A New Titanium–Silica Catalyst for the Epoxidation of Non-functionalized Alkenes and Allylic Alcohols

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Silica treated with $Ti(OPr^i)_4$ is an efficient catalyst for the *tert*-butyl hydroperoxide epoxidation of nonfunctionalized alkenes and allylic alcohols at room temperature; the reactivity of the olefinic substrate depends on the structure, which allows the selective epoxidation of compounds containing different types of double bonds; ^1H and ^{13}C CP-MAS NMR shows the presence of isopropoxide groups in the catalyst.

The direct epoxidation of alkenes is a field of both academic and industrial importance. The epoxide functional group is one of the most useful intermediates in organic synthesis, and epoxides are versatile products that easily undergo ring-opening reactions to form bifunctional compounds.

Excellent results have been obtained in metal-catalysed epoxidations with hydroperoxides,[1] which have led to increased interest in the development of heterogeneous catalysts for these reactions.[2] Vanadium[3] and titanium[4] montmorillonites have been used in the epoxidation of allylic alcohols. Laszlo *et al.*[5] have described the vanadium oxide catalysed epoxidation of non-functionalized alkenes at moderate temperatures and with moderate chemical yields. In recent years a great deal of effort has been directed towards the preparation of catalysts able to promote the epoxidation of alkenes with hydrogen peroxide, such as titanium silicalites.[6] Excellent results are obtained with TS-1,[6,7] but the reaction is limited to unhindered alkenes. Large pore titanium-beta zeolite is useful for the oxidation of bulkier organic molecules, but unfortunately neither the conversion nor the selectivity to the epoxide are high.[8] Up to now, the heterogeneous catalyst with the broadest range of applications has been the titanium–silica developed by Shell.[9] It has been suggested[2] that this catalyst contains titanyl groups ($Ti^{IV}{=}O$) bound to siloxane ligands. It is obtained by impregnation of silica with titanium tetrachloride, followed by hydrolysis and calcination at 800 °C, and it promotes the epoxidation of nonfunctionalized alkenes, allyl chlorides and allylic alcohols with organic hydroperoxides at high temperatures.

Among these catalysts, only the titanium–montmorillonite has been used in asymmetric epoxidation of primary allylic alcohols in the presence of chiral tartrates.[4] In view of its broader applicability, it would be interesting to obtain chiral catalysts related to the titanium–silica, however the calcination process at 800 °C prevents the introduction of a chiral organic ligand. Recently we described the preparation of several titanium–silica and titanium–alumina derivatives and their use as catalysts in Diels–Alder reactions.[10] Here we report a related methodology to obtain a $Ti(OPr^i)_4$–silica derivative which is an efficient catalyst in the epoxidation of alkenes at room temperature.

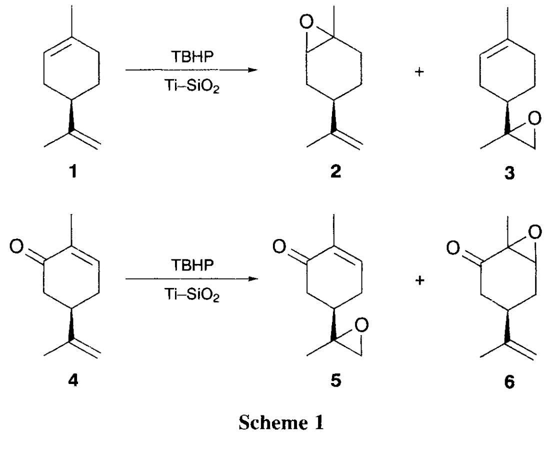
Silica gel (Merck, silica gel 60, 63–200 μm) was treated with $Ti(OPr^i)_4$ (2.5 mmol g^{-1} silica) in toluene under reflux, the solid was separated by filtration, repeatedly washed with toluene and heated under vacuum at 140 °C overnight prior to use. The solid obtained is an efficient catalyst in the epoxidation of alkenes (Table 1) with *tert*-butyl hydroperoxide (TBHP). Cyclic, linear and branched alkenes are converted into the corresponding epoxides at room temperature in moderate to high yields and with high selectivity. With non-functionalized alkenes the reaction rate depends on their structure. Cyclic compounds are more reactive than acyclic compounds, and disubstituted double bonds more than monosubstituted double bonds. The geometry of the double bond also influences the reactivity; *Z*-double bonds are epoxidized more efficiently than *E*-double bonds, and both of these better than *gem*-disubstituted systems. These differences allow the selective epoxidation of compounds with double bonds of different types, so (*R*)-limonene **1** is preferentially oxidized at the cyclic double bond with high selectivity (Scheme 1).

α,β-Unsaturated carbonyl compounds do not react under these conditions, which allows the selective epoxidation of (*R*)-carvone **4** (Scheme 1). In this case the epoxide is obtained with

Table 1 Epoxidation of alkenes with TBHP at room temperature[a]

Alkene	Alkene : TBHP	*t*/h	Conversion of TBHP[b] (%)	Selectivity to epoxide[c] (%)
Hex-1-ene	8 : 1	24	73	62
Styrene	8 : 1	3	95	65[d]
Cyclohexene	8 : 1	1	100	85
Norbornene	3 : 1	4	91	92[e]
Cyclododecene	3 : 1	5	70	71
cis-Hept-2-ene	2 : 1	7	83	96
trans-Hept-2-ene	2 : 1	24	83	72
1-Methylcyclohexene	3 : 1	2	83	94
(*R*)-Limonene	3 : 1	4	93	90[f]
(*R*)-Carvone	1 : 1	30	62	48[g]
Crotyl alcohol[h]	1 : 1.5	1	90	94

[a] TBHP : catalyst ratio was 4 ml (3 mol dm^{-3}) g^{-1}. [b] Determined by gas chromatography (HP-1, 25 m × 0.2 mm × 0.33 μm). [c] Isolated products. Catalyst was filtered off and solvents and reagents evaporated under vacuum. Purification was performed by column chromatography and all the epoxides were characterized by NMR spectroscopy. [d] Acetophenone (15%) and benzaldehyde (3%) are also obtained. [e] *Exo*-epoxide is the only product. [f] **2** : **3** = 7 : 1, **2** is obtained as a 1 : 1 mixture of *cis* and *trans*. [g] **5** is the only product, a 25% de is obtained. [h] Reaction carried out in methylene chloride with double the amount of catalyst.



Scheme 1

25% d.e. The catalyst is also efficient in the epoxidation of primary allylic alcohols, as shown by the excellent results obtained in the reaction of crotyl alcohol.

To confirm that this catalyst is different from the previously described titanium–silica,[9] it was analysed by ^{1}H and ^{13}C CP-MAS NMR. The samples were treated at 140 °C under vacuum (10^{-5} Torr) for 12 h in 5 mm NMR tubes that were sealed at a height of 40 mm under vacuum. A Bruker ASX-200 MHz spectrometer with a specially made probe able to spin 5 mm sealed NMR tubes was used for both ^{1}H and ^{13}C CP-MAS NMR experiments.

The ^{1}H NMR spectrum was obtained at ν_1 = 200 MHz, 30000 full induction decays (FID) were accumulated at a repetition time of 1 s, using 3 kHz MAS, 90° pulses of 2.8 μs, and spectral width (SW) = 4 kHz. The spectrum shows two broad signals at δ 1.4–1.5 and 4.1, the former being larger than the latter [the ^{1}H NMR spectrum of $Ti(OPr^i)_4$ in $CDCl_3$ shows a signal at δ 1.21 (d, 6H, *J* 6 Hz) and another at δ 4.45 (sep, 1H, *J* 6.1 Hz)].

The ^{13}C NMR spectrum was obtained at ν_1 = 50.3 MHz, with a contact time of 10 ms, repetition time of 5 s, spinning rate 3 kHz, SW = 5.5 kHz, 90° pulses of 5 μs and acquisition number of 2600. The spectrum shows a large signal at δ 22.8 and a small signal at δ 66.1 [the ^{13}C NMR spectrum of $Ti(OPr^i)_4$ in $CDCl_3$ shows a large signal at δ 26.5 and a small one at δ 76.1.

In conclusion, a new, easily obtained and efficient catalyst for the epoxidation of alkenes under mild conditions is described. Unfunctionalized alkenes and allylic alcohols are epoxidized with moderate to high yields and with high selectivities. The results obtained open the way to the preparation of titanium–silica catalysts with chiral ligands.

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