, aminopropyl)[6−10] or Me_2SiO units[11,12] were prepared by conventional sol−gel processing (hydrolytic sol−gel), and it was found that the incorporation of both hydrophobic and polar organic groups could dramatically improve catalytic performance.[6−10,12,13] However, the synthesis of these hybrid catalysts by hydrolytic sol−gel procedures remains a challenge, for two main reasons: (i) First, the very different reaction rates of the titanium, silicon, and organosilicon alkoxide precursors lead to heterogeneous samples unless elaborated synthetic procedures are used, such as prehydrolysis of the organosilicon alkoxide,[6,7,14] modification of the titanium alkoxide by a chelating ligand,[7,14,15] strongly acidic conditions,[16] or two-step acid−base catalysis.[14] (ii) More importantly, routine evaporative drying of these hydrolytic gels usually leads to microporous xerogels,[6,7,10,13,14] due to the collapse of the gel network under capillary stresses.[11,17] Low-temperature extraction with supercritical CO_2 at 313 K and 24 MPa is required to obtain mesoporous materials (called aerogels) able to accommodate bulky substrates.[6,7,10,14] Deng and Maier did report the direct synthesis of mesoporous titania−silica xerogels containing $MeSiO_{1.5}$ groups,[16] but they had to resort to extremely long aging and drying times (4 weeks and 3 months, respectively) and to a heat treatment at 523 K with a very low heating rate (0.1 K/min). Such complicated procedures are not compatible with a large-scale production and considerably reduce the industrial interest of these hybrid catalysts. Nonhydrolytic sol−gel processes[18] have been used to prepare

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Table 1. Preparation of the Hybrid Silica−Titania Xerogels[a]

sample	$TiCl_4$ (mmol)	$SiCl_4$ (mmol)	$MeSiCl_3$ (mmol)	Me_3SiCl (mmol)	$^iPr_2O$ (mmol)
TiQ_7T_3	7.22	50.7	21.5	0	146.2
TiQ_4T_6	7.17	27.7	41.1	0	130.8
TiQ_9M	7.12	63.9	0	7.64	145.5
TiQ_8M_2	6.91	55.3	0	13.7	130.8

[a] Conditions: reaction temperature, 110 °C; autogenous pressure, ca. 0.7 MPa; reaction time, 4 days; solvent, 10 mL of CH_2Cl_2.

titania−silica mixed oxides,[19−24] with excellent results in terms of homogeneity and texture. In this communication, we report the nonhydrolytic sol−gel synthesis of highly active and selective hybrid titania−silica epoxidation catalysts. These catalysts were obtained in one step using low-cost chloride precursors and routine evaporative drying, leading to mesoporous xerogels incorporating up to 60 mol % $MeSiO_{1.5}$ (T) units. In addition, it was also possible to incorporate monofunctional $Me_3SiO_{0.5}$ (M) units; to the best of our knowledge, the direct sol−gel synthesis of such materials has not been described previously.

Hybrid titania−silica gels with a Si/Ti molar ratio of 10 were prepared by reaction of chloride precursors with diisopropyl ether as an oxygen donor at 110 °C (cf. Supporting Information). This synthesis is based on the intermediate formation of isopropoxide groups by reaction of diisopropyl ether with chloride groups, followed by nonhydrolytic condensation between chloride and alkoxide groups, leading to the formation of M−O−M bridges with elimination of isopropyl chloride.[18,23,25] The overall synthesis of the samples modified by $MeSiO_{1.5}$ (T) units and $Me_3SiO_{0.5}$ (M) units can be represented by eqs 1 and 2, respectively.

$$TiCl_4 + (10 - a)SiCl_4 + aMeSiCl_3 + (22 - a/2)^iPr_2O \rightarrow (44 - a)^iPrCl + TiO_2(SiO_2)_{10-a}(MeSiO_{1.5})_a \quad (1)$$

$$TiCl_4 + (10 - a)SiCl_4 + aMe_3SiCl + (22 - 1.5a)^iPr_2O \rightarrow (44 - 3a)^iPrCl + TiO_2(SiO_2)_{10-a}(Me_3SiO_{0.5})_a \quad (2)$$

The amounts of reactants used in each synthesis are given in Table 1. In all cases, transparent, yellow monolithic gels were obtained. After washing with CH_2Cl_2, the gels were simply dried under vacuum (10 Pa) at 120 °C for 12 h. In the following, the resulting xerogels have been labeled $TiQ_{10-a}T_a$ or $TiQ_{10-a}M_a$ according to their theoretical content in Q (SiO_2) and T ($MeSiO_{1.5}$) or M ($Me_3SiO_{0.5}$) units.

Table 2. Si/Ti Ratio and Textural Characteristics of the Titania−Silica Xerogels Modified by T or M Units

sample	Si/Ti[a] (exptl)	S_{BET}[b] ($m^2\ g^{-1}$)	V_p[c] ($cm^3\ g^{-1}$)	D_P[d] (nm)
TiQ_7T_3	10.3	1020	1.04	4.1
TiQ_4T_6	10.1	1060	1.28	4.8
TiQ_9M	10.4	950	0.80	3.4
TiQ_8M_2	10.0	930	0.72	3.1

[a] From elemental analysis. [b] BET specific surface area. [c] Total pore volume at $P/P_0 = 0.99$. [d] Average pore diameter ($4V_p/S_{BET}$).

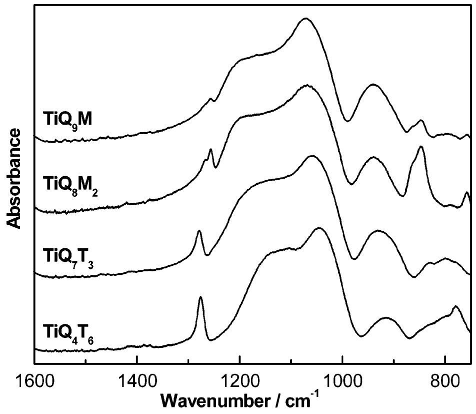

Figure 1. Transmission FTIR spectra (KBr pellets) of titania−silica xerogels modified by T and M units.

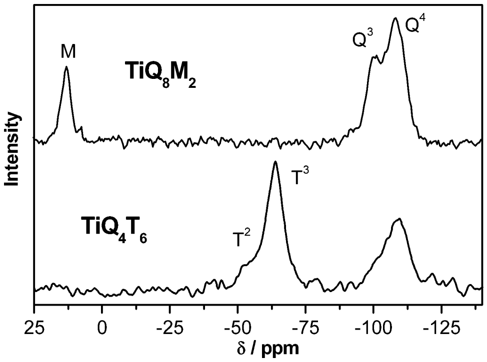

Figure 2. ^{29}Si MAS NMR spectra of TiQ_4T_6 and TiQ_8M_2, recorded using a 30° pulse and a long recycle delay (60 s).

The elemental analysis of the xerogels showed that the experimental Si/Ti ratio of the xerogels was very close to the theoretical one (Table 2), indicating that the various units were quantitatively incorporated in the samples. The incorporation of T and M units could be inferred from the presence of characteristic vibrations in the Fourier transform infrared (FTIR) spectra of the xerogels (Figure 1): symmetric deformation of CH_3 groups at 1280 cm^{-1} (T units) or 1255 cm^{-1} (M units), and Si-C_x stretching and deformation vibrations at 832 cm^{-1} (T units) or at 848 and 756 cm^{-1} (M units).[26] Besides the infrared bands at about 1060 and 1160 cm^{-1} assigned to Si−O−Si vibrations, the spectra of all the samples displayed an intense band at about 945 cm^{-1}. The presence of this band, which is ascribed to Ti−O−Si bonds involving four-coordinated Ti atoms,[2,6,7,16] points to a good dispersion of titanium in the modified silica matrix of our samples.

Quantitative solid-state ^{29}Si magic angle spinning (MAS) NMR spectra of TiQ_4T_6 and TiQ_8M_2 are displayed in Figure 2. The samples have been manipulated in air, and the residual Cl and O^{i}Pr surface groups are easily hydrolyzed to OH groups. It is usually agreed that the −OH and −OTi groups have a similar influence on the chemical shift of a Si site

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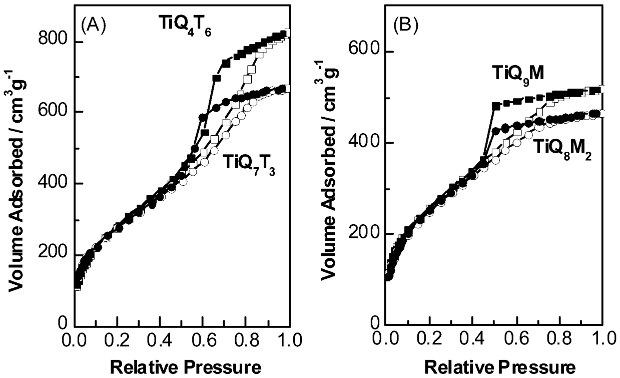

Figure 3. Nitrogen sorption isotherms at 77 K of (A) TiQ_4T_6 and TiQ_7T_3 and (B) TiQ_8M_2 and TiQ_9M.

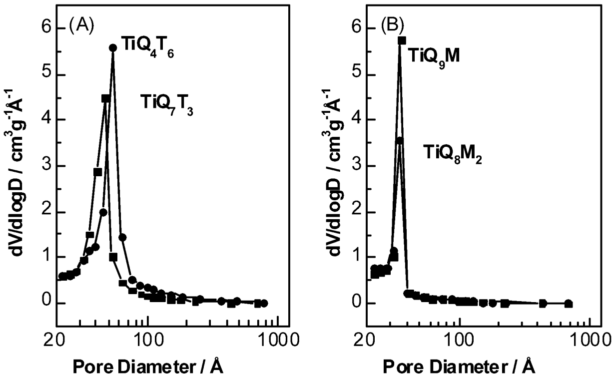

Figure 4. Pore size distributions derived from the desorption branches using the BJH method of (A) TiQ_4T_6 and TiQ_7T_3 and (B) TiQ_8M_2 and TiQ_9M.

and that they should lead to a downfield shift of 4−9 ppm compared to a −OSi group.[2] Accordingly, the resonances at about −109 and −101 ppm in both spectra are ascribed to Q^4 [$Si(OSi)_4$] and Q^3 [$Si(OSi)_3(OX)$] (X = H, Ti) sites, respectively. In the TiQ_4T_6 spectrum, the signals at about −64 and −56 ppm can be likewise assigned to T^3 [$MeSi(OSi)_3$] and T^2 [$MeSi(OSi)_2(OX)$] sites, respectively. In the TiQ_8M_2 spectrum, the signal at about 13.1 ppm is ascribed to M units in $Me_3Si(OSi)$ sites or $Me_3Si(OTi)$ sites, which have been reported at about 11.6 and 16.5 ppm, respectively, in model silsesquioxane compounds.[27] The Q:T (0.66) and Q:M (4.6) ratios obtained from the integration of these spectra were close to the expected ratios (0.67 and 4), which confirms the good incorporation of T and M units in the xerogels.

The N_2 adsorption−desorption isotherms of the hybrid xerogels (Figure 3) were of type IV, indicating that these materials were mesoporous. Analysis of the adsorption data using the *t* plot method confirmed the absence of micropores. All of the hybrid xerogels exhibited very high surface areas around 1000 $m^2\ g^{-1}$ (Table 2) and narrow mesopore distributions (Figure 4). The samples modified by M units showed lower pore volumes and pore diameters. The surface areas and pore volumes of the one-step nonhydrolytic xerogels incorporating T units are much higher than those reported for similar hydrolytic one-step xerogels, which are usually microporous;[13,16] they are even higher than those reported for aerogels obtained by solvent extraction with supercritical CO_2.[6,7]

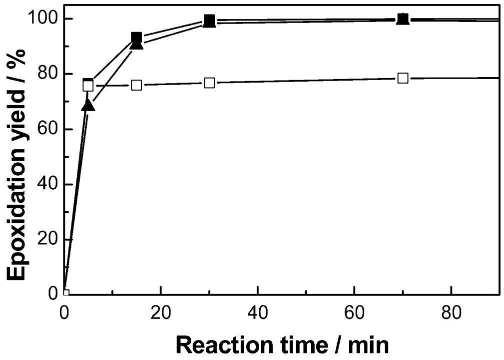

Figure 5. Yield of cyclohexene oxide (based on CHP) for the epoxidation of cyclohexene with TiQ_8M_2 (full squares) and TiQ_4T_6 (full triangles); effect of the removal of the TiQ_8M_2 catalyst after 5 min (open squares). Reactions performed in a batch reactor at 363 K using 100 mg of catalyst, 10 mmol of CHP, 50 mmol of cyclohexene, and 10 mL of toluene.

The outstanding mesoporous texture of our hybrid xerogels can be ascribed to the high degree of condensation typical of nonhydrolytic gels and to the low interaction, compared to water, of the organic liquid phase with the pore surface.[23]

The xerogels TiQ_4T_6 and TiQ_8M_2 were evaluated as catalysts for the epoxidation of cyclohexene by cumyl hydroperoxide (CHP) at 363 K (Figure 5). Both catalysts were highly selective: no secondary product could be detected by GC.

The activity of both catalysts was also excellent, and practically complete conversion (>98%) of cyclohexene to cyclohexene oxide was obtained after only 30 min. The initial epoxidation rates[28] r_0 found with TiQ_8M_2 ($r_0 = 15.3$ mmol $g^{-1}\ min^{-1}$) and TiQ_4T_6 ($r_0 = 13.6$ mmol $g^{-1}\ min^{-1}$) compare well to those reported for the epoxidation of cyclohexene at 90 °C with Si/Ti aerogels modified by $MeSiO_{1.5}$ units ($r_0 = 3.0$ mmol $g^{-1}\ min^{-1}$) or $PhSiO_{1.5}$ units ($r_0 = 7.3$ mmol $g^{-1}\ min^{-1}$).[14] Such high epoxidation rates can likely be explained by the very high surface area of our samples, the good dispersion of Ti, and the high amount of hydrophobic methyl groups incorporated: in both cases, 6 methyl groups for 10 Si atoms. In an additional experiment, the catalyst was filtered off at 90 °C after 5 min of reaction, using a 0.2 μm filter. As shown in Figure 5, the epoxide formation practically stopped, which demonstrates that the activity of this catalyst was not due to the leaching of active Ti species.

In summary, this work shows that the nonhydrolytic sol−gel process offers an extremely simple and efficient one-step route to mesoporous hybrid silica−titania xerogels that are highly active and selective heterogeneous epoxidation catalysts. Contrary to the conventional hydrolytic process, it is possible by this route to simultaneously control not only the Ti dispersion but also the texture and the functionalization of the catalyst, without the use of additives or supercritical drying and starting from inexpensive chloride precursors.

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Supporting Information Available: Experimental section (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(28) r_0: initial rate derived from the amount of epoxide formed during the first 5 min of reaction.