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Effective alkene epoxidation with dilute hydrogen peroxide on amorphous silica-supported titanium catalysts

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The use of amorphous silica-supported titanium catalysts in which the titanium ions display a chemical environment similar to that of Ti-substituted zeolites, afforded excellent activity in the epoxidation of terminal linear and bulky alkenes with dilute solutions of hydrogen peroxide.

Despite numerous reports in the literature, the epoxidation of terminal alkenes remains a challenge in petrochemistry. Many different methods have been developed for the preparation of epoxides. However, in recent years maximum interest has focused on titanium-substituted zeolites in the framework, including TS-1,[1] Ti-β[2] and Ti-incorporated mesoporous silica,[3] which are claimed to be good catalysts for epoxidation with hydrogen peroxide. Although in the presence of methanol as a solvent all these catalysts display high activity and selectivity levels towards epoxide, they have poor mechanical strength and low thermal stability. Non-zeolitic TiO_2–SiO_2-supported catalysts are effective in the epoxidation of alkenes with organic hydroperoxides,[4,5] but it is generally believed that they are not effective in the epoxidation of alkenes with hydrogen peroxide. Nevertheless, titanium silica-supported catalysts have been reported to be active to the epoxidation of alkenes with hydrogen peroxide, but with low selectivity towards epoxide.[6]

Here we report a very simple route for the preparation of TiO_2/SiO_2 catalysts with highly dispersed titanium atoms. These catalysts are relatively inexpensive, easy to synthesise and regenerate, and at the same time show high conversion rates without the requirement of methanol as a solvent. Hitherto, these materials have not been used as catalysts in the epoxidation of alkenes (oct-1-ene, cyclohexene and norbornene) with hydrogen peroxide solutions.

The catalysts were prepared in the following manner:[7] 0.75 g of titanium isopropoxide was dispersed in the solvent (either *n*-decane, toluene or cyclohexanol to produce catalysts C3, C2 and C1, respectively) (150 ml). The solution was heated to 423 K (the boiling point of toluene solution) under stirring and then 5 g of silica (Grace Davison G-952, surface area: 310 $m^2 g^{-1}$, pore volume: 1.5 ml g^{-1}) was added to the solution, which was stirred at 423 K for 2 h. The solid obtained was filtered off and washed twice with 150 ml of hot solvent and subsequently dried at 383 K and calcined at 773 K for 5 h. As reference catalysts, a titanium-supported silica (TiF/SiO_2), as described by Jorda *et al.*,[6] and a titanium silicalite (TS-1), as reported by Taramaso *et al.*,[1] were prepared.

The total amount of titanium introduced into the synthesis solution was incorporated to catalysts TiF/SiO_2, C2 and C3 (Table 1). However, when cyclohexanol was employed as the solvent (C1), only part of the titanium was incorporated into the catalyst. For TS-1, the degree of titanium incorporation was similar to that reported in the literature. The structural FTIR spectra of the catalysts diluted in KBr were inconclusive because the silica support displayed a broad peak at 960 cm^{-1}, which overshadowed the Ti–O–Si vibration mode (960 cm^{-1}).[8]

Table 1 Characteristics of the catalysts

Catalyst	Synthesis	Titanium content (%) (XPS)	XPS ratio (460 eV/ 458.5 eV)
C1	Cyclohexanol	0.8	2.1
C2	Toluene	2.6	0.5
C3	*n*-Decane	2.6	0.1
TS-1[1]		1.7	2.5
TiF/SiO_2[6]		1.1	—[a]

[a] Not determined owing to the presence of fluorinated species.

The DRS UV–VIS spectra (Fig. 1) of catalysts C1, C2, C3 and TiF/SiO_2 were clearly different from that of the TS-1 sample. The spectrum of the latter showed a single peak at 210 nm, which can be taken as a clear indication of isolated Ti(IV) in tetrahedrally coordinated sites. The slight shift in band position and the increase in bandwidth point to a distorted tetrahedral environment of the titanium. The broad adsorption band of the silica-supported samples shifted to high wavelength values; this can be explained in terms of: (i), the presence of titanium atoms in octahedral coordination (values between 290 and 333 nm),[9] as observed in catalysts C2 and C3, and as a small component in TiF/SiO_2; (ii) the hydrophilic nature of the silica surface, which favours the presence of hydrated titanium in tetrahedral coordination (232 nm),[9] as already seen for catalyst C1 and the major proportion of TiF/SiO_2. However, the absence of a band at 370–410 nm rules out the presence of free TiO_2 in all the catalysts.[9]

High resolution photoelectron spectra of Ti 2p core-levels of the *in situ* outgassed samples (Fig. 2) displayed the characteristics Ti $2p_{1/2}$/Ti $2p_{3/2}$ doublet. Although chemical information can be derived from each component, discussion should be based on the most intense Ti $2p_{3/2}$ component. Curve fitting of

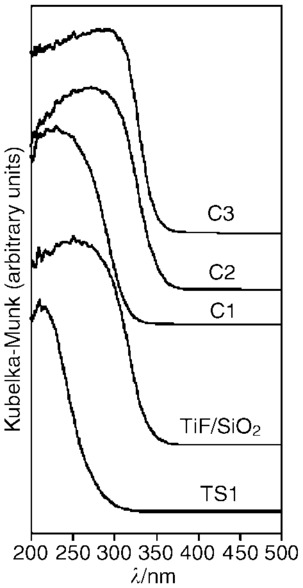

Fig. 1 DRS UV–VIS spectra of solids in ambient conditions recorded with a Shimadzu UV-2100 spectrometer.

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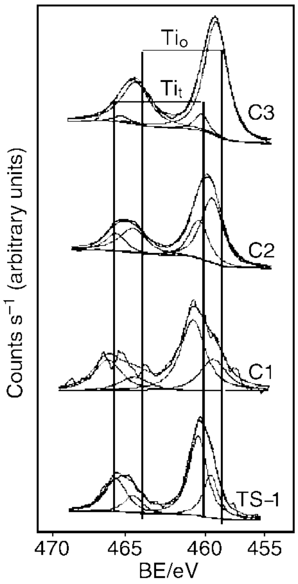

Fig. 2 Ti 2p core-level spectra of outgassed samples *in situ* at 473 K acquired with a VG Escalab 200R spectrometer.

the Ti $2p_{3/2}$ core level to two components shows the highest binding energy component (460.0 eV) can be attributed to titanium in tetrahedral coordination,[10] while the lowest binding energy component (458.5 eV) is usually assigned to titanium in octahedral coordination[10] or in interaction with surface hydroxy groups. Catalyst C3 shows a large part of the titanium in octahedral coordination (Table 1). For catalyst C2, the proportion of titanium in tetrahedral sites is higher than in C3, but most of the titanium still remains in octahedral coordination (Table 1). Catalysts C1 and TS-1 exhibit a titanium peak in tetrahedral coordination that is clearly more intense than the lowest binding energy component. This indicates that titanium ions are in a very similar environment in catalysts C1 and TS-1, although the synthesis route of silica-supported titanium catalyst (C1) is considerably easier than that for the Ti-silicalite sample. Both DRS UV–VIS and XPS spectroscopic techniques pointed to the necessity of carefully controlling the incorporation of titanium into silica (preparation of C1 in cyclohexanol) to obtain titanium in tetrahedral coordination. This is due to the fact that cyclohexanol interacts strongly with the titanium precursor which favours the formation of isolated titanium species, and also that only a fraction of the titanium added is incorporated as a consequence of the equilibrium of adsorption.

These catalysts were tested in the epoxidation of alkenes with dilute aqueous hydrogen peroxide solutions. Epoxidation was performed under ambient pressure in a round-bottomed flask equipped with a condenser and magnetic stirrer. The reaction procedure was as follows: 0.2 mol of alkene, 11 g of *tert*-butyl alcohol and 1 g of catalyst were stirred and heated to the reaction temperature (353 K). Then, 4 g of a dilute solution of hydrogen peroxide (6 wt% in 1-phenylethanol) was added dropwise under stirring over 2 h. Aliquots were taken at regular intervals. H_2O_2 consumption was evaluated by iodometric titration, and organic compounds were analysed by GC to determine their selectivity. The results are summarised in Table 2. The reference catalyst TS-1 showed low selectivity values towards epoxide, which is consistent with the requirement of the presence of methanol to obtain high selectivity values.[11] The method for preparing silica-supported titanium had a strong effect on performance for the epoxidation of oct-1-ene. The TiF/SiO_2 catalyst showed similar conversion and selectivity values to those reported in previous work,[6] but lower than those of TS-1. Catalysts C3 and C2 showed very low selectivity towards epoxide, in agreement with the high proportion of octahedrally coordinated titanium, as revealed by DRS UV–VIS and XPS spectroscopic techniques. Nevertheless, catalyst C1 had very high (95%) selectivity values towards epoxide, related to the high proportion of titanium in tetrahedral coordination as revealed by the DRS UV–VIS technique, and specifically by XPS spectroscopy. Finally, catalyst C1 also displayed very good performance in the epoxidation of bulky alkenes with hydrogen peroxide. In cyclohexene and norbornene, 91 and 98% selectivity towards epoxide, respectively, were reached. Used catalyst C1 was analysed and the Ti content found to be the same as in the fresh sample, thus excluding leaching.

Table 2 Data for alkene epoxidation with hydrogen peroxide after 1 h of reaction ($T = 353$ K)

Catalyst	Alkene	Conversion of H_2O_2 (%)	Selectivity to epoxide^a (%)
TS-1	Oct-1-ene	96	70
TiF/SiO_2	Oct-1-ene	75	65
C3	Oct-1-ene	96	32
C2	Oct-1-ene	97	56
C1	Oct-1-ene	97	95
C1	Cyclohexene	98	91
C1	Norbornene	98	98

[a] Selectivity to epoxide = mol of epoxide formed/mol of H_2O_2 consumed.

In short, using a very simple route, we have prepared titanium-supported amorphous silica catalysts in which the chemical environment of titanium atoms is very similar to Ti-substituted zeolites. The use of cyclohexanol is pivotal to the production of very active and selective catalysts in the reaction of alkene epoxidation with hydrogen peroxide. These catalysts also display excellent performance with linear as well as larger or bulky alkenes.

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