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# Novel amine-modified $TiO_2$–$SiO_2$ aerogel for the demanding epoxidation of substituted cyclohexenols

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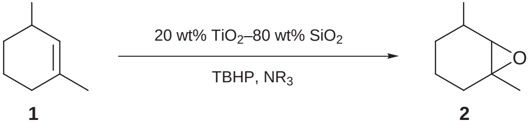
**Amine additives provided high selectivity (up to 98%) in the epoxidation of sensitive alkyl-substituted cyclohexenols with a $TiO_2$–$SiO_2$ aerogel and $Bu^tOOH$; heterogenization of the catalyst system resulted in a new bifunctional catalyst.**

Recently, active and selective titania–silica epoxidation catalysts have been prepared by the solution sol-gel technique.[1–4] The advantages of this preparation method are the intimate molecular-scale mixing of Ti in the silica matrix and high surface area of the materials. The drying conditions have also been recognized to play an important role: removal of the solvent entrapped in the tenuous gel network by semicontinuous extraction with supercritical $CO_2$ at near ambient temperature results in mesoporous textural properties, providing access of bulky reactants to the active sites.[2] An aerogel with a $TiO_2$ content of 20 wt% (20LT), prepared by this method, showed outstanding performance in the epoxidation of cyclic olefins with alkyl hydroperoxides.[5,6]

In the epoxidation of primary and secondary allylic alcohols, high selectivities were achieved in the presence of (basic) zeolite 4 Å or $NaHCO_3$ used as additives.[7] There are also some other examples in the literature on the enhancement of epoxide selectivity when the acidity of a Ti- and Si-containing catalyst is tuned by alkali metal exchange or addition of an inorganic base to the reaction mixture.[8–11] In the epoxidation of alkyl-substituted cyclohexenols, such as 3-methylcyclohex-2-en-1-ol **1** and 3,5,5-trimethylcyclohex-2-en-1-ol (isophorol), 20LT provided the epoxides only as minor products ($<10\%$ selectivity). Unfortunately, the acid-catalyzed side reactions could not be suppressed by any of the known methods. For comparison, good to high yields of the epoxides of alkyl-substituted cyclohexenols were obtained by stoichiometric oxidations,[12–15] but no efficient catalytic method is available yet for this type of epoxidation reaction.[16]

Here we report a new strategy for the selective epoxidation of alkyl-substituted cyclohexenols by adjusting the surface properties of titania–silica with small amounts of amines. The epoxidation of 3-methylcyclohex-2-en-1-ol **1** with TBHP (*tert*-butyl hydroperoxide) was chosen as a model reaction (Scheme 1).

A 20LT aerogel was prepared by the solution sol-gel method as described previously.[2] The solvent was extracted semicontinuously with supercritical $CO_2$ at 40 °C and 240 bar. The raw aerogel was calcined in air at 400 °C for 5 h. X-Ray analysis showed that the amorphous material possessed a good Ti dispersion, high surface area ($S_{BET} = 680\ m^2\ g^{-1}$) and mesoporous structure (mean pore diameter: 9 nm, pore size maximum: 40 nm, pore volume: 1.5 $cm^3\ g^{-1}$).



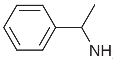
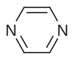
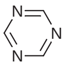
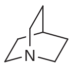
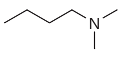
**Scheme 1**

Prior to epoxidation, 0.1 g 20LT was dried *in situ* in Ar at 200 °C for 16 h. Under standard conditions, epoxidation was carried out at 60 °C in Ar using 10 mmol substrate, 2.5 mmol TBHP, 0.1 g activated molecular sieves 4 Å, the amine modifier, 0.5 ml dodecane (internal standard) and toluene (total volume: 10 ml). Conversion and selectivities were determined by GC analysis and iodometric titration. The conversion of **1** is related to the stoichiometric initial amount of TBHP (4:1) and given in mol% of the maximal attainable value, and the epoxide selectivity is quoted with reference to the substrate consumed.

In the absence of amine the allylic alcohol **1** was readily converted non-oxidatively, and the epoxide **2** was only a minor product (Table 1). Major reactions were the acid-catalyzed isomerization and dehydration of **1**, and oligomerization of **1** and **2**. Note that the epoxidation activity of titania–silica is attributed to the Lewis acidity of the $(Si–O)_4Ti$ sites, whereas the surface silanol groups represent Brønsted acidic sites active in the aforementioned side reactions.[17,18] Addition of 1 or 10 mol% amine (related to **1**) suppressed the acid-catalyzed side reactions and good to high epoxide selectivity was achieved. Interestingly, no correlation between the basicity of the amine additive and the epoxide selectivity could be established.

The amount of amine additive played an important role in the selectivity enhancement, as illustrated in Fig. 1. Only 1 mol% of triazine was sufficient to suppress the acid-catalyzed reactions and reduce the conversion of **1** to 100% or below. Note that the substrate:TBHP molar ratio was 4:1, and that the conversion is related to the initial amount of TBHP. Addition of 5 mol% of triazine afforded the highest epoxide yield of 56%, correspond-

**Table 1** Epoxidation of 3-methylcyclohex-2-en-1-ol **1** using amines as additives (under standard conditions)

| | | | | Epoxide selectivity (%) related to[b] | |
|---|---|---|---|---|---|
| Entry | Additive | $pK_a$ | $t_{30\%}{}^{a}$/min | **1** | Peroxide |
| 1 | — | — | 1.3 | 3 | 34 |
| 2[c] |  | 9.4 | 120 | 82 | 49 |
| 3[c] |  | 0.65 | 36 | 90 | 80 |
| 4[c,d] |  | –1.7 | 9.2 | 92 | 86 |
| 5[e] |  | 10.9 | 43 | 73 | 83 |
| 6[e] |  | 10.0 | 9 | 98 | *ca.* 100 |

[a] Time needed for 30% conversion of **1**. [b] Determined at $t_{30\%}$. [c] 10 mol% amine (based on **1**) was used. [d] Ethylbenzene was used as internal standard. [e] 1 mol% amine (based on **1**) was used.

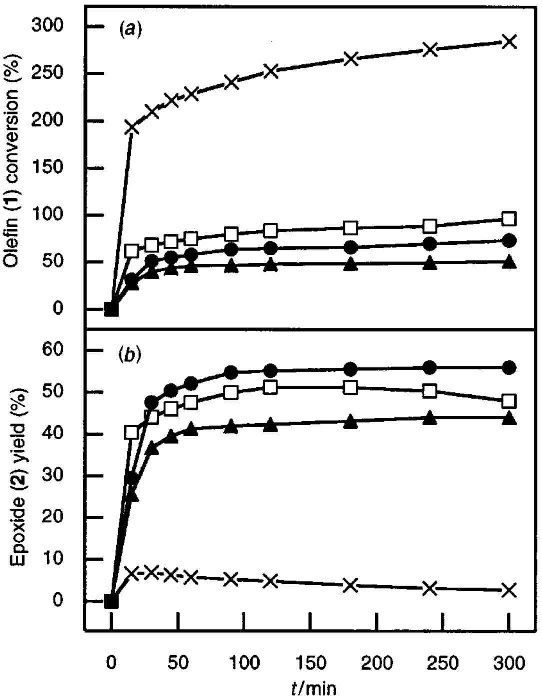


**Fig. 1** Influence of the amount of triazine on (*a*) the conversion of **1** (related to the initial amount of TBHP) and (*b*) the yield of **2**: (×) 0, (□) 1, (●) 5 and (▲) 10 mol% based on **1**.

ing to over 90% epoxide selectivity at medium conversion. The results show that the amounts of amine additives quoted in Table 1 may be far from the optimum values.

On the basis of preliminary kinetic studies we propose that the amines have a rather complex effect. At low concentrations they interact mainly with the surface silanol groups, and deactivate (block) these Brønsted sites. This positive effect on selectivity depends only marginally on the p$K_a$ value of the amine, as all amines tested are more basic than the oxygen atom of **1**. At higher concentrations, interaction of the amines with the Ti site seems to be dominant, leading to lower epoxidation activity. This effect is similar to the detrimental influence of alcoholic solvents, which was suggested to be due to their competition with TBHP for the active sites.[17] Also, at high amine concentrations (usually $\geqslant$5mol%) the base-catalyzed ring opening of **2** became important.

Intrigued by the good results of the epoxidation of **1** with Me$_2$NBu as additive, we prepared a new catalyst with immobilized aminoalkyl groups. An aerogel containing 10 wt% TiO$_2$ was designed with surface Me$_2$N(CH$_2$)$_3$ groups (designated 10LT$_A$). To a solution of (MeO)$_4$Si (135 mmol) and Ti(acac)$_2$(OPr$^i$)$_2$ (12.5 mmol) (75% in Pr$^i$OH) in Pr$^i$OH (10 ml), the hydrolysant consisting of water (750 mmol) and HNO$_3$ (15 mmol) in Pr$^i$OH (40 ml) was added at room temperature. After 6 h stirring, a solution of Me$_2$N(CH$_2$)$_3$Si(OMe)$_3$ (15 mmol) in Pr$^i$OH (82 ml) was added. The solution gelated within 12 h. After ageing for 7 days at room temperature, the solvent was removed by extraction with supercritical CO$_2$ at 40 °C and 230 bar. On the basis of a thermoanalytical investigation, the amine-modified aerogel was calcined only at 100 °C for 1 h, in order to avoid decomposition of the Me$_2$N(CH$_2$)$_3$ groups. The BET surface area of the mesoporous calcined sample amounted to 312 m$^2$ g$^{-1}$. The pore volume was 1.0 cm$^3$ g$^{-1}$ and the average cylindrical pore diameter was calculated to be 11.6 nm. The good titania dispersion (relative contribution of Si–O–Ti entities) was confirmed by FT-IR from the ratio of Si–O–Ti (950 cm$^{-1}$) and Si–O–Si (1210 cm$^{-1}$) peak areas.

This catalyst also converted the allylic alcohol **1** selectively to the epoxide **2**. At 30% conversion of **1**, which was attained in 18 min, the epoxide selectivity was 78%. As compared to the reaction with 20LT and Me$_2$NBu (Table 1), the lower epoxide selectivity of 10LT$_A$ is likely due to the too high amine content. The catalyst was also tested in the epoxidation of *trans*-hex-2-en-1-ol. Under conditions similar to the oxidation of **1** but at 90 °C, the epoxide yield was 48% after 1 h reaction time. Recycling 10LT$_A$ twice (after washing and drying) afforded 33 and 31% yields. The lower yields were partly due to catalyst loss during recycling (17%), and the difference between the performance of fresh and used catalysts decreased at higher reaction times. Epoxide selectivity was barely influenced by recycling (70 and 72% for the first and third runs, respectively). Besides, 10LT$_A$ did not catalyze the epoxide ring opening reaction, indicating the suppressed acidity of this amine-modified catalyst.

We have attempted to apply amine modifiers in the epoxidation of other cyclic allylic alcohols. The epoxidation of isophorol over 20LT without amine additive at 363 K resulted in byproducts mainly by non-oxidative reactions, and only 10% epoxide selectivity at 221% conversion (related to initial TBHP concentration) was obtained in 1h. Using PhMeCHNH$_2$ (1 mol%) the side reactions were diminished and 58% epoxide selectivity at 72% substrate conversion was achieved. The influence of alkyl substituents on the epoxidation of cyclohexenols is presently under investigation.

In conclusion, in the epoxidation of alkyl-substituted cyclic allylic alcohols with a titania–silica aerogel and TBHP, small amounts of amines suppress the acid-catalyzed, non-oxidative side reactions. In the best case, 1 mol% of Me$_2$NBu (related to 3-methylcyclohex-2-en-1-ol reactant) afforded 98% epoxide selectivity at 30% conversion, and over 70% epoxide yield at high conversion. On the basis of this observation, a novel bifunctional, recyclable catalyst has been developed. This modified aerogel contains both Lewis acidic [(SiO)$_4$Ti] and Lewis basic [C$_3$H$_6$N(CH$_3$)$_2$] sites. It is hoped that tuning the acid–base and redox properties will further improve the performance of this catalyst.

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