JOURNAL OF CATALYSIS **157**, 665–675 (1995)

Titania-Silica Mixed Oxides

III. Epoxidation of α-Isophorone with Hydroperoxides

R. Hutter, T. Mallat, and A. Baiker[1]

Department of Chemical Engineering and Industrial Chemistry, Swiss Federal Institute of Technology, ETH-Zentrum, CH-8092 Zürich, Switzerland

The epoxidation of an α-keto olefin, α-isophorone, has been studied using high-surface-area, amorphous titania-silica aerogels. The mixed oxides were prepared by the alkoxide–sol-gel route and the solvent was removed by semicontinuous extraction with supercritical CO_2. The morphology of the catalysts was studied by HRTEM. The influence of the following reaction parameters was investigated: temperature, the chemical nature of hydroperoxide and solvent, and the ratio of olefin to catalyst or peroxide. The highest reaction rate and selectivity were obtained in alkylaromatic solvents of low polarity. Polar solvents compete for the active coordination sites and lower the reaction rate. All tested aerogels provided high epoxide selectivity (98–100%) at 333 K, using *t*-butyl hydroperoxide as oxidant in an olefin : peroxide molar ratio of 5 : 1. No epoxide formation was observed with H_2O_2. A considerable leaching of titanium in the aqueous oxidizing medium (evidenced by FTIR and ICP-AES analysis) is attributed to the hydrolysis of the Ti–O–Si bonds. The aerogels containing 20 or 2 wt% TiO_2 show the highest rate, related to the amount of catalyst or TiO_2, respectively. There is a positive correlation between oxidation rate and Ti–O–Si connectivity, characteristic of Ti-dispersion in the silica matrix. The suppressed reactivity of α-isophorone compared to cyclohexene is attributed to the electron-withdrawing effect of the carbonyl group, whereas the influence of the 2-methyl group (steric hindrance and electron release) is of secondary importance. The best titania-silica aerogel proved to be superior to TiO_2-on-SiO_2, TS-1, and titania-silica xerogels. © 1995 Academic Press, Inc.

INTRODUCTION

Considerable effort has been expended in the past decades to developing heterogeneous epoxidation catalysts that can substitute the conventional stoichiometric and homogeneous catalytic oxidation of olefins. The first truly heterogeneous catalyst (TiO_2-on-SiO_2) was discovered in the late sixties by Shell researchers (1) and is used in industrial scale for propylene epoxidation. This supported titania catalyst is active with alkylhydroperoxides as oxidant and at least as selective as the best homogeneous molybdenum catalysts (2, 3). It is assumed that the active species are the surface Ti-alkylperoxo groups, isolated by O–Si^{IV} fragments (4). The chemical stability of the catalyst and the absence of leaching problems are likely due to compound formation (Ti–O–Si bonds) between the Ti-precursor and silica during the calcination step (5). Other silica-supported oxides (such as V_2O_5, MoO_3, and ZrO_2) have also been tested but either their activity or the chemical stability of the oxide catalysts were inferior to the TiO_2-on-SiO_2 system (5, 6).

A major progress has been achieved recently in the Enichem laboratory by synthesising a titanium-substituted silicalite (TS-1), in which titanium is assumed to be uniformly distributed in the silicalite framework (7–9). The big advantage of this new material is the use of the cheap oxidant aqueous H_2O_2 under mild conditions (10–13). The range of organic compounds that can be oxidized with TS-1 is, however, greatly limited by the relatively small average diameter (about 0.55 nm) of the channel system, where most of the active sites are located (10, 14). The scope of using Ti-zeolites as epoxidation catalysts has been broadened when zeolites of larger pore size, such as a Ti-zeolite isomorphous with Zeolite β (15) or with MCM-41 (16), have been synthesized. Although they have been shown to be able to oxidize bulky cycloalkenes, their intrinsic activity is moderate and some further development is needed to improve their catalytic performance (17–21).

Other types of solid catalysts, such as vanadium-pillared clays (22), Mo–Y zeolites (23, 24), and the V-analog of the ALPO-31 molecular sieve (25), have also been described recently, but some leaching of active component was observed or was not studied at all. The catalytic performance of "supported reagents" is usually well below that of Ti-zeolites (26). Polymer-supported metal complexes (e.g., V- and Mo-compounds on polystyrene) provide good to excellent selectivities toward the epoxide and in some cases no loss of activity was observed after recycling them (27).

Titania-silica mixed oxides are usually considered to be

---

[1] To whom correspondence should be addressed.

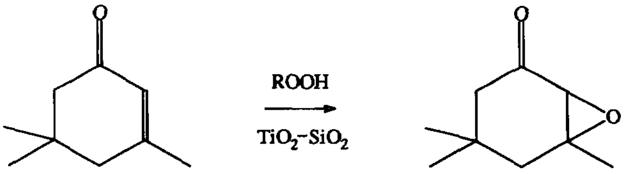
0021-9517/95 $12.00

materials of poor epoxidation activity (12, 13, 28). On the contrary, we have shown recently that highly active and selective epoxidation catalysts can be prepared by the sol-gel–aerogel technique (29–31). The amorphous, mesoporous titania-silica aerogels of high surface area (>400 m^2/g) were developed by tuning the synthesis parameters to the requirements of the oxidation reaction, using cyclohexene as model compound and an alkyl- or alkylaromatic hydroperoxide as oxidizing agent. The sample containing 20 wt% TiO_2 possessed the highest activity for the oxidation of various cyclic olefins, including cyclododecene, norbornene, and limonene, with selectivities up to 93% to peroxide and ca. 100% to epoxide. Astonishingly, this catalyst was found to be more active and selective than other Ti- and Si-containing solid catalysts (29, 31).

During the development of heterogeneous epoxidation catalysts, usually simple linear or cyclic olefins (e.g., propene, 1-octene, cyclohexene) have been used as model compounds. The metal-catalyzed epoxidation with alkylhydroperoxides is known to proceed by a heterolytic mechanism, with an electrophilic attack on the olefin by the active oxidizing species (4, 5, 32). The rate increases with increasing substitution of the olefin with alkyl or other electron-donating groups. On the contrary, electron-withdrawing groups retard the rate of epoxidation. Substitution at the C=C double bond can influence the reaction rate by more than three orders of magnitude (5). Conjugation of the olefin with other multiple bonds or an aromatic ring decreases the reaction rate as the delocalization of π-electrons reduces the electron density at the double bond (33). Accordingly α-keto olefins are difficult to epoxidize by the electrophilic metal catalyst/alkylhydroperoxide systems (32).

It seemed to be of interest to test our new sol-gel titania-silica aerogels in the epoxidation of an electron-deficient olefin that contains two functional groups susceptible to oxidation. The transformation of α-isophorone (3,5,5-trimethyl-2-cyclohexene-1-one) to the corresponding epoxide (3,5,5-trimethyl-2,3-epoxy-cyclohexanone, α-isophorone oxide) was chosen as an example (Scheme 1). To our knowledge, no heterogeneous catalytic oxidation of α-isophorone has been reported so far. A homogeneous catalytic process, the $Pd(OAc)_2$-catalyzed oxidation of α-isophorone with α-silyloxyalkyl peroxybenzoate, provided only 17% epoxide (34). The use of alkaline hydrogen peroxide (70–72% yield (35)), alkaline t-butyl hydroperoxide (59% yield (36)), dimethyl- or cyclohexanone dioxirane (83–86% yield (37, 38)), and N-bromosuccinimide (52% yield (39)) as stoichiometric oxidants has been suggested for this reaction.

In the present study we focus on the influence of reaction conditions on the rate and selectivity of the epoxidation of α-isophorone, using a 20 wt% TiO_2 : 80 wt% SiO_2 aerogel (30). The performance of this catalyst is compared to other well-known Ti- and Si-containing epoxidation catalysts.



SCHEME 1

EXPERIMENTAL

Catalyst Preparation

Analytical and purum grade reagents and doubly distilled water after ion exchange were used. The Ti-contents of the catalysts were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

An amorphous sol-gel–aerogel titania-silica catalyst [20LT], containing 20 wt% nominal TiO_2 was prepared by the sol-gel method under acidic preparation conditions and dried by semicontinuous extraction with supercritical CO_2 at 313 K (low-temperature aerogel, LT) (30). An acidic hydrolysant was added to an isopropanolic solution of tetraisopropoxytitanium (IV) modified by acetylacetone (in a molar ratio of 1 : 1) and tetramethoxysilicon (IV). The resulting titania-silica gel was subsequently dried under supercritical conditions. A part of it was calcined in a flow of dry air at 473–1073 K. The 20LT aerogel, calcined at 873 K, possessed a BET surface area of 550 m^2/g, a pore volume $V_{p(N_2)}$ of 1.3 cm^3/g, and a mean pore diameter $\langle d_p \rangle$ of 10 nm (30). Other samples containing 2, 5, and 10 wt% TiO_2 (2LT, 5LT and 10LT, respectively) were prepared similarly. More details on the synthesis and characterization of sol-gel titania-silica by means of FTIR, UV-vis, N_2-physisorption, X-ray diffraction, and thermal analysis have been reported previously (30, 31).

A sol-gel titania-silica xerogel (10X, 10 wt% TiO_2) was prepared the same way, except that the resulting gel was conventionally dried in vacuum at 373 K and partly calcined in air at 673–873 K. The xerogel, calcined at 673 K, possessed a BET surface area of 473 m^2/g, a pore volume $V_{p(N_2)}$ of 0.03 cm^3/g and was made up predominantly of micropores ($\langle d_p \rangle < 2$ nm) (30). A silica-supported titania catalyst (TiO_2-on-SiO_2, 2 wt% TiO_2) has been prepared by grafting tetraisopropoxytitanium (IV) on Aerosil 200 (Degussa, S_{BET} = 200 m^2/g, $V_{p(N_2)}$ = 1.5 cm^3/g), followed by calcination at 873 K (31).

Titanium silicalite (TS-1; 3.1 wt% TiO_2, S_{BET} = 420 m^2/g) has been synthesized according to the procedure described in Ref. (40).

Oxidation Reactions

Cumene hydroperoxide (CHP, ca. 3 *M* in cumene), *t*-butyl hydroperoxide (TBHP, ca. 3 *M* in toluene or in isooctane), and purum or analytical grade reagents (α-isophorone, >99 wt%) and solvents were used.

The oxidation reactions were performed in a closed, mechanically stirred glass batch reactor fitted with reflux condenser, thermometer, septum for withdrawing samples, and dropping funnel for addition of the peroxide. All reactions were carried out strictly under argon (99.999%) to avoid the presence of oxygen and moisture. Typically, the peroxide was charged in the dropping funnel. Catalyst, solvent, and olefin were introduced into the reactor. Most of the catalytic runs were carried out using an olefin : catalyst weight ratio of 53. The slurry was heated to the reaction temperature. The reaction was started by adding the peroxide to the vigorously stirred slurry ($n = 1000\ \text{min}^{-1}$).

Conversion and selectivity were determined by gas chromatography in the presence of an internal standard (31). Selectivities are calculated as follows:

$$S_{\text{peroxide}}\,(\%) = 100 \cdot [\text{epoxide}]/([\text{peroxide}]_0 - [\text{peroxide}])$$

$$S_{\text{olefin}}\,(\%) = 100 \cdot [\text{epoxide}]/([\text{olefin}]_0 - [\text{olefin}]).$$

The initial rate (r_0) is defined as the epoxide formation in the first 20 min. Hydroperoxide conversion was determined by iodometric titration using a Metrohm 686 titroprocessor.

The minimum energy conformation of CHP and the olefins was calculated by MM+ force field (Hyperchem, Release 3 from Hypercube Inc.).

Spectroscopic Analysis

The infrared measurements were performed at room temperature using a Perkin–Elmer 2000 FTIR; 100 scans were accumulated for each spectrum at a spectral resolution of 4 cm^{-1}. A 1-mg sample in 100 mg KBr was pressed to a wafer and placed directly into the IR beam. For the study of leaching of Ti^{IV} from the solid, 0.2 g 20LT aerogel was suspended in 2 ml H_2O_2 (30% in water) and 5 ml methanol, stirred at 343 K for 5 and 130 min, filtered, and dried at 373 K in vacuum to decompose the peroxo-complexes.

High-Resolution Transmission Electron Microscopy (HRTEM)

The fine powder of the mixed oxide was deposited onto a holey carbon foil. The electron micrographs were obtained by a Philips CM30 ST microscope at 300 kV. The elemental microanalysis of the particles was carried out by a Tracor TN-5500 energy dispersive X-ray spectrometer (EDX).

TABLE 1

Epoxidation of α-Isophorone with Different Hydroperoxides[a]

Peroxide	r_0 (mmol min^{-1} (g cat)$^{-1}$)	S_{olefin} (%)[b]	S_{peroxide} (%)[b]
CHP[c]	0.13	98	85
TBHP[d]	0.17	98	83
TBHP[e]	0.16	99	83

[a] Reaction conditions: 0.2 g 20LT aerogel, 77 mmol α-isophorone, 13.4 mmol peroxide, 9 ml ethylbenzene (solvent), 333 K.

[b] At 50% conversion.

[c] Ca. 3 *M* in cumene.

[d] Ca. 3 *M* in toluene.

[e] Ca. 3 *M* in isooctane.

RESULTS

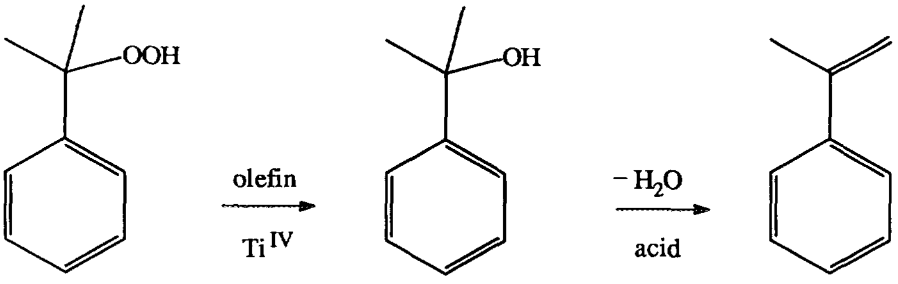
The Role of Peroxide Structure

The epoxidation of α-isophorone with the titania-silica aerogel 20LT was investigated using various peroxides. The uncalcined (raw) sample was used here and in the further catalytic experiments, because a decrease in activity (by 10–20%) after calcination in air at 473–1073 K was observed in the epoxidation of cyclohexene (31) and α-isophorone.

No oxirane was obtained with H_2O_2 (35 wt% in water), but cumene hydroperoxide and *t*-butyl hydroperoxide in apolar solvents provided high selectivities ($S_{\text{olefin}} \geq 98\%$), as illustrated in Table 1. Thus, the multifunctional olefin α-isophorone is selectively oxidized to the epoxide with this catalyst. Note that the oxidation of α,β-unsaturated ketones with peracids usually does not lead to oxirane formation (32).

TBHP is more reactive by about 20% than CHP. A similar relation concerning the reactivity of these hydroperoxides toward propene has been reported (41). Another disadvantage of using alkylaromatic hydroperoxides is the dehydration of the alcohol coproduct (2-phenyl-2-propanol in the case of CHP), catalyzed by acidic sites, as shown in Scheme 2. The formation of this olefinic by-product was observed only when CHP was used at temperatures above 343 K. It has been reported that using TiO_2-on-SiO_2 this side reaction is important only in the epoxidation of unreactive olefins (e.g., allyl chloride) at temperatures above 350 K (2, 5). The Brønsted and Lewis acidity of titania-silica and the influence of acidic sites of Ti-containing solid catalysts on the epoxidation selectivity have been discussed elsewhere (2, 10, 11, 42, 43).

Regardless of solvent and calcination temperature of the catalyst, no oxirane was obtained with aqueous H_2O_2. The absence of epoxidation activity using titania-silica and H_2O_2 is in agreement with earlier observations (4). The only exception is the epoxidation of olefins possessing a



SCHEME 2

hydrophilic functional group (e.g., unsaturated alcohols), the reaction in which some minor epoxide formation can be expected (12, 13). A comparison of TS-1 (hydrophobic nature of the internal channel system and active with aqueous H_2O_2) and titania-silica mixed oxides (hydrophilic relative to TS-1 and hardly or not active with aqueous H_2O_2) revealed that the competitive adsorption of water hinders the epoxidation reaction in the latter case (12, 13). Note that water is a strong inhibitor also in the (homogeneous) metal-catalyzed epoxidations with alkylhydroperoxides (4).

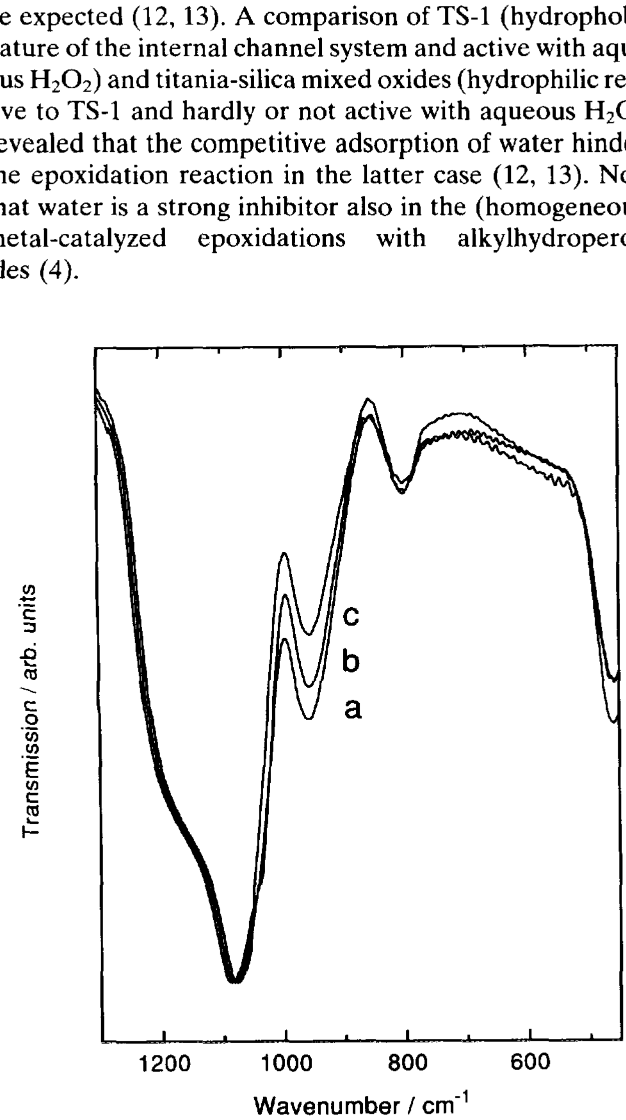


FIG. 1. Influence of catalyst treatment with H_2O_2 on the FTIR spectra of 20LT aerogel (calcined at 873 K); before treatment (a); after 5 min treatment with aqueous-methanolic H_2O_2 and drying at 373 K (b); after 130 min treatment and subsequent drying (c).

A further difficulty with aqueous H_2O_2 is the major leaching of Ti from the mixed oxide during reaction, which was indicated by the yellow color of the slurry (homogeneous Ti-peroxo-complexes). For comparison, the chemical stability of titania-silica aerogels in apolar medium is excellent, similar to that of TiO_2-on-SiO_2 (Shell-type catalyst) (4, 5, 31). The limited stability of the aerogel (raw or calcined) in the simultaneous presence of water and oxidizing agent was proved by FTIR analysis. Figure 1 shows the irreversible decrease of the relative intensities of the characteristic band around 950 cm^{-1} (attributed to Ti–O–Si linkages (30, 44–46)) after treating the catalyst with the oxidant. The leaching process is especially fast in the first period of the oxidative treatment. Calcination procedures at temperatures between 473 and 1173 K did not suppress leaching. The loss of titanium during epoxidation with H_2O_2 was also confirmed by ICP-AES analysis.

We assume that in aqueous oxidizing medium the Si–O–Ti structural parts of the aerogel (evidenced by FTIR analysis) dissociate according to possible pathways depicted in Scheme 3, resulting in the formation of "mobile" Ti-species. It has already been reported that considerable structural changes of sol-gel-derived titania-silica mixed

TABLE 2

Epoxidation of α-Isophorone with Various Solvents[a]

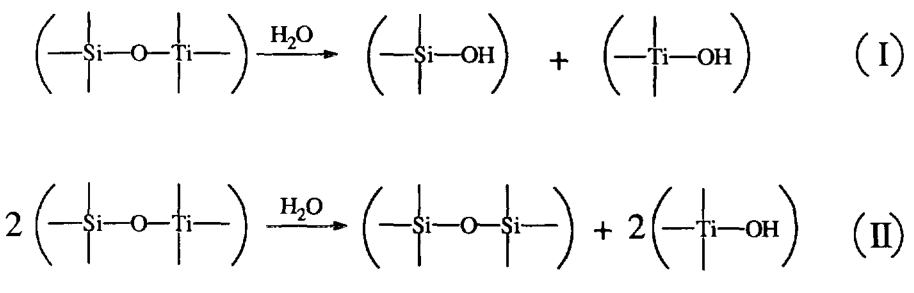
Solvent	E_T^N [b]	r_0 (mmol min^{-1} (g $cat)^{-1}$)	S_{olefin} (%)[c]	$S_{peroxide}$ (%)[c]
Isooctane	0.012	0.10	95	79
Ethylbenzene	ca. 0.1[d]	0.16	99	83
Cumene	ca. 0.1[d]	0.16	99	82
1,2-Dichlorobenzene	0.225	0.15	93	75
1,1,2,2-Tetrachloroethane	0.269	0.15	90	73
t-BuOH	0.389	0.01	78	53
H_2O	1.000	0.00	—	—

[a] Reaction conditions: 0.2 g 20LT aerogel, 77 mmol α-isophorone, 13.4 mmol TBHP (ca. 3 *M* in isooctane), 9 ml solvent, 333 K.

[b] Normalized solvent polarity parameter (48).

[c] At 50% conversion.

[d] Value for methylbenzene.



SCHEME 3

oxides can be expected at above 400 K in the presence of water vapor and air (47). Restructuring was attributed to the hydrolysis of the Ti–O–Si bonds, the migration of Ti from the network to the adsorbed water layer, and the formation of new Ti–O–Ti bonds. Note that the advantage of working under dry conditions has also been shown for propylene epoxidation catalyzed by TiO_2-on-SiO_2 (1).

Solvent Effect

The influence of solvents on the epoxidation of α-isophorone with TBHP is shown in Table 2. The solvent polarity is characterized by the empirical solvent parameter E_T^N, derived from the solvatochromism of a pyridinium-*N*-phenoxide betaine (48). The highest selectivities and reaction rates were obtained in alkylaromatic solvents of low polarity. Both selectivity and activity were somewhat lower in the strongly apolar isooctane, likely due to the poor wetting of the hydrophilic titania-silica catalyst (12, 13). Interestingly, the reaction rate and especially the selectivities decreased in the moderately polar chlorinated hydrocarbons, compared to the alkylaromatic solvents. It has been suggested earlier that polar but noncoordinating solvents, such as polychlorinated hydrocarbons, are ideal for the epoxidations catalyzed by homogeneous transition metal catalysts or TiO_2-on-SiO_2 (2, 5).

The performance of the sol-gel catalyst dropped in protic polar solvents and there was no detectable oxirane formation in H_2O (the upper extreme of the polarity scale). It is known for homogeneous metal-catalyzed epoxidations with hydroperoxides that strongly polar protic solvents, such as water and alcohols, can form stable complexes with the catalyst (2, 5). The strong coordination of the solvent to the catalyst hinders the formation of the catalyst–hydroperoxide complex and impedes the approach of the hydrophobic olefin to the catalyst surface. The former leads to a reduced reaction rate and the latter to a reduced selectivity to the epoxide.

Influence of Olefin : Peroxide Ratio

The olefin : peroxide molar ratio has a crucial influence on the rate and selectivity of the epoxidation reaction, as shown in Table 3. When keeping the hydroperoxide concentration and the total volume of the reaction mixture at a constant level, the reaction rate decreases with decreasing olefin : peroxide rate. At an olefin : peroxide ratio of 1 : 1 only 20% conversion was obtained after 18 h and the selectivity based on the olefin was only 70% even at this low conversion. However, further conclusions concerning the kinetics of the reaction cannot be drawn, as the initial rate is defined as the epoxide formation in the first 20 min (in order to include the influence of a possible early catalyst deactivation). For comparison, the transition metal-catalyzed homogeneous epoxidation reactions have generally been found to be first order in olefin (5, 49).

At high olefin : hydroperoxide molar ratio (5 : 1) the selectivities to epoxide, based on the olefin converted, were nearly 100% and S_{peroxide} was also high (Table 3). With the decreasing olefin : hydroperoxide ratio the selectivities are significantly lower. These results are in good agreement with earlier observations using homogeneous transition metal or heterogeneous TiO_2-on-SiO_2 catalysts and alkylhydroperoxides as oxidant (3–5). The main reason for low selectivity at low olefin concentration is the competing homolytic decomposition of the hydroperoxide yielding radicals, e.g., *tert*-butoxy and *tert*-butylperoxy radicals from

TABLE 3

Influence of Olefin : Peroxide Molar Ratio on the Epoxidation of α-Isophorone[a]

α-Isophorone : ROOH	r_0 (mmol min^{-1} (g cat)$^{-1}$)	S_{olefin} (%)[b]	S_{peroxide} (%)[b]
6 : 1	0.17	99	83
5 : 1	0.16	99	83
4 : 1	0.14	96	80
3 : 1	0.09	90	76
2 : 1	0.05	84	64
1 : 1	0.02	70[c]	50[c]

[a] Reaction conditions: 0.2 g 20LT aerogel (raw), 0.54 *M* TBHP (in isooctane), ethylbenzene (solvent; total liquid volume: 25 ml), 333 K.
[b] At 50% conversion.
[c] At 20% conversion.

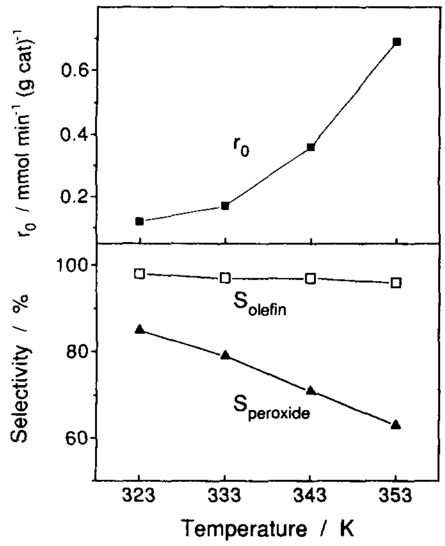


FIG. 2. Influence of reaction temperature on the initial rate (top) and selectivity (bottom). S_{olefin} and $S_{peroxide}$ are determined at 70% peroxide conversion (conditions: 0.2 g 20LT aerogel, 77 mmol α-isophorone, 13.4 mmol TBHP (in isooctane), 9 ml ethylbenzene (solvent)).

TBHP. These radicals can react with the olefin, the solvent, and the hydroperoxide, depending on the conditions and the chemical nature of the reaction components.

Influence of Temperature

As depicted in Fig. 2, the rate of α-isophorone epoxidation increases and the peroxide selectivity ($S_{peroxide}$) decreases when the temperature is raised from 323 to 353 K. The selectivity related to the olefin (S_{olefin}) remains high even at 353 K, but only at moderate peroxide conversions. The conversion dependence of S_{olefin} at two different catalyst : reactant ratios is illustrated in Fig. 3. Up to 50% peroxide conversion, the selectivity is about 99%. At around 80–90% conversion (depending on the catalyst : reactant ratio) the reaction almost stops and the decomposition of epoxide to a variety of products becomes the dominant reaction.

The catalyst deactivation at about 80–90% conversion and 350 K is likely due to the dimerization and polymerization of the product epoxide and/or the reactant olefin. This assumption is supported by the high-molecular-weight byproducts (oligomers) detected with GC/MS analysis. The monotonous decrease of peroxide selectivity ($S_{peroxide}$) with increasing reaction temperature (Fig. 2) is attributed to the competition by the homolytic decomposition of the oxidant (5).

Optimization of Reaction Parameters

An attempt was made to find an optimum in reaction conditions for the epoxidation of α-isophorone using the 20LT aerogel. The following reaction parameters have been varied: temperature, concentration of reactants, catalyst : reactant ratio, and chemical nature of peroxide and solvent. The key problem of optimization is the low reaction rate under mild conditions (electron-deficient olefin) and the drop in selectivity at higher temperature. Accordingly, two optima have been found, depending on the optimized parameter. The conditions of the fastest reaction (I) with fair selectivities and the most selective reaction (II) with acceptable reaction time are shown in Table 4.

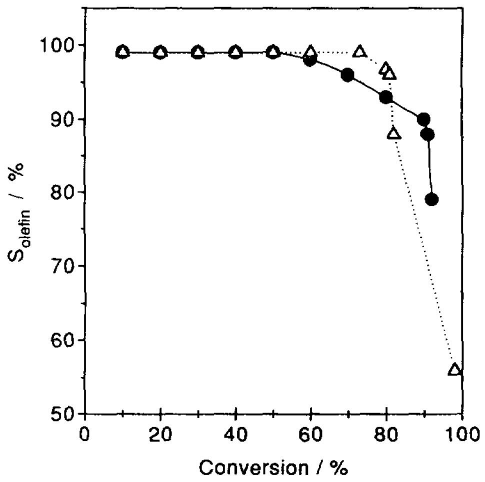


FIG. 3. Selectivity based on α-isophorone vs peroxide conversion (conditions: 0.2 g (△) or 0.4 g (●) 20LT aerogel, 77 mmol α-isophorone, 13.4 mmol TBHP (in isooctane), 9 ml ethylbenzene (solvent), 353 K).

Epoxidation of α-Isophorone with LT Aerogels of Different Ti-Content

The correlation between the catalytic performance of uncalcined (raw) LT aerogels and their titania content is shown in Fig. 4. The higher the titanium content of the mixed oxides between 2 and 20 wt%, the higher the initial rate, although the rate enhancement is not proportional with the titanium content. The selectivity of the olefin → epoxide transformation is high, 98–99% for all aerogels.

Comparison of Some Ti-Containing Heterogeneous Catalysts

Very few examples can be found in the literature where the performance of heterogeneous catalysts of different origin are compared. In the epoxidation of α-isophorone we tested a series of LT aerogels and the best catalyst 20LT was also compared to a titania-silica xerogel, a Ti-zeolite (TS-1), and TiO_2-on-SiO_2 (Shell-type) catalyst.

The initial rate of epoxidation and the selectivities related to either the peroxide or the olefin are shown in Fig. 5. The selectivity (measured at 50% peroxide conversion) of the TiO_2-on-SiO_2 catalyst is almost as good as that of

TABLE 4

Epoxidation of α-Isophorone[a]

Code	Olefin : catalyst (g/g)	Temperature (K)	r_0 (mmol/(g_{cat} min))	$X_{peroxide}$ (%)	Time (min)	S_{olefin} (%)	$S_{peroxide}$ (%)
I	26.5	353	0.47	50	28	99	69
				90	168	90	61
II	53	323	0.12	50	350	ca. 100	89 (92[b])
				70	1100	98	85

[a] Reaction conditions: catalyst, 0.4 g (I) or 0.2 g (II) 20LT aerogel (raw); olefin: peroxide molar ratio 6:1 (3 *M* TBHP in isooctane); solvent, 9 ml ethylbenzene.

[b] With CHP as peroxide.

20LT, but its activity is lower by more than a factor of two. Note that, in contrast to the aerogels, the activity of the Shell-type catalyst cannot be improved by increasing the overall Ti-content above 2.3 wt% (31), which corresponds to a TiO_2-content at the surface of approximately 10–14% of the theoretical monolayer density (50). Some deactivation at temperatures above 340 K was also observed for the TiO_2-on-SiO_2. TS-1 provided less than 2% converson after 18 h. A conventionally dried sol-gel xerogel 10X containing 10 wt% TiO_2 was totally inactive in the reaction, independent of the calcination temperature. The inactivity of TS-1 and 10X is due to their microporosity: ca. 0.55-nm channel size is characteristic for the former and ≤2 nm for the latter (10, 14, 30, 31). For comparison, the calculated sizes of α-isophorone, TBHP, and CHP in their minimum energy conformation *in vacuo* are 0.75 × 0.58 × 0.84, 0.51 × 0.60 × 0.67 and 0.55 × 0.63 × 0.93 nm, respectively.

Morphology of Sol-gel Mixed Oxides

Electronmicroscopy of sol-gel aerogels and xerogels revealed some characteristic morphological differences. The micrographs of the same magnification shown in Figs. 6a–6c illustrate the influence of the titanium content of LT aerogels. The morphology of the 2LT aerogel is mainly determined by the silica matrix. The size of the particles (primary structure) is substantially bigger than those of aerogels containing 5–20 wt% TiO_2. All samples were fully amorphous except 20LT, which contained very few crystalline particles in the range 1–2 nm, which were not detectable by XRD (30). This observation is in agreement with the earlier conclusion derived from FTIR and UV-vis analysis, that the Ti-dispersion in silica decreases with increasing Ti-content and at 20 wt% TiO_2-content a considerable fraction of Ti is located in titania nanodomains (30, 31). Despite the presence of these nanodomains, no fluctuation

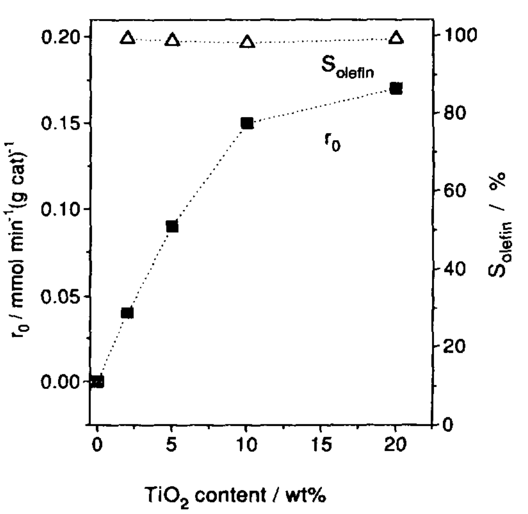


FIG. 4. Initial rate of α-isophorone epoxidation with LT aerogels as a function of TiO_2-content and selectivity based on olefin at 50% peroxide conversion (conditions: 0.2 g catalyst, 77 mmol α-isophorone, 13.4 mmol TBHP (in toluene), 9 ml ethylbenzene (solvent), 333 K).

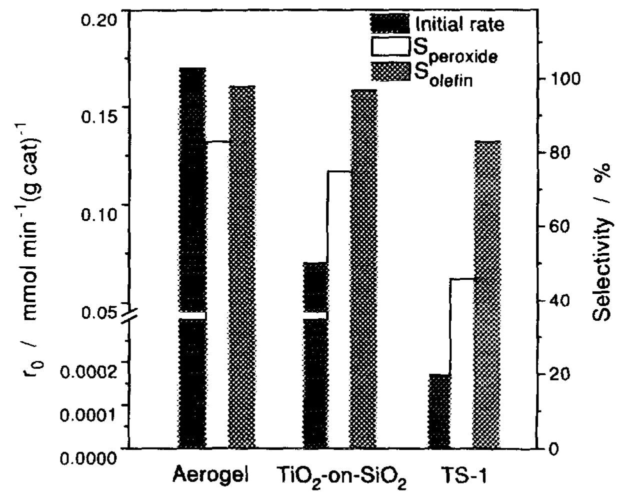


FIG. 5. Comparison of initial rates and selectivities (related to olefin and peroxide) observed for the epoxidation of α-isophorone using the uncalcined aerogel (20LT), titania-on-silica and TS-1 (conditions: 0.2 g catalyst, 77 mmol olefin, 13.4 mmol TBHP (in toluene), 9 ml ethylbenzene (solvent), 333 K).

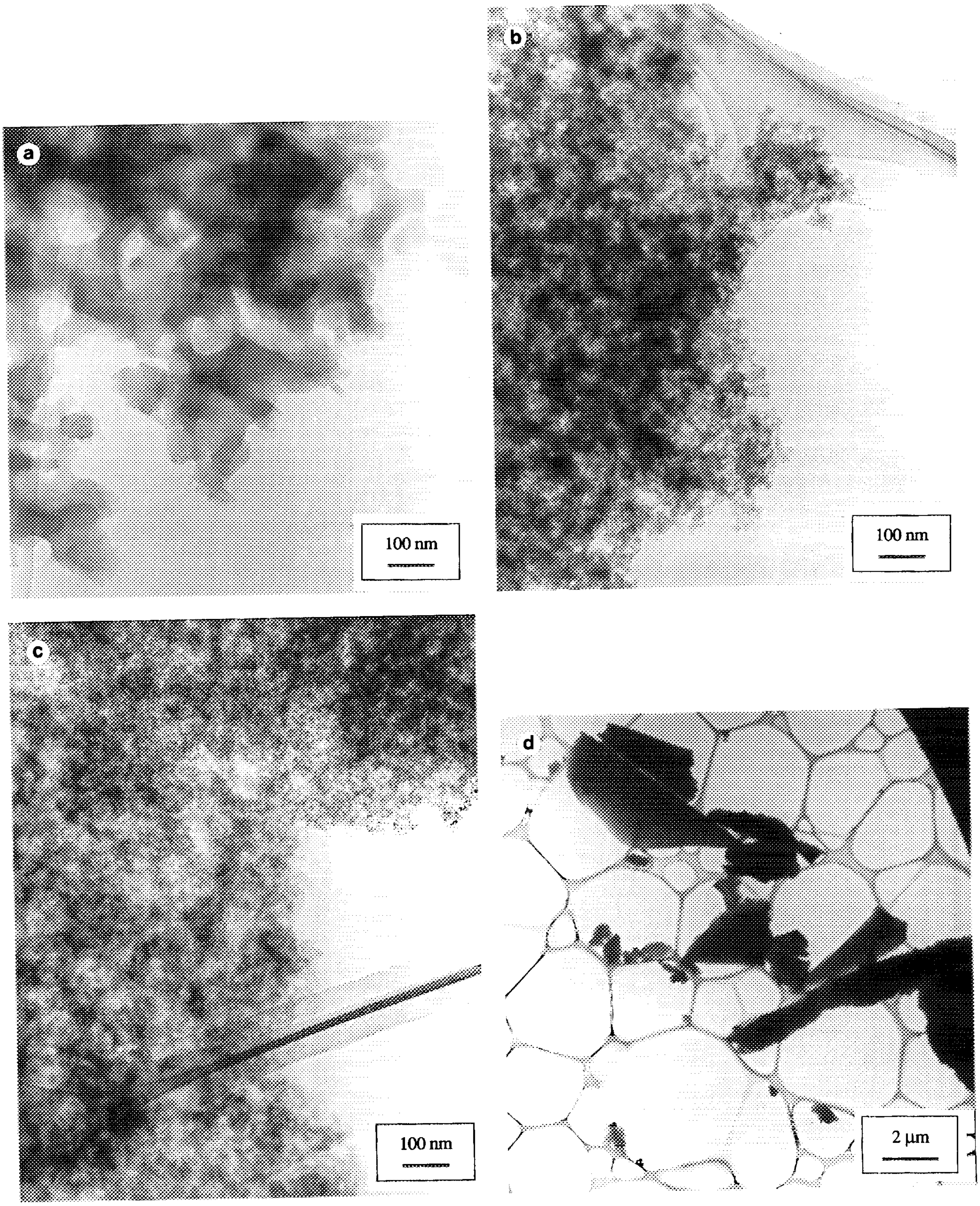
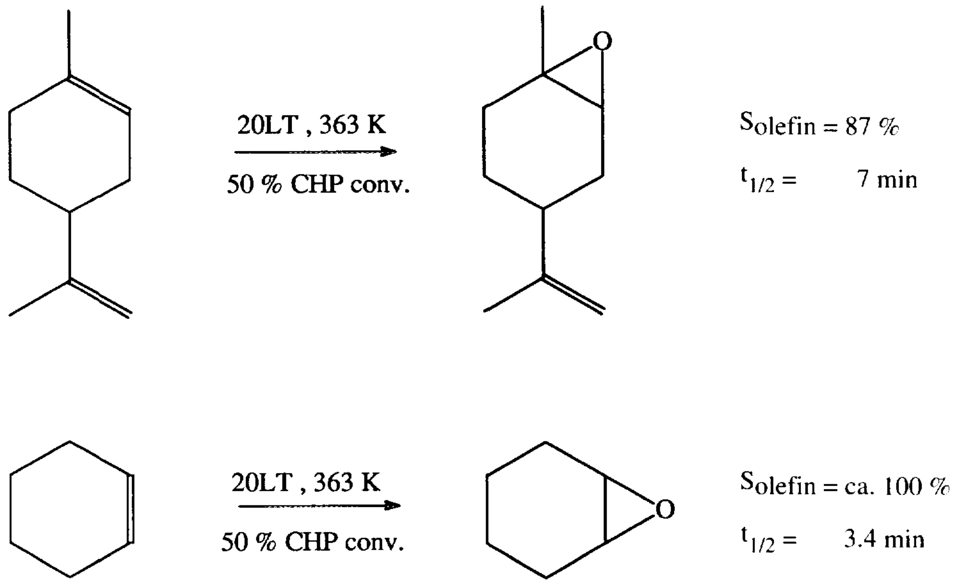


FIG. 6. High-resolution electron micrographs depicting morphological features of: aerogels 2LT (a), 5LT (b), 20LT (c), and xerogel 10X (d) (assignments of samples are explained in the Experimental section).



SCHEME 4

in the Ti : Si ratio could be detected by TEM-EDX analysis. This is an indication that the Ti-distribution in silica is very even in the 10 to 100-nm range or above.

Figure 6d illustrates the detrimental effect of conventional drying of the titania-silica sol-gel. The morphology of 10X xerogel resembles that of broken glass pieces with a rather uneven particle size in the range of about 0.1–5 μm. These samples possess a microporous structure and hardly any epoxidation activity (30, 31).

DISCUSSION

The aerogels, prepared by the alkoxide–sol-gel route and dried by semicontinuous extraction with supercritical CO_2 at low temperature proved to be very selective in the epoxidation of α-isophorone. The oxidation of this α-keto olefin (Scheme 1) is about 40–60 times slower than the oxidation of cyclohexene under the same conditions (31). An important question is whether the low reaction rate is due to the electron deficiency of the C=C bond (delocalized π-electrons) or due to steric hindrance represented by the methyl group at the C^3 atom. When limonene (4-isopropenyl-1-methyl-1-cyclohexene) was oxidized, the rate of reaction decreased only by a factor of 2, compared to the rate of cyclohexene oxidation (Scheme 4). Moreover, limonene was selectively oxidized at the sterically more hindered, but more nucleophilic double bond to give 4-isopropenyl-1-methyl-1-cyclohexene-1,2-epoxide (31). On the basis of these comparisons we can conclude that the electron deficiency of the C=C double bond in α-isophorone is crucial in the retardation of the epoxidation reaction and the influence of the 2-methyl group (steric hindrance and electron release) is of secondary importance.

We have found earlier in the epoxidation of cyclic olefins with sol-gel mixed oxides that the Ti-distribution in the silica matrix is a crucial parameter in determining the catalytic activity (31). The Ti-distribution (Ti–O–Si connectivity) was characterized by the ratio of the deconvoluted peak area of the ν(Ti–O–Si) vibration at ca. 940 cm^{-1} and that of ν(Si–O–Si) vibration at ca. 1210 cm^{-1} (30). This ratio (*D*), normalized to the Ti-content of the mixed oxide, is shown in Fig. 7. There is a good correlation between the

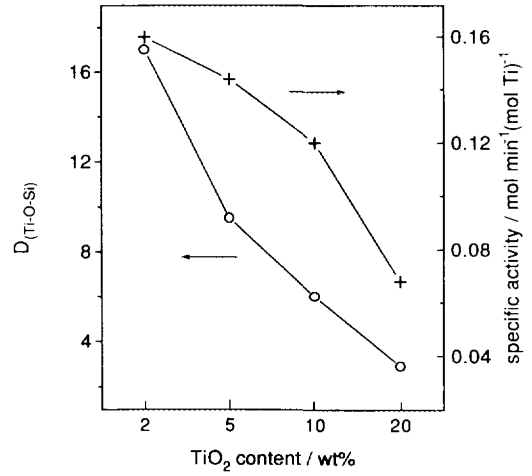


FIG. 7. Specific activity of LT aerogels and the relative contribution of Ti–O–Si connectvity ($D_{Ti-O-Si}$; see text) as a function of TiO_2-content (for conditions see Fig. 4 legend).

relative Ti-distribution (D) and the specific activity in α-isophorone epoxidation, related to the molar amount of Ti-content of the LT aerogels.

A different relationship was obtained in the epoxidation of cylohexene (31). In that reaction the specific activity of 5LT and 10LT catalysts was higher than that of 2LT. This unexpected behavior was explained by the pore size limitations in the latter catalyst. The average pore diameter of the 2LT sample is only 2–4 nm (depending on the calcination temperature) and around 8–14 nm for the samples of higher TiO_2-content (30). Comparing the epoxidation of cyclohexene and α-isophorone we can conclude that in the latter case the microporous structure of 2LT does not hinder the reaction, likely due to its considerably lower rate.

CONCLUSIONS

The epoxidation of α-isophorone, which represents an electron-deficient α-keto olefin, has been investigated using the previously developed (30, 31) low temperature titania-silica aerogels. Using t-butyl hydroperoxide as oxidant, the aerogels provide excellent epoxide selectivity (98–100%) under mild conditions. The electron-deficiency of the olefin seems to effect mainly the reaction rate, whereas the selectivity to olefin and peroxide remains high. Comparative tests in epoxidation with bulky olefins indicate that the catalytic performance of aerogels, derived from the sol-gel route combined with extraction of the solvent with supercritical CO_2, is better than that of zeolite TS-1 and the Shell-type silica-supported titania. The outstanding performance of the aerogel is attributed to its favorable mesoporous texture and the optimal abundancy of Ti–O–Si connectivity at 20% nominal TiO_2 content. It remains to be tested how these aerogels compare to the newly developed large pore Ti-zeolites (15, 16).

ACKNOWLEDGMENTS

The authors are grateful to D. Dutoit for kindly supplying the aerogels and to R. Wessicken (Department of Solid State Physics, Swiss Federal Institute of Technology, Zürich) for the HRTEM measurements. Financial support of this work by F. Hoffmann-La Roche AG, Switzerland, and the *Kommission zur Förderung der wissenschaftlichen Forschung* is gratefully acknowledged.

REFERENCES

1. Brit. Pat. 1 249 079 (1971).
2. Sheldon, R. A., van Doorn, J. A., Schram, C. W. A., de Jong, A. J., *J. Catal.* **31,** 438 (1973).
3. Sheldon, R. A., and van Doorn, J. A., *J. Catal.* **31,** 427 (1973).
4. Sheldon, R. A., *J. Mol. Catal.* **7,** 107 (1980).
5. Sheldon, R. A., *in* "Aspects of Homogeneous Catalysis" (R. Ugo, Ed.), Vol. 4, p. 3, Reidel, Dordrecht, Holland, 1981.
6. Brit. Pat. 1 248 709 (1971).
7. U.S. Pat. 4 410 501 (1983).
8. Notari, B., *Stud. Surf. Sci. Catal.* **37,** 413 (1988).
9. Notari, B., *Catal. Today* **18,** 163 (1993).
10. Clerici, M. G., and Ingallina, P., *J. Catal.* **140,** 71 (1993).
11. Hutchings, G. J., and Lee, D. F., *J. Chem. Soc. Chem. Commun.* 1095 (1994).
12. Khouw, C. B., Dartt, C. B., Labinger, J. A., and Davis, M. E., *J. Catal.* **149,** 195 (1994).
13. Tatsumi, T., Yako, M., Yanagisawa, K., and Asano, K., *in* "Catalysis of Organic Reactions" (M. G. Scaros and M. L. Prunier, Eds.), p. 341, Dekker, New York, 1995.
14. Tatsumi, T., Nakamura, M., Yuasa, K., and Tominaga, H., *Chem. Lett.*, 297 (1990).
15. Camblor, M. A., Corma, A., Martínez, A., and Pérez-Pariente, J., *J. Chem. Soc. Chem. Commun.*, 1589 (1992).
16. Corma, A., Navarro, M. T., and Pérez-Pariente, J., *J. Chem. Soc. Chem. Commun.*, 147 (1994).
17. Corma, A., Camblor, M. A., Esteve, P., Martínez, A., and Pérez-Pariente, J., *J. Catal.* **145,** 151 (1994).
18. Corma, A., Navarro, M. T., Pérez-Pariente, J., and Sanchez, F., *Stud. Surf. Sci. Catal.* **84,** 69 (1994).
19. Sato, T., Dakka, J., and Sheldon, R. A., *J. Chem. Soc. Chem. Commun.*, 1887 (1994).
20. Rigutto, M. S., de Ruiter, R., Niederer, J. P. M., and van Bekkum, H., *Stud. Surf. Sci. Catal.* **84,** 2245 (1994).
21. Camblor, M. A., Corma, A., Martínez, A., Pérez-Pariente, J., and Valencia, S., *Stud. Surf. Sci. Catal.* **82,** 531 (1994).
22. Choudary, B. M., Valli, V. L. K., and Prasad, D., *J. Chem. Soc. Chem. Commun.*, 721 (1990).
23. Sohn, J. R., and Lunsford, J. H., *J. Mol. Catal.* **32,** 325 (1985).
24. Dai, P. S. E., and Lunsford, J. H., *J. Catal.* **64,** 184 (1980).
25. Venkatathri, N., Hegde, S. G., and Sivasanker, S., *J. Chem. Soc. Chem. Commun.*, 151 (1995).
26. Clark, J. H., "Catalysis of Organic Reactions with Supported Inorganic Reagents," p. 95, VCH, New York, 1994.
27. Sherington, D. C., *Pure Appl. Chem.* **60,** 401 (1988).
28. Neumann, R., Chava, M., and Levin, M., *J. Chem. Soc. Chem. Commun.*, 1685 (1993).
29. Hutter, R., Dutoit, D. C. M., Mallat, T., Schneider, M., Baiker, A., *J. Chem. Soc. Chem. Commun.*, 163 (1995).
30. Dutoit, D. C. M., Schneider, M., and Baiker, A., *J. Catal.* **153,** 165 (1995).
31. Hutter, R., Mallat, T., Baiker, A., *J. Catal.* **153,** 177 (1995).
32. House, H. O., *in* "Modern Synthetic Reactions," 2nd ed., Benjamin/Cummings, California, 1972.
33. Sheng, M. N., Zajacek, J. G., *J. Org. Chem.* **35,** 1839 (1970).
34. Nagata, R., Matsuura, T., and Saito, I., *Tetrahedron Lett.* **25,** 2691 (1984).
35. Wasson, R. L. and House, H. O., "Org. Synth.", Coll. Vol. IV, p. 552, 1963.
36. Wynberg, H., and Marsman, B., *J. Org. Chem.* **45,** 158 (1980).
37. Adam, W., Hadjiarapoglou, L., and Nestler, B., *Tetrahedron Lett.* **31,** 331 (1990).
38. Murray, R. M., Singh, M., and Jeyaraman, R., *J. Am. Chem. Soc.* **114,** 1346 (1992).
39. Baret, P., Pierre, J. L., and Heilmann, R., *Bull. Soc. Chim. France*, 4735 (1967).
40. Martens, J. A., Buskens, Ph., Jacobs, P. A., van der Pol, A., van Hooff, J. H. C., Ferrini, C., Kouwenhoven, H. W., Kooyman, P. J., van Bekkum, H., *Appl. Catal. A* **99,** 71–84 (1993).

41. Farberov, M. I., Stozhkova, G. A., Bondarenko, A. V., Kirik, T. M., and Ognevskaya, N. A., *Neftekhim.* **11,** 404 (1971).
42. Liu, Z., Tabora, J., and Davis, R. J., *J. Catal.* **149,** 117 (1994).
43. Imamura, S., Nakai, T., Kanai, H., and Ito, T., *Catal. Lett.* **28,** 277 (1994).
44. Mukherjee, S. P., *J. Non-Cryst. Solids* **42,** 477 (1980).
45. Best, M. F., and Condrate, R. A., *J. Mater. Sci. Lett.* **4,** 994 (1985).
46. Bellussi, G., and Fattore, V., *Stud. Surf. Sci. Catal.* **69,** 79 (1991).
47. Matsuda, A., Kogure, T., Matsuno, Y., Katayama, S., Tsuno, T., Tohge, N., and Minami, T., *J. Am. Ceram. Soc.* **76,** 2899 (1993).
48. Reichardt, C., *in* "Solvents and Solvent Effects in Org. Chem.," 2nd ed., VCH, 1988.
49. Gould, E. S., Hiatt, R. R., and Irwin, K. C., *J. Am. Chem. Soc.* **90,** 4573 (1968).
50. Srinivasan, S., Datye, A. K., Hampden-Smith, M., Wachs, I. E., Deo, G., Jehng, J. M., Turek, A. M., and Peden, C. H. F., *J. Catal.* **131,** 260 (1991).