A hydrophobic gel for epoxidation of olefins with organic peroxides

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The epoxidation of cyclooctene by *tert*-butyl hydroperoxide (*t*-BuOOH) over a TiO_2–SiO_2 xerogel made from a permethylated cyclooligosiloxane, tetraethylorthosilicate, and a Ti chloroalkoxide, was carried out in acetonitrile as the reaction solvent. The organic moieties of the hybrid gel (in this case, –CH_3 groups) and the Ti content of the catalyst appear to be stable on prolonged exposure to the reaction medium. Besides very good stability, the hybrid catalyst in this study displays 100% selectivity toward cyclooctene epoxide production. Solid state ^{29}Si magic angle spinning NMR (^{29}Si MASNMR), diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS), and chemical analysis were used to monitor the stability of the hybrid material. The kinetics of olefin epoxidation was studied in a batch reactor in the 313–343 K range.

KEY WORDS: hybrid gels; epoxidation; Ti; *tert*-butyl hydroperoxide

1. Introduction

For the heterogeneously catalyzed epoxidation of olefins, the pioneering work of Taramasso *et al.* [1] on the synthesis of Ti-substituted zeolites still plays a pivotal role in the field. Amorphous TiO_2–SiO_2 gels on the other hand, have sparked some interest, but it is generally difficult to synthesize such catalysts in a state where Ti leaching is not a serious concern [2]. On the other hand, the inherent pore limitations of zeolites are perhaps the primary motivation for research on TiO_2–SiO_2 gels as epoxidation catalysts. The latter have average pore sizes in the 20 Å range even in their "xerogel" state [2]. Another approach that has also proven very attractive is that presented by Corma [3,4], and later by van der Waal [5], who overcame pore size limitations by synthesizing Ti-containing mesoporous sieves.

Within the field of sol–gel derived amorphous materials, hybrid (organic–inorganic) gels are a sub-class that exhibits unique properties [6–8]. A most salient feature of this family of porous solids is that their hydrophobicity and mechanical properties can be fine-tuned rather easily [6]. For their use as catalysts, as for all other sol–gel derived materials, one must remain on guard against liquid-phase leaching of the active function [9]. In some cases, as Vanoppen *et al.* [10] also observed in the autoxidation of cyclohexane with a Co-containing molecular sieve as a catalyst, zeolitic materials are also subject to active-function leaching. It is generally believed that leaching is the result of solvolysis of metal–oxygen bonds [9]. Another consideration for utilizing hybrid gels as catalysts is that of cost of materials processing [9]. Unless a sol–gel catalyst displaying long-term stability is obtained, such material would not be able to compete with a Ti-zeolite in the epoxidation of small size olefins.

In this paper, we examine the behavior of the same hybrid gel catalyst we reported on before for cyclooctene epoxidation [2], this time using *tert*-butyl hydroperoxide (*t*-BuOOH) and acetonitrile as the oxidant and solvent, respectively, instead of H_2O_2 and *tert*-butanol (*t*-BuOH) as the oxidant/reaction medium. Based on our previous experience, the titanium content in hybrid gels becomes stable after 48 h under reaction conditions, regardless of whether *t*-BuOOH or H_2O_2 play the oxidant role. However, further studies done in our laboratory pointed to the fact that methyl groups from the "organic silicon" centers (the material is made from tetraethylorthosilicate and $[(CH_3)_2SiO]_3$ rings as sol–gel precursors) are not entirely immune to long-term hydrogen peroxide (H_2O_2) attack, in light of solid state ^{29}Si nuclear magnetic resonance data. Furthermore, even though one would tend to favor the use of H_2O_2 from a cost viewpoint [11], the unimolecular decomposition of H_2O_2 is an undesirable competing reaction that can hardly be avoided with this type of hybrid Ti-based gels [12]. For example, we have found that that nearly 20% of the H_2O_2 was lost to this side reaction during cyclooctene epoxidation with H_2O_2 and *t*-BuOH as the solvent [13]. In addition, Holmes *et al.* [12] indicated that the selectivity of *t*-BuOOH based epoxidations by Ti/silica catalysts is typically improved relative to those observed in the same reactions using H_2O_2.

Thorough spectroscopic, gas adsorption, and thermal behavior characterization work on these hybrid gels has been reported in previous papers [8,15,16]. In brief, we found that that the Ti function in a stable catalyst, upon proper thermal and gaseous treatments [15], exists as small TiO_x aggregates. This was counter-intuitive at first sight, since it has long been argued that isolated, tetrahedral Ti is responsible for epoxidation catalysis. Our materials preparation protocol is identical to that of Neuman and Levin-Elad [16], except for the replacement of about one third of the prescribed amount of tetraethylorthosilicate (TEOS) by

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an organic silicon source, namely $[(CH_3)_2SiO]_3$, or the corresponding 4- and 5-member cyclooligosiloxane rings. Use of cyclic siloxanes leads to higher surface area hybrid materials than the non-cyclic $(CH_3)_2Si(OMe)_2$, presumably due to a better match in hydrolysis reactivity between the organic and the inorganic (TEOS) Si sources [15]. The presence of Ti catalyzes the oxidation of unreacted alkoxy groups in air at high temperatures, but the Si–C bonds in the $=Si(CH_3)_2$ moieties are remarkably stable [8,16]. The kinetic results reported on this paper provide a more complete picture in regard to the potential of hybrid TiO_2–SiO_2 based materials made from permethylated cyclooligosiloxanes as the organic silicon source.

2. Experimental

2.1. Sample preparation, chemical analysis, and reaction studies

The preparation of hybrid TiO_2–SiO_2 gels from cyclic siloxanes is described in greater detail elsewhere [2,8]. Briefly, the hybrid gel support used in this study was made from a TEOS:$[(CH_3)_2SiO]_3$ mixture at a Si molar ratio of 2. The finished catalyst was labeled as Si_3–Ti, where the "3" subscript denotes the cyclooligosiloxane precursor ring size. The Ti source is $TiCl_x(i\text{-PrO})_y$ species resulting from contacting anhydrous isopropanol with $TiCl_4$. The TEOS and $[(CH_3)_2SiO]_3$ were first partially co-hydrolyzed at 333 K in the presence of a HCl 0.12 M solution that provided $1/2$ the total amount of water required by stoichiometry for complete hydrolysis. Subsequently, an adequate amount of $TiCl_x(i\text{-PrO})_y$ isopropanolic solution to yield a material with a Ti wt% of approximately 3.0 was added, in conjunction with the remaining amount of water required to reach stoichiometric levels for complete hydrolysis. A vitreous solid was thus obtained, and the oven-dried material was ground to fine powder, and subsequently treated thermally prior to reaction as previously described [2]. The Ti content of our samples, before and after reaction, was measured at Galbraith Laboratories (Knoxville, TN). The Ti loading of our sample fell in the 2.8–3.1 wt% range.

The reaction was carried out in a Pyrex®, batch liquid-phase reactor equipped with a reflux condenser [2]. The catalyst powder remained suspended by the action of efficient stirring. In this study, *cis*-cyclooctene 95% purity (balance, cyclooctane), acetonitrile 99.8% (reaction solvent), hexadecane 99% (GC internal standard), and 5.73 M t-BuOOH from Aldrich® were used without further purification. The concentration of t-BuOOH was determined by an iodometric titration method adapted from that of Gao *et al.* [17]. An 8610B SRI gas chromatograph equipped with a 30 m ethylene glycol capillary column and FID detection was used for product and reactant quantification. The *cis*-cyclooctene and cyclooctene epoxide signals were properly calibrated. The temperature of a mixture consisting of catalyst (200 mg), solvent (22.5 ml), internal standard (0.1 ml), and t-BuOOH (1.2 ml) was first stabilized in the reactor. The *cis*-cyclooctene was added later *via* a septum-capped side port. Since the mass of cyclooctene added (typically in the 1–2 ml range) at $t = 0$ was very small relative to the mass of the reactor plus those of all of the other species present, the reaction temperature was essentially unaffected by the late addition of the olefin. The catalyst used for the kinetic measurements is actually the thermally treated solid that had been pre-exposed to reaction conditions for 48 h, and oven dried at 383 K. Kinetic measurements were performed at 313, 323, 333, and 341 K. Reaction orders in *cis*-cyclooctene and t-BuOOH were also obtained. For reaction order measurements, the relatively large amount of solvent employed in this study permits its use as a "volume compensator" when varying one of the reactants' concentration, without dramatically affecting the chemical nature of the reaction (solvent) medium.

2.2. Characterization studies

Detailed descriptions of the diffuse reflectance Fourier transform infrared spectrometer (DRIFTS) and its environmental cell, and of the ^{29}Si magic angle spinning (MAS) nuclear magnetic resonance (NMR) equipment are given elsewhere [8]. In brief, the DRIFTS cell operates under the flow-through packed bed principle, and it allows for precise control of temperature and gas environment. For the ^{29}Si MAS/NMR experiments, different contact time and cross-polarization experiments were carried out.

3. Results and discussion

Table 1 shows the Ti content of the material in its "fresh" state, and after 24 and 48 h under reaction conditions. Deviations of approximately 0.1–0.2% had been observed before [8], and are primarily due to experimental error associated with sample handling at the analysis site, not to an obvious Ti leaching effect. This was confirmed by running duplicate analyses. In fact, the Ti wt% appears to counter-intuitively increase with reaction time, which could only be explained by either loss of other components in the "spent" solid relative to the "fresh" catalyst, or to experimental error, as indicated above. We favor the latter, in light of spectroscopic arguments presented later.

The presence of the two low-frequency bands at 800–820 cm^{-1} (Si–C stretching) and 865 cm^{-1} (Si–CH_3 deformation) on the material exposed to 48 h reaction time was confirmed by DRIFTS. Figure 1 shows the ^{29}Si MASNMR spectra (with and without proton cross-polarization) after exposure to the *cis*-cycooctene/t-BuOOH/solvent reaction environment at 333 K for 48 h. The spectra are remarkably

Table 1
Ti wt% analysis of Si_3–Ti, recovered after 0 ("fresh" state), 24 and 48 h under reaction.

Washing time (h)	0	24	48
Ti (wt%)	2.8	3.0	3.1

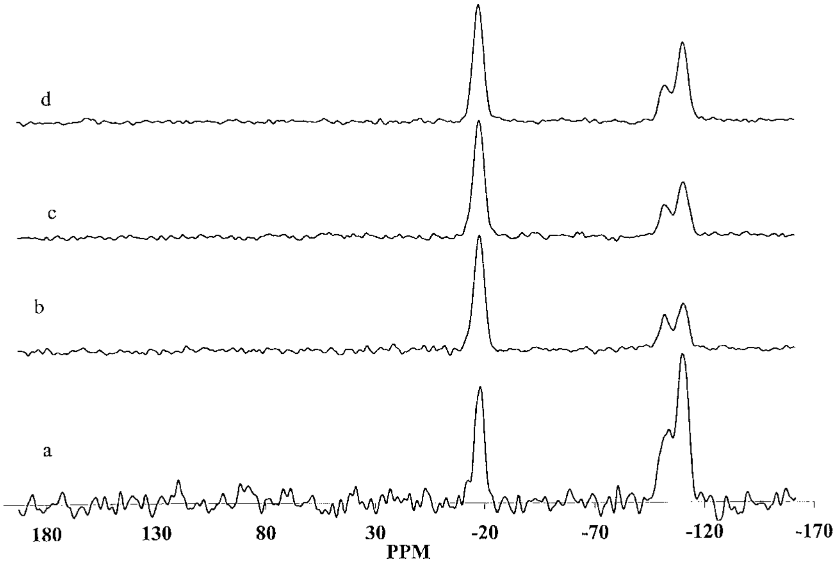

Figure 1. ^{29}Si MAS NMR spectra of Si_3–Ti after 48 h reaction. (a) One pulse, 240 s delay, and CP/MAS with CT equal to (b) 1.5 ms, (c) 3.0 s, and (d) 8.0 ms.

similar to those of the “fresh” sample [8], its most salient feature being the preservation of the so-called D^2 resonance (-18 ppm), which is assigned to $(CH_3)_2Si(OX)_2$ centers (where “X” is most likely Si, rather than Ti, given the low Ti loading) [8]. As mentioned earlier [8,15], the Q^3 resonance (-98 ppm) from $(OR)Si(OX)_3$ centers, where R can be H, Et, or *i*-Pr, and the Q^4 line at -107 ppm, ascribed to $Si(OX)_4$, are influenced by proton cross-polarization, indicating that the Si centers sense a proton-rich environment. The latter primarily comes from the presence of unreacted alkoxy groups. Complete elimination of alkoxy groups requires treatment in air at temperatures that are too high to avoid active phase sintering and surface area losses [8]. In addition to the preservation of the D^2 signal, a lack of T^n-type resonances (monoalkylated Si) also indicates that the “organic silicon” centers do not undergo partial degradation in the presence of *t*-BuOOH. Similar studies with H_2O_2 revealed that the D^2 resonance is indeed affected in Si_3–Ti upon prolonged exposure to this aqueous oxidant.

At this point, it must be mentioned that one of the chemical transformations that is difficult to track by our ^{29}Si MAS-NMR setup is that of exchange of unreacted isopropoxide and ethoxide groups with *t*-BuO– from the *t*-BuOH produced during reaction [18]. However, we safely assume that such an alteration would have occurred during the 48 h “washing” (exposure to the reacting mixture) cycle, and that the catalyst remains stable afterwards. Unlike in our hybrid material, loss of Ti in liquid-phase reactions by solvolysis of oligomeric $[Ti_xSi_yO_z]^{n-}$ species in “all-inorganic” Ti–Si gels has long been recognized as a major limitation for their use in olefin epoxidation. It is conceivable that such Ti loss mechanism is suppressed in our material because its high surface hydrophobicity might lead to very low water surface coverages.

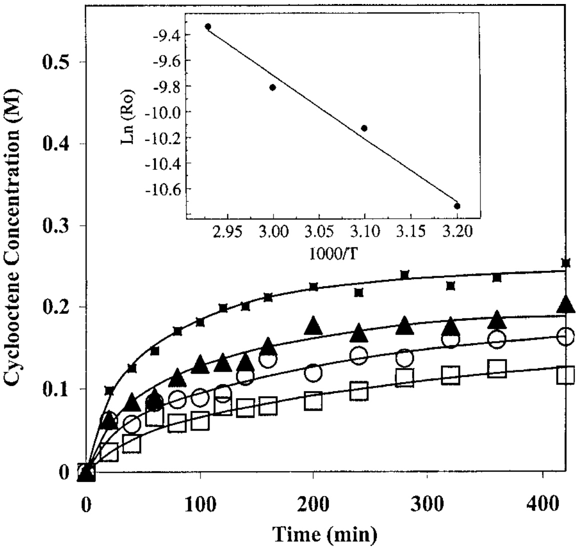

Figure 2. Cyclooctene epoxide concentration as a function of reaction time at different temperatures. The inset is the corresponding initial-rate Arrhenius plot. *T* (K) are: 313 (□), 323 (○), 333 (▲), and 341 (■) K.

Figures 2–4 summarize the performance of Si_3–Ti for cyclooctene epoxidation under the solvent/oxidant pair chosen in this study. The choice of solvents was not in any way arbitrary. We must point to the fact that we observed a number of partially oxidized by-products when running the reaction with *t*-BuOH or methanol as solvents, some of them presumably arising from oxidation of the solvent themselves. The activity plateaus observed in some of the curves are due to total oxidant consumption, not equilibrium. More importantly, a number of *t*-BuOOH titration experiments done before and after reaction reveal that oxidant consumption is essentially stoichiometric, *i.e.*, *t*-BuOOH does not undergo (unlike H_2O_2) unimolecular decomposition under the chosen reaction conditions to any appreciable extent. We have always observed some extent of “bubbling” (O_2 production) when using H_2O_2 for cyclooctene oxidation with this type of hybrid materials as catalysts. A lack of oxidant loss by uni-

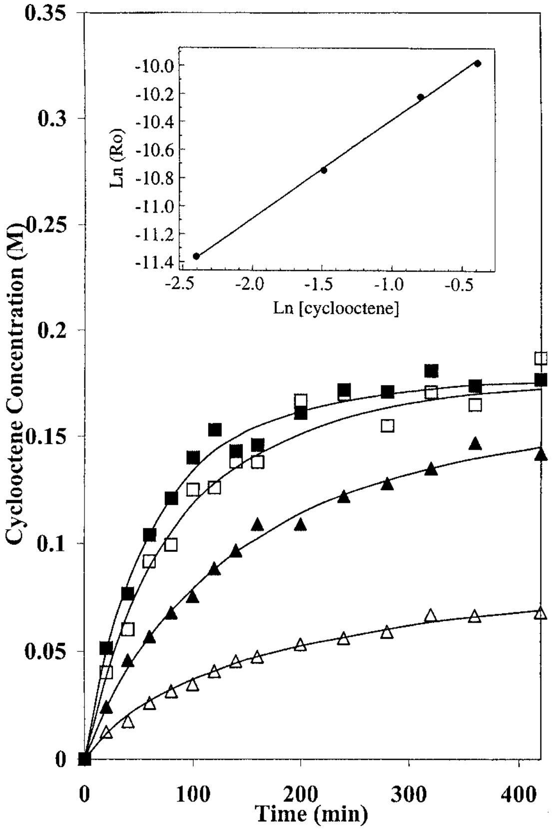

Figure 3. Effect of *cis*-cyclooctene initial concentration on the rate of epoxide production. Inset is the corresponding reaction order plot. Concentrations are: 0.0903 (△), 0.226 (▲), 0.451 (□), and 0.677 (■) M.

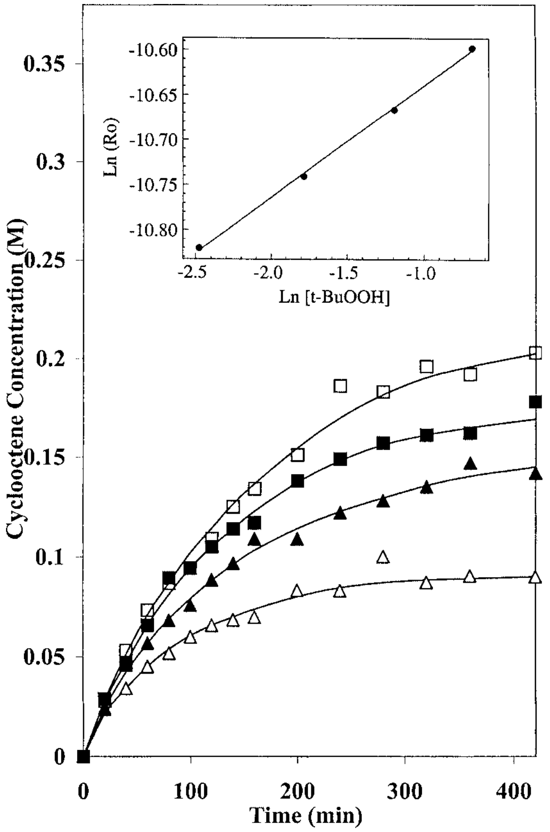

Figure 4. Effect of *t*-BuOOH initial concentration on the rate of epoxide production. Inset is the corresponding reaction order plot. Concentrations are: 0.0841 (△), 0.168 (▲), 0.303 (■), and 0.504 (□) M.

Table 2

Dependence of the reaction rate constant on temperature.

k ($mol^{0.2}/l^{0.2}$ min g_{cat})	0.0088	0.00287	0.0228	0.0323
T (K)	313	323	333	341

molecular decomposition in the case of *t*-BuOOH allowed us to track the reaction by simple quantification of hydrocarbon product and reactant. No products other than cyclooctene epoxide were observed. Non-linear fitting was necessary in each case to derive kinetic parameters, given the apparent scattering of data in figures 2–4.

The activation energy for cyclooctene oxidation was found to be 41.3 kJ/mol. The power rate law obtained was of the form

$$R = k[t\text{-BuOOH}]^{0.1}[\text{cyclooctene}]^{0.7}. \qquad (1)$$

Values for all four reaction rate constants are given in table 2.

In the absence of unimolecular decomposition of the oxidant, and in the initial-rate limit, product inhibition effects on the overall kinetics, as suggested by Milchert and Zawarski [18], are not expected to occur. The small dependence of the initial reaction rate on *t*-BuOOH concentration suggests that, at the catalyst/oxidant ratio employed in this study, the catalytic sites have a strong preference for *t*-BuOOH adsorption. By the same token, and despite this materials' demonstrated hydrophobicity [2], the reaction order in cyclooctene suggests that this hydrocarbon likely approaches the *t*-BuOOH-active site complex from the solution to form the transition state.

Romano *et al.* [19], and later Corma and collaborators [20] underlined the inability of Ti-silicalite to catalyze olefin epoxidations using *t*-BuOOH as oxidant, most probably due to pore size constraints that make it impossible for a transition state involving the active site, the olefin, and *t*-BuOOH to accommodate inside the silicalite channels. Ti-β on the other hand, was found to be an effective catalyst for the *t*-BuOOH-meadiated epoxidation of olefins at 323 K in the presence of acetonitrile [20]. At that temperature, Corma's group [20] found initial rates in the range 0.60–3.5 × 10^{-6} mol of (C_6–C_{10}) olefins converted per gram per second, and selectivities approaching 100% with acetonitrile as the reaction solvent. Interestingly, in our case the data from figure 2 at 323 K, once adjusted to the actual mass of reactants, solvent, internal standard and catalyst gives an initial rate value of 3.5 × 10^{-6} mol of cyclooctene converted per gram of hybrid catalyst per second. Comparison with Corma *et al.*'s data on Ti-β is valid since their reaction data was obtained using 10 g acetonitrile as solvent, 0.3 g. Ti-β, 25 mmol of olefin and 6.25 mmol of *t*-BuOOH, which are in the same order of magnitude as the quantities used in our study (see section 2). The Ti/(Ti + Si) ratio in the Ti-β catalyst from [20] was 0.025, which is also comparable to that of our hybrid solid. Thus, it is apparent that the specific activity of our materials is in the same range as that of Ti-substituted zeolites.

In summary, TiO_2–SiO_2 hybrid gels, which possess larger pores than Ti-substituted zeolites, are effective and stable *t*-BuOOH-based olefin epoxidation catalysts. We underline the fact that here are primarily two degrees of freedom that can be exploited in the design of such sol–gel catalysts, namely pore size and hydrophobicity level. These are viewed as key parameters that must be manipulated according to the size of the molecule to be epoxidized, and on its accompanying functional groups.

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