Selective Epoxidation of α-Isophorone with Mesoporous Titania–Silica Aerogels and tert-Butyl Hydroperoxide

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Amorphous, mesoporous TiO_2–SiO_2 mixed oxides, synthesised using a sol–gel process followed by extraction with supercritical CO_2, show high selectivities (98%) in the heterogeneous epoxidation of α-isophorone in ethylbenzene at 60 °C.
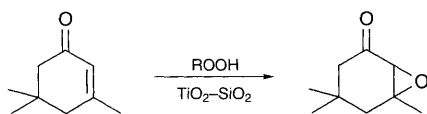
Epoxidation is of great importance in organic synthesis due to the usefulness of oxiranes as intermediates. Substantial effort has been expended to substitute stochiometric or homogeneous transition-metal catalysed epoxidations by solid catalysed processes.[1] The first really efficient heterogeneous catalyst TiO_2-on-SiO_2, utilised for industrial propene oxide production,[2] was prepared by anchoring a titanium compound onto the surface of silica support. A titanium-substituted silicalite TS-1, isomorphous to ZSM-5 zeolite, has been reported to be an excellent catalyst for the epoxidation of small organic compounds with H_2O_2.[3] There is an intensive search for new large pore titanium-containing zeolites, such as Ti-β[4] or Ti-MCM-41,[5] in order to overcome the steric restriction of TS-1.

Recently we have shown[6] another way of preparing solid catalysts which are active in the epoxidation of bulky cyclic olefins. Titania–silica mixed oxides, generally found as poor epoxidation catalysts,[7–9] can surpass TiO_2-on-SiO_2 and Ti-containing zeolites when prepared by the sol–gel aerogel method. Key factors for high activity and selectivity are the good dispersion of titania in the silica matrix, mesoporous structure and high surface area.

Usually simple unfunctionalised alkenes are chosen as test reactants during catalyst development and little is known about the performance of heterogeneous catalysts in the epoxidation of olefins of more complex structures. For example, olefins with an electron-withdrawing carbonyl group in α-position are difficult to epoxidise with electrophilic metal catalyst–alkyl hydroperoxide systems. Here we show that α-isophorone (3,5,5-trimethylcyclohex-2-en-1-one) can be selectively epoxidised with tert-butyl hydroperoxide under mild conditions (Scheme 1). This is the first case that an electron-deficient (deactivated) α-keto olefin could be selectively oxidized to the corresponding oxirane using a solid catalyst. To our knowledge, there is no efficient catalytic method for the epoxidation of α-isophorone. A homogeneous catalytic process, the Pd(OAc)$_2$-catalysed oxidation of isophorone with α-silyloxyalkyl per-oxybenzoate provided only 17% epoxide.[10]

A sol–gel aerogel process[11] was used for the preparation of titania–silica mixed oxides. In brief, tetraisopropoxytitanium(IV) chemically modified with acetylacetone (molar ratio 1 : 1) was combined with a solution of tetramethoxysilicon(IV) in isopropanol. Then aqueous hydrochloric acid in isopropanol was added under vigorous stirring to start hydrolysation employing a molar ratio H_2O : alkoxide : acid of 5 : 1 : 0.09. After gelation the sample was dried by semicontinuous extraction with supercritical CO_2 at 40 °C and 240 bar. Samples with different Ti : Si ratios have been prepared. Raw samples were used for epoxidation, as they are slightly more active than the material calcined in an air-flow at 800 °C.

The synthesis of a titania-on-silica catalyst (2 mass% TiO_2) was based on a patent to Shell.[2] Tetraisopropoxytitanium(IV) served as precursor for the impregnation of the silica support (aerosil 200). Calcination at 800 °C is a crucial step for developing the active catalysts.

Ti-contents have been determined by ICP-AES. Nitrogen adsorption and capillary condensation revealed in all cases a mesoporous structure (average pore size up to 10 nm for aerogels and 30 nm for TiO_2-on-SiO_2) with BET surface areas varying from ca. 200 m^2 g^{-1} (TiO_2-on-SiO_2) up to ca. 800 m^2 g^{-1} (aerogels). All samples were X-ray amorphous even after calcination at 800 °C.

The structural deviation between titania–silica aerogel and TiO_2-on-SiO_2, both possessing the same Ti-content (2 mass%), is shown by the FTIR spectra in Fig. 1. The well-developed band at around 950 cm^{-1} in the aerogel spectrum is attributed to framework titanium[12] in the silica matrix. The intensity of this band increases with increasing Ti-content up to 20 mass% titania, indicating a good Ti-distribution (Ti–O–Si connectivity). This band is characteristic of amorphous TiO_2–SiO_2 aerogels and crystalline Ti-silicalites such as TS-1, but is not present in TiO_2-on-SiO_2. Pure amorphous silica (aerosil) and the 2 mass% TiO_2-on-SiO_2 have almost identical spectra. The weak shoulder at ca. 985 cm^{-1} has been assigned to surface O_3SiOH groups.[12] It has been found that the activity and stability of TiO_2-on-SiO_2 are due to compound formation (Ti–O–Si bonds) between the Ti-precursor and the silica support during calcination.[1]

Under standard conditions epoxidation was carried out at 60 °C in Ar, using 77 mmol α-isophorone, 13.4 mmol tert-butyl hydroperoxide, 9 ml solvent (usually ethylbenzene) and 200 mg catalyst. Conversion and selectivities were determined by GC
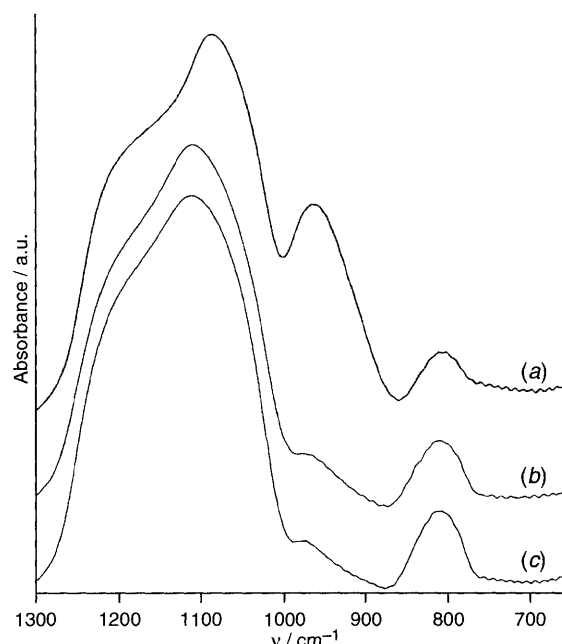

Scheme 1

Fig. 1 FTIR spectra of (a) sol–gel TiO_2–SiO_2 mixed oxide (2 mass% TiO_2, calcined at 800 °C), (b) TiO_2-on-SiO_2 catalyst (2 mass% TiO_2, calcined at 800 °C) and (c) pure silica (Aerosil 200)

analysis and iodometric titration. The (initial) rate is defined as the epoxide formation in the first 20 min.

Fig. 2 demonstrates that the activity of sol–gel titania–silica catalysts increases with increasing Ti-content up to 20 mass% TiO_2. Epoxide selectivity varying between 97 to 99% based on olefin (at 50% conversion) is not affected by the titanium content. The 2 mass% TiO_2-on-SiO_2 catalyst shows higher
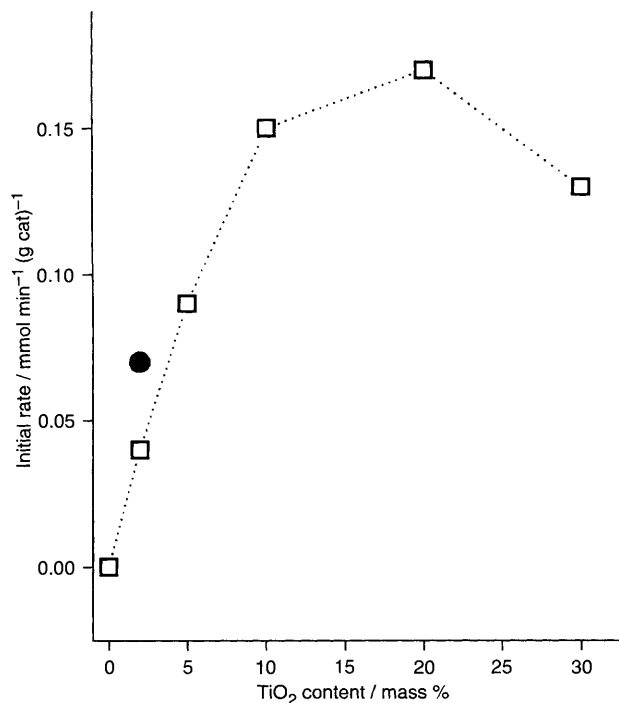

Fig. 2 Rate of α-isophorone epoxidation as a function of TiO_2-content of titania–silica aerogels (□; raw) and TiO_2-on-SiO_2 catalyst (●; calcined at 800 °C); standard conditions
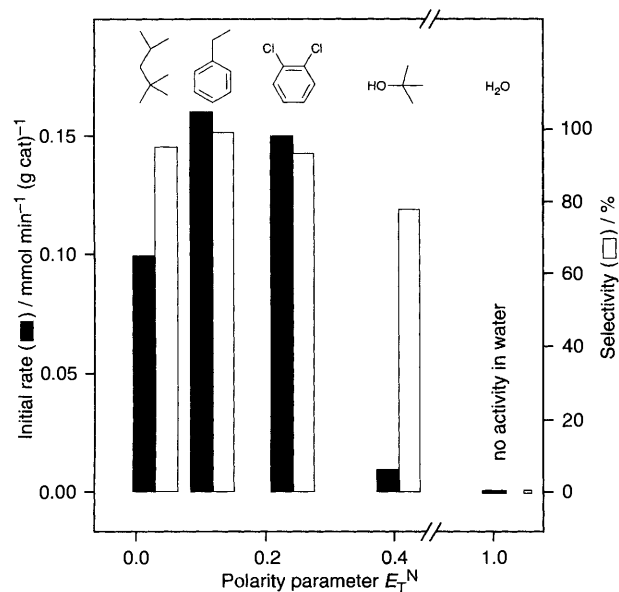

Fig. 3 The influence of solvent polarity on the reaction rate and selectivity in the epoxidation of α-isophorone; standard conditions, selectivity is determined at 50% conversion

activity than the aerogel of the same composition. However, the Ti-loading and the performance of TiO_2-on-SiO_2 could not be improved by applying greater amounts of Ti-precursor, in agreement with the original description of the preparation technique.[1] It is likely that the limit is the number of free surface OH groups on the silica support available for anchoring. Note that the epoxidation of the bulky α-isophorone (0.75 × 0.58 × 0.84 nm) cannot be expected in the narrow channels of TS-1 (0.56 × 0.53 nm).

Selectivity and reaction rate are markedly influenced by the solvent polarity, characterised by the empirical solvent parameter[13] E_T^N. Ethylbenzene proved to be the best solvent with regard to both reaction rate and selectivity (Fig. 3). Epoxide selectivities of 98% based on olefin and 85% based on peroxide (at 70% conversion) have been reached in ethylbenzene at 50 °C. (Major by-product is β-isophorone formed by isomerization of the reactant.) Coordinating, polar solvents cause a significant drop in activity by hindering the formation of the catalyst–hydroperoxide complex and the advance of the hydrophobic olefin to the active sites. Accordingly, there is no oxirane formation in water (E_T^N = 1.0).

The performance of sol–gel titania–silica aerogels in the epoxidation of cyclohexene has been reported previously.[6] Although oxirane formation is highly selective in cases of both α-isophorone and cyclohexene (up to 98 and ca. 100% based on olefin, respectively), the reaction is about 60 times slower in the former under identical reaction conditions. The suppressed reaction rate is likely due to the electron-withdrawing carbonyl group in α-position, whereas the influence of the 2-methyl group (electron release and steric hindrance) is of secondary importance.

Titania–silica mixed oxides are generally considered as poor epoxidation catalysts possessing low activity and selectivity.[7–9] Our study shows that the proper selection of preparation conditions results in catalysts of outstanding selectivity with acceptable reaction rate in the rather demanding oxidation of an electron-deficient (deactivated) α-keto olefin.

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