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# Titania–silica epoxidation catalysts modified by acetoxypropyl groups

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Mesoporous titania–silica aerogels with $TiO_2 : SiO_2 = 1 : 9$ weight ratio and varying amounts of covalently bound 3-acetoxypropyl groups were prepared from 3-acetoxypropyltrimethoxysilane, tetramethoxysilane and titanbisacetylacetonatdiisopropoxide. The textural properties of the hybrid aerogels were strongly influenced by the concentration of acetoxypropyl groups. The BET surface area and specific pore volume were significantly lowered upon introduction of the polar organic modification. Despite these less favorable textural properties, all modified aerogels were remarkably more active epoxidation catalysts, and in the epoxidation of cyclohexenol also more selective, than the unmodified titania–silica aerogel. For example, incorporation of only 2 mol% acetoxypropyl groups lowered the BET surface area from 813 to 339 $m^2\,g^{-1}$, whereas the selectivity to 2,3-epoxy-cyclohexenol increased from 76 to 90%, and the reaction time (required to achieve 70% TBHP conversion) decreased from 46 to 5 min. The higher epoxide selectivity and the small enhancement in *cis*/*trans* ratio in the epoxide may indicate an electron pair donor interaction between the ester carbonyl group and the Ti active site.

**Keywords:** titania–silica hybrid aerogel, organic modification, acetoxypropyltrimethoxysilane, epoxidation, cyclohexene, cyclohexenol, *tert*-butylhydroperoxide

## 1. Introduction

Epoxidation of bulky olefins is an important application of titania–silica mixed oxides. The reaction requires a mesoporous structure and high Ti dispersion in the silica matrix (“site isolation” [1,2]). The performance of the catalyst and choice of oxidant are influenced also by the surface properties such as acidity and hydrophobicity [1,3,4]. Recent research activities have focused on the use of the cheap oxidant aqueous hydrogen peroxide by hydrophobization of the catalysts. Good results have been achieved by introducing covalently bound methyl and phenyl groups [5–7], or by silylation [8,9].

In the production of bulk chemicals, the choice of a cheap oxidant is crucial, but in fine chemistry the aim is usually to obtain the highest possible yield of the valuable product. Accordingly, we focused on epoxidations in non-aqueous medium with alkylhydroperoxides, which method affords remarkably higher rates and selectivities compared to oxidation with aqueous $H_2O_2$ [5,6]. Recently, we have synthesized a series of titania–silica aerogels with a wider range of covalently bound modifying groups [10]. Besides methyl and phenyl groups, new group classes such as halogenides (chloropropyl), amines (dimethylaminopropyl) and esters (acetoxypropyl) were successfully incorporated into the matrix by the use of the solution sol–gel process.

Some of these aerogels modified by polar organic groups were shown to be significantly more active and selective than the similarly prepared, unmodified titania–silica catalyst. This was the first evidence for a beneficial effect of polar organic functions immobilized on the surface of an epoxidation catalyst. The aim of the present study was to elucidate the potential and limitations of these aerogels in the epoxidation of bulky cyclic olefins. A series of titania–silica catalysts with different concentration of acetoxypropyl groups were prepared and tested in the epoxidation of cyclohexene and cyclohexenol with *tert*-butylhydroperoxide (TBHP).

## 2. Experimental

### 2.1. Catalyst preparation

Acronyms used for the different catalysts are listed in table 1 together with important information concerning the compositions of sol–gel solutions applied in synthesis. The numbers in the abbreviations indicate the percentage of modified silicon precursor based on the total amount of silicon. The aerogels were prepared according to procedures previously published [7,11]. Prehydrolysis of acetoxypropyltrimethoxysilane (ACOPTMS, ABCR) in $i$-PrOH with aqueous $HNO_3$ hydrolysant under vigorous stirring (1000 rpm) lasted 6 h. The prehydrolysis was necessary to compensate for the different sol–gel reactivity of the precursors [7,12]. Subsequently, tetramethoxysilane (TMOS, Fluka, puriss.) and titanbisacetylacetonatdiisopropoxide (TIBADIP, 75% in $i$-PrOH, Aldrich, puriss.) in $i$-PrOH were added. The titania loading of all aerogels was 10 wt% $TiO_2$ for a theoretical catalyst $TiO_2$–$SiO_2$. After 24 h, trihexylamine (THA, Fluka, >97%) in $i$-PrOH was

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Table 1
Components used for sol–gel preparations.[a]

| Aerogel | Components added | | | Theoretical $TiO_2$ content[b] (wt%) |
|---|---|---|---|---|
| | At start | After 6 h | After 24 h | |
| ACOP2 | 62 ml $i$-PrOH<br>3 mmol R–Si–$(OMe)_3$<br>750 mmol $H_2O$<br>15 mmol $HNO_3$ | 10 ml $i$-PrOH<br>147 mmol TMOS<br>12.5 mmol TIBADIP | 60 ml $i$-PrOH<br>22.5 mmol THA | 9.7 |
| ACOP5 | 62 ml $i$-PrOH<br>7.5 mmol R–Si–$(OMe)_3$<br>750 mmol $H_2O$<br>15 mmol $HNO_3$ | 10 ml $i$-PrOH<br>142.5 mmol TMOS<br>12.5 mmol TIBADIP | 60 ml $i$-PrOH<br>22.5 mmol THA | 9.3 |
| ACOP10 | 62 ml $i$-PrOH<br>15 mmol R–Si–$(OMe)_3$<br>750 mmol $H_2O$<br>15 mmol $HNO_3$ | 10 ml $i$-PrOH<br>135 mmol TMOS<br>12.5 mmol TIBADIP | 60 ml $i$-PrOH<br>22.5 mmol THA | 8.8 |
| ACOP20 | 62 ml $i$-PrOH<br>30 mmol R–Si–$(OMe)_3$<br>750 mmol $H_2O$<br>15 mmol $HNO_3$ | 10 ml $i$-PrOH<br>120 mmol TMOS<br>12.5 mmol TIBADIP | 60 ml $i$-PrOH<br>22.5 mmol THA | 7.8 |

[a] Abbreviations: $i$-PrOH – 2-propanol, TMOS – tetramethoxysilane, TIBADIP – titanbisacetylacetonatediisopropoxide, THA – trihexylamine.

[b] Calculated by assuming that the amount of chemically bound water, present in SiOH groups, is zero.

added and the stirring speed reduced (500 rpm). Gelation to an opaque monolithic body occurred within 1 h.

Sol–gel processes were carried out in a glass reactor at room temperature under a He atmosphere. The total volume of the liquid was ca. 170 ml and the corresponding molar ratios water : silicon alkoxide : acid : THA were 5 : 1 : 0.1 : 0.15.

Semicontinuous extraction with supercritical $CO_2$ was carried out at 40 °C and 230 bar. A glass liner was used to prevent contamination originating from the steel autoclave. The as-prepared aerogel clumps were ground in a mortar and calcined in a tubular reactor with upward flow at 100 °C. All samples were heated at a rate of $10\,°C\,min^{-1}$ in an air flow of $5\ l\,min^{-1}$, and kept at the final temperature for 1 h. The calcination temperature was limited by the stability of the organic functional group, as indicated by former thermal analytical investigations [10]. This temperature is not sufficiently high for the complete removal of residual THA, as confirmed by $^{13}C$-NMR spectroscopy.

Composition of the samples with regard to Si, Ti and Fe was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The Si to Ti ratio was nominal and the Fe content was below 0.01% (detection limit).

## 2.2. Nitrogen physisorption

The specific surface area ($S_{BET}$) and specific desorption pore volume ($V_p(N_2)$), assessed by the BJH method, were determined by nitrogen physisorption at −196 °C using a Micromeritics ASAP 2000 instrument. Prior to measurement, the sample was degassed at 100 °C until a final constant pressure below 0.1 Pa was achieved. BET surface area was calculated in a relative pressure range between 0.05 and 0.2, assuming a cross sectional area of $0.162\ nm^2$ for the nitrogen molecule. Pore size distribution was calculated applying the BJH method to the desorption branch of the isotherm [13].

## 2.3. Electron microscopy

For TEM investigation, the sample was crushed and deposited on a holey carbon foil supported by a copper grid. The Philips CM30 microscope, operated at 300 kV, was equipped with a Supertwin lens (cs = 1.2 mm, point resolution <0.2 nm).

## 2.4. Epoxidation procedure

2-cyclohexen-1-ol (Fluka, ca. 97%), cyclohexene (Fluka, >99.5%) and *tert*-butylhydroperoxide (TBHP, Fluka, ca. 5.5 M solution in nonane, stored over molecular sieve 4 Å) were used as received. Toluene (Riedel–de Haën, >99.7%) was distilled and stored over molecular sieve.

All reactions were carried out under purified He to avoid the presence of oxygen and moisture. In the standard procedure, 70 mg catalyst was transferred into a 50 ml glass reactor, equipped with a magnetic stirrer, thermometer and reflux condenser, and heated in a He flow to 200 °C for 2 h (100 °C for DMAP10 and ACOP10). After cooling to ambient temperature, 20 mmol reactant, an internal standard (decane or pentadecane), and 2 ml of toluene (solvent) were added. The reaction was started at 90 °C by addition of 5 mmol TBHP (reactant/peroxide molar ratio = 4/1).

Samples were analyzed by an HP 6890 gas chromatograph (cool on-column injection, HP-FFAP column). Selectivities and yield were calculated as follows (the subscript 0 denotes initial concentrations):

- selectivity of the epoxide related to the olefin converted:

$$S_{\text{olefin}} = \frac{[\text{epoxide}]}{[\text{olefin}]_0 - [\text{olefin}]} \times 100\ (\%); \qquad (1)$$

- selectivity of the epoxide related to the peroxide converted:

$$S_{\text{peroxide}} = \frac{[\text{epoxide}]}{[\text{peroxide}]_0 - [\text{peroxide}]} \times 100\ (\%). \qquad (2)$$

The initial rate was defined as the epoxide formation in the first 5 min.

No leaching was observed when filtering off the catalyst during the reaction and testing the filtrate for epoxidation activity. The catalyst exhibited the same activity as before filtering. Besides, no change of modifier structure has been observed by $^{13}$C-NMR of a used catalyst.

## 3. Results

### 3.1. Catalyst characterization

Characterization of ACOP10 by FTIR, $^{29}$Si-NMR and $^{13}$C-NMR spectroscopic methods, and $NH_3$ adsorption has been described elsewhere [10]. These methods confirmed that the covalently bound acetoxypropyl groups mostly preserved their integrity during catalyst preparation. The Ti dispersion was estimated using the ratio $R$ between the intensities of the signals Ti–O–Si (940 cm$^{-1}$) and Si–O–Si (1210 cm$^{-1}$) in the IR spectrum [11]. Although this measurement gives only semiquantitative values due to overlapping with Si–O$^{-}$ vibrations [14], the data are useful for comparison of similarly prepared mixed oxides. For the ACOP10 catalyst, Ti dispersion in the silica matrix was high ($R = 0.55$, determination see [10]), comparable to that achieved with the unmodified aerogel (0.47).

The influence of increasing amount of acetoxypropyl functional groups on the textural properties of titania–silica is shown in table 2. The nitrogen physisorption measurements were carried out on calcined materials. The pore size distributions of ACOP2 and ACOP20 with the corresponding t-plots are presented in figure 1. The BET surface areas decreased significantly from 339 m$^2$ g$^{-1}$ for ACOP2 to 181 m$^2$ g$^{-1}$ for the ACOP20 material. This drop is even more striking when comparing to the surface area of the unmodified titania–silica reference catalyst [10]. It has been found recently that introduction of organic functional groups can have a detrimental impact on the surface area of titania–silica mixed oxides [7,10].

The pore volume decreased from 2.1 cm$^3$ g$^{-1}$ for ACOP2 to 1.2 cm$^3$ g$^{-1}$ for ACOP20. The micropore volume for all modified catalysts was nearly zero, which is also reflected by the minor negative deviations of the measured volumes from the fitted line in the t-plots (figure 1, right) for higher thickness $t$. The maxima of the pore size distribution decreased significantly with increasing loading of acetoxypropyl groups. This is illustrated in figure 1 (left) which compares the pore size distribution of two aerogels having the highest (ACOP20) and lowest (ACOP2) acetoxypropyl content.

The morphology of the uncrushed aerogel clumps of ACOP10 was investigated by scanning electron microscopy

Table 2
Physico-chemical properties of the aerogels.

| Aerogel | $S_{\text{BET}}$ (m$^2$ g$^{-1}$) | $V_p$[a] (cm$^3$ g$^{-1}$) | $V_m$[b] (cm$^3$ g$^{-1}$) | $d_{\max}$[c] (nm) |
|---|---|---|---|---|
| Unmodified | 813 | 2.3 | 0.1 | 62 |
| ACOP2 | 339 | 2.1 | 0 | 75 |
| ACOP5 | 253 | 1.3 | 0 | 68 |
| ACOP10 | 251 | 1.6 | 0 | 65 |
| ACOP20 | 181 | 1.2 | 0 | 54 |

[a] Designates the BJH cumulative desorption pore volume of pores in the maximum range 1.7–300 nm diameter.

[b] Micropore volume from t-method analysis.

[c] Graphically assessed maximum of the desorption branch pore size distribution.

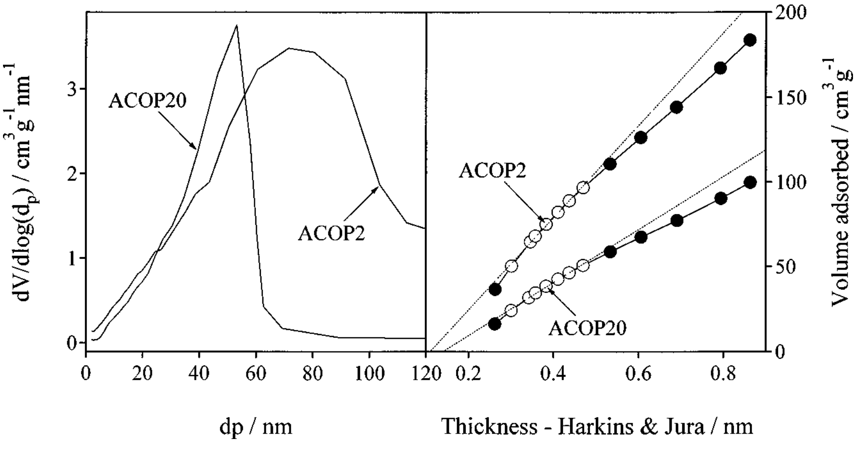

Figure 1. Pore size distributions (left) and t-plots (right), of ACOP2 and ACOP20 aerogels, determined by $N_2$ adsorption.

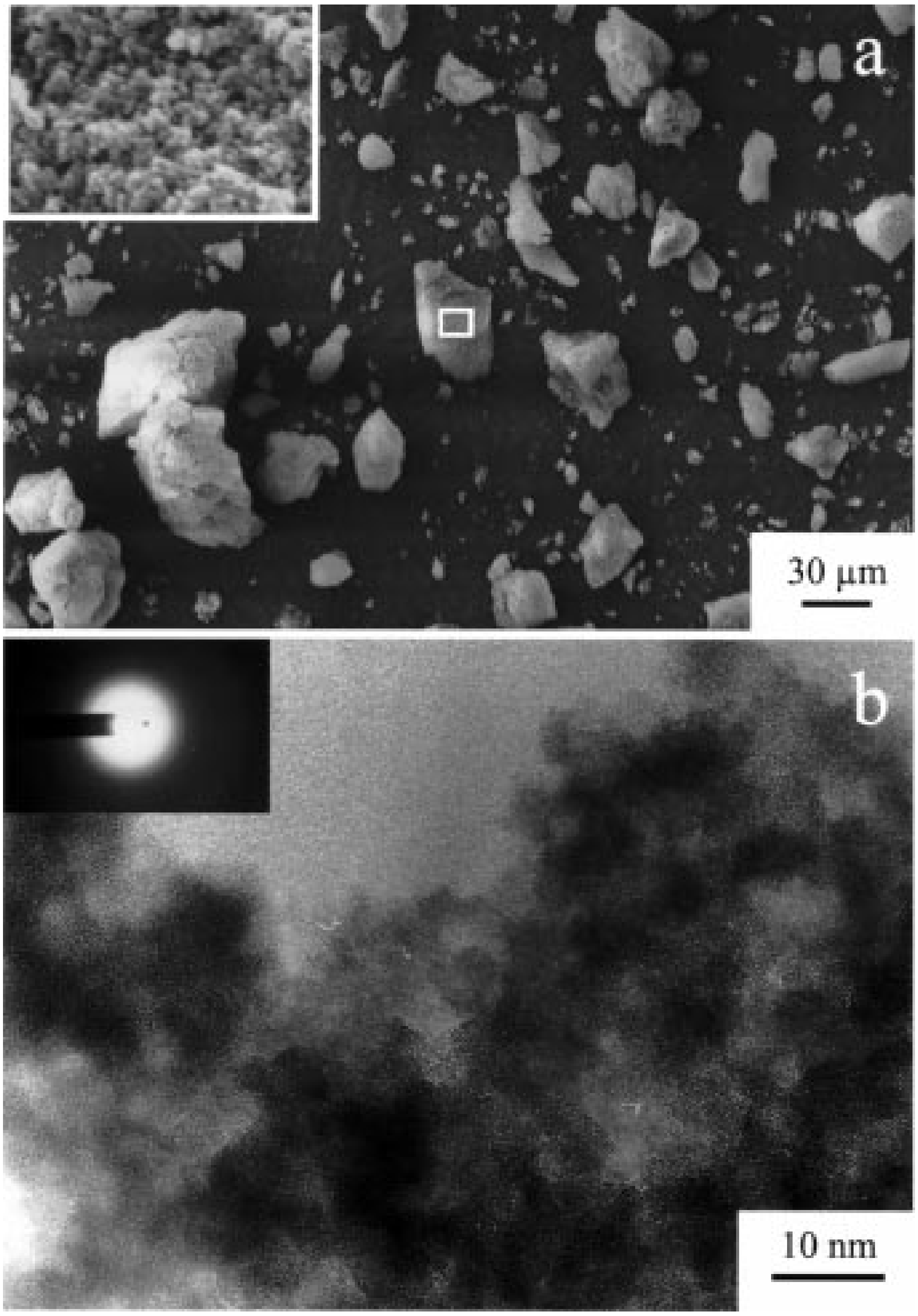

Figure 2. Scanning (a) and transmission (b) electron micrographs of ACOP10 aerogel. Inset in (a): magnification of white box (horizontal length corresponds to 10 $\mu$m), inset in (b): electron diffractogram.

(figure 2(a)). The majority of the particles had sizes above 10 $\mu$m. The inset in figure 2(a) shows the magnification of the white box. The microstructure of the aerogel was made up of smaller units in the range 0.1–1 $\mu$m, which formed larger particles upon further condensation.

The morphology in the nanoscale is shown in figure 2(b). Both the transmission electron micrograph and electron diffractogram indicate the typical amorphous aerogel structure that has been observed before also for methyl-modified titania–silica aerogels [7]. No crystalline nanodomains could be perceived.

### 3.2. *Catalytic activity – epoxidation of cyclohexene and cyclohexenol*

In all cases, conversion of cyclohexene and cyclohexenol over the five different aerogels and the formation of the corresponding epoxides were followed for 2 h by GC analysis. These kinetic curves (not shown here) can be well characterized by the initial rate and the time required to reach 70% conversion of TBHP. For the sake of reliable comparison, the olefin and peroxide selectivities are also compared at identical (70%) peroxide conversion.

Table 3
Epoxidation of cyclohexene in toluene with TBHP at 90 °C.

| Aerogel | Initial rate (mmol g$^{-1}$ min$^{-1}$) | Time of reach 70% TBHP conversion (min) | $S_{\text{olefin}}$ at 70% TBHP conversion (%) | $S_{\text{peroxide}}$ at 70% TBHP conversion (%) |
|---|---|---|---|---|
| Unmodified | 5.9 | 20 | 96 | 91 |
| ACOP2 | 8.2 | 8 | 97 | 94 |
| ACOP5 | 7.7 | 8 | 97 | 89 |
| ACOP10 | 8.1 | 7 | 98 | 90 |
| ACOP20 | 6.6 | 9 | 97 | 90 |

Table 4
Epoxidation of cyclohexenol in toluene with TBHP at 90 °C.

| Aerogel | Initial rate (mmol g$^{-1}$ min$^{-1}$) | Time of reach 70% TBHP conversion (min) | $S_{\text{olefin}}$ at 70% TBHP conversion (%) | $S_{\text{peroxide}}$ at 70% TBHP conversion (%) | *Cis*/*trans* at 70% TBHP conversion |
|---|---|---|---|---|---|
| Unmodified | 4.9 | 46 | 76 | 77 | 72 : 28 |
| ACOP2 | 6.8 | 5 | 90 | 80 | 80 : 20 |
| ACOP5 | 6.5 | 10 | 82 | 77 | 79 : 21 |
| ACOP10 | 8.2 | 7 | 88 | 80 | 80 : 20 |
| ACOP20 | 6.3 | 10 | 90 | 86 | 83 : 17 |

The results of the epoxidation of cyclohexene with TBHP are presented in table 3. The initial rate (in the first 5 min) increased moderately upon introduction of acetoxypropyl groups. The differences are bigger when comparing the time necessary to achieve higher peroxide conversions. Taking 70% TBHP conversion as a representative value, the performance of all organically modified aerogels is rather similar, but 2–3 times better than that of the unmodified aerogel. The epoxidation selectivity of the unmodified aerogel is already high, related either to the olefin or TBHP consumed, and barely influenced by the presence of acetoxypropyl groups.

The activities and selectivities of the aerogels in cyclohexenol epoxidation are compared in table 4. As concerns the activity, the correlation is similar to that observed in the more facile epoxidation of cyclohexene. Introduction of the ester groups results in only moderate enhancement in the initial rate, but the reaction time until 70% TBHP conversion is reduced dramatically, by a factor of 4.5–9. Besides, there is no correlation between the reaction rate, or time, and the concentration of organic modification. The epoxide selectivity related to cyclohexenol improved from 76% for the unmodified catalyst to 90% for ACOP2 and ACOP20. The peroxide selectivity was influenced to a lesser extent and reached its highest value for ACOP20 with 86%. A small but significant change by 7–11% in stereoselectivity (*cis*/*trans* ratio) was observed by the introduction of organic functional groups.

## 4. Discussion

The catalytic test of organically modified titania–silica aerogels revealed that the influence of acetoxypropyl groups on the epoxidation reactions was barely dependent on their concentration in the range 2–20 mol%. For example, substitution of only 2 mol% of tetramethoxysilane precursor by 3-acetoxypropyltrimethoxysilane was sufficient to reduce the reaction time in the epoxidation of cyclohexenol by a factor 9, and increase $S_{\text{olefin}}$ from 76 to 90% (at 70% conversion). Further increase in the concentration of ester groups did not lead to considerable improvement in the catalytic performance.

The reaction rates and times in tables 3 and 4 are compared based on identical amounts of catalyst. The differences in the modified and unmodified aerogels are even more striking when considering also the changes in BET surface area (table 2). The presence of 2–20 mol% acetoxypropyl groups diminished the original surface area by a factor 2.5–4.5. Unfortunately, the real number of surface Ti active sites cannot yet be determined. Hence, turnover frequencies, which would allow a more reliable comparison of the catalytic activity could not be calculated.

A possible explanation for the positive effect of acetoxypropyl groups on the epoxidation activity and selectivity of titania–silica mixed oxides could be an electron-pair–donor interaction of the carbonyl O atom with the Ti sites. The small enhancement in *cis*/*trans* ratio of epoxycyclohexenol (table 4) may support this assumption, as the increased crowdedness around the active site can favor the formation of *cis*-epoxide. However, this interaction is expected to reduce the Lewis acidity, and thus the epoxidation activity, of the Ti active site [15].

Summarizing the results we can conclude that incorporation of acetoxypropyl groups into titania–silica is detrimental for the textural properties but enhances dramatically the performance of aerogels in epoxidation reactions. A feasible explanation for these effects, which contrast to earlier observations [1], requires further research.

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