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RESEARCH NOTE

Epoxidation of α-Isophorone with Amine-Modified Titania–Silica Hybrid Aerogel: Evidence for Ti–Amine Interaction

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The epoxidation of isophorone with TBHP over unmodified and dimethylaminopropyl-modified titania–silica aerogels is studied. Organic modification diminishes the epoxidation activity of titania–silica, but it also eliminates the activity in acid-catalyzed side reactions, such as epoxide and peroxide decomposition. Addition of MeOH to an unmodified aerogel has a similar effect. These catalytic experiments suggest that (i) electron donation by the alkylamino groups or MeOH to the Ti active site (Lewis acid) suppresses its acidity and thus the rate of acid-catalyzed oxidation and isomerization reactions, and (ii) the surface Si–OH groups (Brønsted sites) of titania–silica are poor catalysts for epoxide decomposition.

Key Words: **titania–silica aerogel; organic modification; dimethylaminopropyltrimethoxysilane; epoxidation; isophorone; *tert*-butylhydroperoxide.**

1. INTRODUCTION

Titania–silica aerogels modified by soluble bases have recently been shown to be excellent catalysts for the epoxidation of various olefins (1). The benefits of dissolved organic amine modifiers could be preserved after heterogenization by incorporation of amines via the thermally and chemically stable Si–C bond (2, 3). Because excess acidity is known to reduce epoxidation selectivity by catalyzing side reactions of substrate and consecutive reactions of the product (4, 5), the positive effect has mainly been attributed to the neutralizing effect of amine bases (1, 3). However, based on the ability of titanium to form complexes with amines (6), it can be conceived that a direct interaction between the organic surface modification and the titanium active site exists. An indication for this type of interaction is the shift of the UV-vis band characteristic of isolated Ti sites from 220–230 to 260 nm, when quinoline is adsorbed on a hydrophobic titania–silica (7). In case of TS-1, the interaction of Ti with volatile polar compounds, such as NH_3, H_2O, and CH_3OH, has been evidenced by FTIR, DRUV, EXAFS, and XANES (8).

The selective epoxidation of α,β-unsaturated carbonyl compounds is difficult because the electron-withdrawing effect of the carbonyl moiety decreases the electron density at the double bond. Epoxidation of α-isophorone (Scheme 1) has been catalyzed by different catalytic systems (9–11). Up to 99% epoxide selectivity at 50–70% peroxide conversion could be attained with an aerogel containing nominal 20 wt% TiO_2 (12).

In order to test the newly developed organically modified aerogels in the epoxidation of deactivated olefins and to elucidate the role of organic modification in the epoxidation reaction, the oxidation of α-isophorone has been chosen as a test reaction in this work. The catalyst used is an *N*,*N*-dimethyl-3-aminopropyl-modified titania–silica mixed oxide containing ca. 9 wt% TiO_2. This aerogel showed exceptional activity and 94% epoxide selectivity at 91% peroxide conversion in the epoxidation of cyclohexenol with TBHP (3).

2. EXPERIMENTAL

Catalyst Preparation

Synthesis of the DMAP10 catalyst has been described elsewhere (3). The Ti- and Si-precursors were titanium bisacetylacetonatediisopropoxide and tetramethoxysilane, and 10 mol% of the silicon precursor was replaced by *N*,*N*-dimethyl-3-aminopropyltrimethoxysilane. Hydrolysis was catalyzed by aqueous HNO_3 in 2-propanol, and in the second-step gelation was forced by trihexylamine (and the modifier precursor) at room temperature. Semicontinuous extraction with supercritical CO_2 was performed at 40°C and 230 bar. The aerogel was calcined in flowing air at 100°C. The aerogel contained 8.9 wt% TiO_2, taking into account the weight of the organic modification. The unmodified reference catalyst was prepared analogously to the modified catalyst to ensure comparability (3, 13). This

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SCHEME 1. Epoxidation of α-isophorone by TBHP.

material contained 10 wt% TiO_2. Both catalysts were characterized by N_2 physisorption, thermal analysis, and FTIR, DRIFT, and NMR spectroscopy (3, 13). Some important features are collected in Table 1. The data show that both catalysts are dominantly mesoporous, but organic modification led to a lower surface area and Ti dispersion in the silica matrix.

Epoxidation Procedure

The α-isophorone (Fluka, purum.), α-isophorone oxide (Aldrich, >99%), and *tert*-butylhydroperoxide (TBHP; Fluka, ca. 5.5 M solution in nonane, stored over molecular sieve 4 Å) were used as received. The toluene was distilled and stored over molecular sieve.

All reactions were carried out under purified He. 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 an He flow to 100°C for 2 h. After cooling to ambient temperature, 20 mmol of olefin, pentadecane (internal standard), 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). For the epoxide decomposition measurements the catalyst was pretreated in the same way as described above. After cooling, 5 mmol of isophorone oxide, an internal standard, and 2 ml of toluene were added. The reaction was started at 90°C by addition of 5 mmol TBHP. When noted, 5 mmol of MeOH was added or no catalyst was used. Samples were analyzed by an HP 6890 gas chromatograph (cool on-column injection, HP-FFAP column). Epoxide selectivity was related to the olefin consumed.

TABLE 1

Textural Properties of Aerogels

Aerogel	S_{BET}	$V_p{}^a$	$V_m{}^b$	$\langle d_p \rangle^c$	R^d
Unmodified	813	2.3	0.10	8.5	0.47
DMAP10	312	1.0	0	11.6	0.35

[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] $\langle d_p \rangle = 4V_p/S_{BET}$.

[d] Ti dispersion; $R = S_{(Si\text{–}O\text{–}Ti)}/S_{(Si\text{–}O\text{–}Si)}$, determined from FTIR spectra (for details, see (22)).

TABLE 2

Epoxidation of α-Isophorone (IP) in Toluene with TBHP at 90°C

Aerogel	Average rate in 5 min (μmol m^{-2} min^{-1})	Average rate in 120 min (μmol m^{-2} min^{-1})	$S_{epoxide}$ at 10% TBHP conversion (%)
Unmodified	0.20	0.12	>99
DMAP10	0.13	0.10	93

3. RESULTS

It has been shown earlier (3) that organic modification of titania–silica aerogels by *N*,*N*-dimethyl-3-aminopropyl functional groups enhances the specific reaction rate and selectivity in the epoxidation of cyclohexenol, but the positive effect is minor in the oxidation of cyclohexene. Here, in the epoxidation of α-isophorone organic modification of titania–silica has an unambiguously negative impact on the catalytic performance. As illustrated in Table 2, the epoxide selectivities were high, but the initial rate of olefin conversion was considerably reduced by organic modification of the aerogel. Kinetic analysis indicated that with increasing conversion the difference in average rates decreased monotonously, likely due to some deactivation of the unmodified aerogel. Due to the slow reaction, the selectivities are compared at 10% TBHP conversion. Clearly, organic modification of titania–silica by aminopropyl groups has no advantage in the epoxidation of the electron-deficient olefin α-isophorone.

In order to learn more about the behavior of the organically modified aerogel, two important side reactions, the decomposition of the product isophorone oxide and the oxidant TBHP, have been investigated in more detail. Consumption of the epoxide via acid-catalyzed ring opening reactions (14) is shown in Table 3. The conditions were chosen to mimic the situation during the epoxidation reaction described above. The initial amount of isophorone oxide (5 mmol) corresponds to 100% epoxide yield. Despite the high reaction temperature (90°C), no decomposition of isophorone oxide was observed in the absence of

TABLE 3

Isophorone Oxide Conversion under Epoxidation Reaction Conditions, in the Presence and Absence of Catalyst (90°C, 2 h Reaction Time)

Catalyst	Additive	Epoxide conversion (%)	TBHP conversion (%)
No	no	0	15
Unmodified	no	22	39.5
Unmodified	MeOH	0	18
DMAP10	no	0	10.5

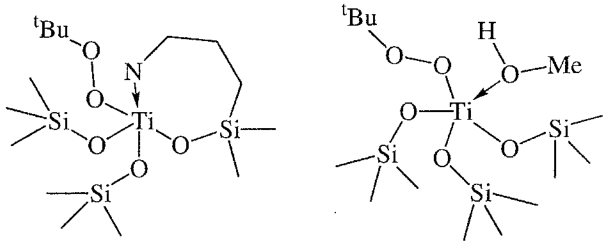
catalyst. (Careful removal of water from the system before reaction is very important.) The unmodified aerogel is a good catalyst for the decomposition of isophorone oxide. In 2 h, 22% of the maximum possible amount of product is consumed by consecutive reactions. Note that during epoxidation the reactant isophorone competes for the Ti active sites, which explains the high epoxide selectivity up to 60–70% TBHP conversion (15). Addition of MeOH completely stops the decomposition of isophorone oxide, although the acid-catalyzed reaction of the epoxide with MeOH to form the corresponding hydroxy-ether would be possible. Modification of the aerogel with dimethylaminopropyl groups had the same effect as addition of MeOH: no consumption of isophorone oxide was observed, compared to the reference reaction in the absence of catalyst.

A similar picture was obtained from studying the effect of catalysts and additive on TBHP decomposition (Table 3). Without any catalyst present, TBHP decomposes slowly at the high reaction temperature. The unmodified catalyst enhanced remarkably the reaction rate compared to the uncatalyzed decomposition, but addition of MeOH compensated this effect. Interestingly, the amine-modified aerogel DMAP10 had no activity in peroxide decomposition. Furthermore, analysis of the reaction mixture at any reaction time indicated the same order of TBHP decomposition in the four systems investigated.

4. DISCUSSION

Organic modification of titania–silica aerogels by *N*,*N*-dimethyl-3-aminopropyl functional groups (DMAP10) had a small positive effect on the epoxidation of cyclohexene, as compared to the performance of the unmodified aerogel (16). The results in Table 2 demonstrate that the aminoalkyl functional groups had a negative impact on the epoxidation of α-isophorone, which molecule possesses an electron-withdrawing (deactivating) carbonyl group in an α position to the C=C bond. Considering the specific initial rates related to unit surface areas of the aerogels, DMAP10 was more active in the epoxidation of cyclohexene by 40% (16), but less active in the epoxidation of isophorone by more than 30%. Epoxidation of the two substrates was carried out under almost identical conditions. The average pore diameter of the organically modified aerogel was higher than that of the unmodified catalyst, and microporosity was completely eliminated in the modified catalyst. Hence, the observed changes cannot be attributed to differences in substrate diffusion in the pores of the aerogels.

It is clear from the results in Table 3 that the titania–silica aerogel is active in the decomposition of isophorone oxide and TBHP, but organic modification by covalently bound dimethylaminopropyl functional groups completely eliminated these side reactions on the catalyst. It seems likely that the incorporated aminoalkyl group as Lewis base can interact with a neighboring Ti active site (strong Lewis acid) and/or a surface silanol group (weak Brønsted site). Unfortunately, no direct evidence for these interactions can be provided yet.



SCHEME 2. Possible interactions of the amine functional group and MeOH with the Ti active site (simplified drawing, further interactions to obtain the favored octahedral coordination of Ti are not shown).

Surface silanol groups (Si–OH) are characteristic of titania–silica mixed oxides, being responsible for the hydrophilicity of these materials (17, 18). It is clear from the inactivity of the unmodified aerogel after the addition of MeOH that silanol groups are not involved in epoxide decomposition (ring opening) reactions of α-isophorone oxide. Apparently, epoxide decomposition is catalyzed by the Ti active sites of the unmodified aerogel. It has been shown before that formation of the peroxo complex enhances the activity (acidity) of Ti in epoxide decomposition (19, 20). We propose that the absence of epoxide decomposition after addition of MeOH or when the unmodified catalyst is replaced with DMAP10 has the same origin: the suppressed acidity of the Ti–peroxo complex due to electron donation by MeOH or the surface aminoalkyl functional groups (Scheme 2). The same conclusion concerning the acidity of the Ti–peroxo complex can be drawn from the peroxide decomposition experiments (Table 3). This is the first experimental evidence that the amine functional groups in the organically modified titania–silica mixed oxide interact directly with the Ti active sites under reaction conditions.

It is known that alcohols are poor solvents for epoxidations with titania–silica, but the low reactivity was explained by competition between the alcoholic solvent and the alkylhydroperoxide oxidant for the Ti sites (21). Our results suggest that the suppressed Lewis acidity of the Ti active sites should also be taken into account for the interpretation of the low epoxidation rate in alcoholic solvents.

5. CONCLUSIONS

Epoxidation of α-isophorone and decomposition of isophorone oxide and TBHP provide the first experimental evidence for an electron donor interaction of the amine functional group with the Ti active site in an organically modified titania–silica mixed oxide. This interaction can account for suppressed acidity of the Ti active site, resulting in suppression of the acid-catalyzed side reactions, and also for the lower activity in the epoxidation of the deactivated olefin α-isophorone. These observations demonstrate why amine modification of titania–silica is an effective tool for tuning the acidity of mixed oxides for specific epoxidation reactions (2, 3).

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