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Efficient catalytic epoxidation of olefins with silylated Ti-TUD-1 catalysts

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ABSTRACT

Various silylated Ti-TUD-1 samples were synthesized by treating Ti-TUD-1 samples of differing Ti loadings with hexamethyldisilazane (HMDS). The silylation of silanol (Si–OH) and titanol groups (Ti–OH) on the mesoporous silica was confirmed by FTIR spectroscopy, hydrophobicity (TGA), and NH_3-TPD measurements. The relatively unreactive olefins, such as 1-octene and *p-tert*-butylphenylallyl ether, were epoxidized using both silylated and unsilylated Ti-TUD-1 samples with different Ti loadings in the range of 1–10 wt% Ti. The catalytic epoxidation reactions were performed with commercial solutions of organic hydroperoxides as oxidants without the addition of any other organic solvent. The selectivities in peroxide utilization were found to depend on the type of olefin, oxidant, and catalyst. Using unsilylated Ti-TUD-1, low selectivity to epoxide was achieved for cumyl hydroperoxide (CHP), which is attributed to its facile acid-catalyzed decomposition to phenol and acetone under the reaction conditions. However, both *t*-butyl hydroperoxide (TBHP) and cumyl hydroperoxide yielded high selectivity to epoxide (based on converted hydroperoxide) with silylated Ti-TUD-1 samples. The selectivity to epoxide was lower for the electron-poor olefin *p-tert*-butylphenylallyl ether than for simple 1-octene. The experiments with CHP as the oxidant were used as a diagnostic tool to demonstrate that the enhanced epoxidation activity and selectivity of the silylated samples with TBHP can be credited to two effects of silylation. The elimination of protic Ti–OH sites of the Ti-TUD-1 catalyst resulted in a significant reduction of the competing acid-catalyzed decomposition of the peroxide, whereas the enhanced hydrophobicity of the catalyst surface enhanced the accommodation of the apolar olefinic substrate.

1. Introduction

Selective catalytic epoxidation is an important transformation in the synthesis of many organic chemicals. A significant achievement in the development of epoxidation catalysts occurred in the 1970s with the discovery of Ti/SiO_2 catalysts, which have been used for the epoxidation of propylene using alkylaromatic hydroperoxides as oxidants [1,2]. In various processes with Ti/SiO_2 catalysts, propylene oxidation to propylene oxide (PO) operates at low (∼10%) conversions to achieve maximum selectivity to PO, which is then separated by fractional distillation. The currently available processes for PO, as well as the developments in this area, have been discussed in a recent review [3]. In 1983, the Enichem Company discovered the framework Ti-substituted silicates (TS-1), one of the most important innovations in oxidation catalysis in the last several decades [4]. Isolated tetracoordinated titanium sites in the hydrophobic framework of MFI silicate exhibited spectacular catalytic properties for such oxidations as hydroxylation and epoxidation with dilute H_2O_2 [5]; however, the application of these microporous titanium silicate materials is confined to small molecules, due to their small pore size.

The discovery of mesoporous MCM-41 has opened up avenues for the oxidation of more bulky substrates [6,7]. Several framework Ti-substituted mesoporous silicates, including Ti-MCM-41 [8,9], Ti-HMS [10,11], Ti-MCM-48 [12,13], and Ti-SBA-15 [14,15], have demonstrated promising activity for the epoxidation of bulky olefins using alkyl hydroperoxides as oxidants. Nevertheless, compared with the microporous MFI titanium silicates, the mesoporous materials exhibit low activities for epoxidation reactions. The hydrophilic nature of Ti-isomorphous substituted mesoporous silica catalysts is postulated to be one of the major reasons for the low activity [16].

In a different synthetic procedure, Ti-grafted MCM-41 has been prepared with more accessible Ti active sites for selective epoxidation [17,18]. In recent work, a modified procedure was developed for the synthesis of high-Ti Ti-MCM-41, in which activities for the epoxidation of olefins were improved significantly due to the incorporation of a large amount of titanium [19]. The catalytic epoxidation with these catalysts requires nonaqueous oxidants to obtain satisfactory activity. A number of recent reports have described the advantages of silylation/organic functionalization of the surface of the of Ti-MCM-41 materials, thus making them more

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hydrophobic to improve the activity during epoxidation [9,12,13, 20–23]. The epoxidation activity of metal-substituted mesoporous silicates has been enhanced significantly by silylation of the surface silanol (–Si–OH) and –Ti–OH groups. Various metal (mainly Ti)-substituted molecular sieves have been made hydrophobic in two ways: by postsynthesis modification using different silylating agents [12,13,20–28] and by direct organic functionalization during synthesis using monoalkylsilanes or dialkylsilanes [29–31].

The development of the molecular sieve TUD-1 has opened up a new route for obtaining inexpensive mesoporous titanium silicates in contrast to the various mesoporous silicates discussed above [32–35]. These materials have shown superior epoxidation activity to Ti-MCM-41. The activity has been studied mainly in the epoxidation of relatively reactive olefins, such as cyclohexene and cyclooctene. In contrast, few studies have been investigated the epoxidation of such olefins as 1-octene [21,36] and arylallyl ethers, which are known to be relatively inert against epoxidation and in general react with lower peroxide selectivity. The epoxidation of arylallyl ethers may find application in the synthesis of epoxy resins [37].

Catalytic epoxidation using isomorphous Ti-substituted mesoporous silicates with alkylaromatic hydroperoxides as oxidants has not been reported to date. For instance, cumyl hydroperoxide (CHP) is a more attractive oxidant than *t*-butyl hydroperoxide (TBHP), due to its relatively easy reuse (dehydration of the product alcohol, followed by hydrogenation recovers cumene) during epoxidation sequences of propylene [38]. In the present work, the silylation of Ti-TUD-1 samples was carried out with hexamethyldisilazane (HMDS). The epoxidation of such olefins as 1-octene and arylallyl ether catalyzed by these silylated Ti-TUD-1 catalysts has been studied using the organic oxidants *t*-butyl hydroperoxide (TBHP) and cumyl hydroperoxide (CHP). An attempt has been made to rationalize the activity and epoxidation selectivity based on peroxide of the silylated catalysts compared with the unsilylated catalysts. The differences have been correlated to the surface properties of the catalyst and are discussed on the basis of several reports that have proposed the enhanced hydrophobicity as the sole reason for the improved activity for silylated samples.

2. Experimental

2.1. General

The various Ti-loaded Ti-TUD-1 samples used in this study were obtained from the original study; their synthesis and full characterization are described in detail elsewhere [32]. The anhydrous TBHP (66.4% in decane on molecular sieves) used in these studies was purchased from Aldrich, and CHP (80% in cumene) was obtained from Acros Organics.

2.2. Silylation of the Ti-TUD-1 samples

Silylation was carried out using HMDS as the silylating agent. The HMDS was boiled at 125 °C in a three-necked round-bottomed flask, and the resulting gas was carried over the catalyst with a nitrogen stream. The Ti-TUD-1 samples were pretreated at 350 °C for 2 h in a nitrogen stream. Then the temperature was lowered to 200 °C, and the samples were treated with HMDS. A total of 4 mL of HMDS was passed through a vertical reactor at 200 °C containing 4 g of a Ti-TUD-1 sample. The exothermicity of the reaction induced a temperature rise of approximately 20 °C during silylation. The Ti-TUD-1 samples Ti-1.5, Ti-2.5, Ti-5, and Ti-10 silylated in this manner are designated Ti-1.5 S, Ti-2.5S, Ti-5S, and Ti-10S, respectively. After the treatment with HDMS, the modified supports were treated with a nitrogen stream at 200 °C for nearly 2 h to remove pore-filled and adsorbed HDMS.

2.3. Characterization of the Ti-TUD-1 samples

The amount of water loss (wt%) from the Ti-TUD-1 samples was determined by thermogravimetric analysis (TGA). No specific pretreatment was performed before the TGA. The samples were stored in capped glass tubes under atmospheric conditions. The samples were heated from 15 to 150 °C at a ramp rate of 1 K/min in the presence of inert gas and then rehydrated to 15 °C at the same ramp rate.

NH_3-TPD analysis was performed on a Micromeritics TPD/TPR-2900 analyzer. The samples were dried in situ at 525 K in a flow of helium gas before the measurement and then cooled to 393 K, at which point they were saturated with 30 cm^3/min pure NH_3 gas for 10 min. Desorption was measured in a flow of He (50 cm^3/min) in the temperature range 363–823 K (10 K/min) using a thermal conductivity detector. Samples of equal initial weight were analyzed. The differences in the amounts of desorbed NH_3 from the different samples were much larger than the limits of experimental error.

ICP determination of the Ti content of the Ti-TUD-1 samples was performed on a Varian Vista-MPX spectrometer. The carbon content of the silylated samples was analyzed with a Perkin-Elmer series II CHNS/O Analyzer 2400.

IR absorption spectra of the solid samples were recorded using a Thermo Nicolet Nexus spectrometer equipped with a liquid N_2-cooled MCT detector and a Spectratech diffuse reflectance accessory, including a high-temperature cell. Water was removed from the catalyst surface to facilitate the characterization of the OH group composition by recording the spectra at 120 °C after equilibration for 1 h in He flow (30 mL/min). All spectra were obtained by collecting 128 scans with 4 cm^{-1} resolution against a KBr background (also measured at 120 °C in flowing He).

2.4. Epoxidation reactions

In a typical reaction, 10 mmol of the olefin, 3.33 mmol of the oxidant, and 50 mg of the catalyst were mixed in cylindrical 25-mL vessels in a reaction station equipped with magnetic stirrer bars and cooling condenser using circulation of cold water. The reactions were performed in batch conditions in air at atmospheric pressure under stirring at 250 rpm at 60 °C for several hours. At specific time intervals, aliquots of the reaction mixture were taken into ethanol for gas chromatography (GC) analysis. For all experiments, the product mixtures were sampled for GC analysis after the epoxidation reaction (8 h). For the experiments shown in Fig. 6, 100-μL aliquots of the product mixture were obtained for GC analysis at specified time intervals; this had no influence on the final outcome after 8 h, as can be seen from entry 4 in Table 2. The quantitative analysis of product samples was performed on a HP 6890 series gas chromatograph equipped with a 25-m-long WCOT column with CP-Sil-5 CB stationary phase, capped with fused silica ends using an flame ionization detector. The epoxide products were identified by GC-mass spectroscopy (MS) by comparison with known compounds. The percentage yield of epoxide and turnover numbers (TONs) were determined as follows: yield of epoxide (%) $= (\text{mmol of epoxide}_{\text{final}}/\text{mmol of olefin}_{\text{initial}}) \times 100$; TON $= (\text{mmol of epoxide}_{\text{final}}/\text{mmol of Ti present in the catalyst})$. It is assumed that all of the Ti centers present in the sample are acting as active sites. The amount of peroxides present in the reaction mixtures was determined by iodometric titration. In a typical titration, 2 mL of saturated KI and 15 mL of glacial acetic acid were added to a known amount of the reaction mixture. This mixture was placed in the dark for 15 min before being titrated against 0.2 M sodium thiosulfate solution. The disappearance of the brown-colored iodine to colorless KI was considered the end point. The conversion

Table 1
Physico-chemical properties of the Ti-TUD-1 samples.

Sample	Ti (wt%)	$I_{960\ \mathrm{cm}^{-1}}/I_{1060\ \mathrm{cm}^{-1}}$	Weight loss (wt%)	C (wt%)
TUD-1	0	0.44	7.7	0
Ti-1	0.88	0.51	10.5	0
Ti-1.5	1.16	0.54	10.3	0
Ti-2	1.47	0.52	10.5	0
Ti-2.5	2.51	0.54	10.5	0
Ti-5	4.03	0.63	9.3	0
Ti-10	9.34	0.73	n.d.[a]	0
Ti-1.5S	1.09	0.32	3.3	7.6
Ti-2.5S	1.78	0.49	2.5	4.5
Ti-5S	3.11	0.45	2.4	7.0
Ti-10S	6.18	0.61	3.6	5.4

[a] n.d.: not determined.

of the peroxide (%) and selectivity (%) are calculated by the following formulas:

$$\text{conversion} = \big[\big((\text{mmol of the peroxide in the mixture})_{t=0} - (\text{mmol of peroxide in the mixture})_{t=8\,\mathrm{h}}\big) / (\text{mmol of peroxide in the mixture})_{t=0}\big] \times 100,$$

$$\text{selectivity} = \frac{(\text{mmol of epoxide produced})_{t=8\,\mathrm{h}}}{(\text{mmol of peroxide consumed})_{t=8\,\mathrm{h}}} \times 100.$$

3. Results and discussion

3.1. *Characterization of the catalyst samples*

3.1.1. *General*

The various titanium-loaded Ti-TUD-1 samples are designated Ti-1, Ti-1.5, Ti-2, Ti-2.5, Ti-5, and Ti-10 for the respective Ti-TUD-1 samples containing 1–10 wt% of Ti. The Ti-TUD-1 samples silylated with HMDS are designated Ti-1.5S, Ti-2.5S, Ti-5S, and Ti-10S (see the Section 2). The full characterization of the Ti-TUD-1 samples used in this study has been reported previously [32]. Based on these studies, it was concluded that in the Ti-TUD-1 samples with low Ti loading (Ti-1, T-1.5, Ti-2, and Ti-2.5), titanium is present in the framework of the mesoporous silica, whereas the Ti-TUD-1 samples with high Ti loading must contain some nanocrystalline TiO_2 along with the framework Ti [39]. Silylation of the Ti-TUD-1 samples with HMDS resulted in an increase in the weight of the samples; this increase was 5.9 wt% for Ti-2.5, 7.3 wt% for Ti-5, and 8.6 wt% for Ti-10. The amount of Ti present in the samples was determined by ICP analysis; the values are presented in Table 1. The effect of silylation on such characteristics as porosity and surface area of the TUD samples was not investigated.

3.1.2. *FTIR spectroscopy*

The FTIR spectra of the TUD-1 samples display a strong absorption band at 960 cm^{-1}, which has been attributed to Si–O stretching frequencies of both Si–O–Ti and Si–OH groups in titanium isomorphously substituted mesoporous molecular sieves [27,28,34]. A prominent peak is present at 1060 cm^{-1} due to Si–O–Si asymmetric stretching of the silica framework in TUD-1. The increase in the ratio of $I_{960\ \mathrm{cm}^{-1}}/I_{1060\ \mathrm{cm}^{-1}}$ gave evidence for the increase in the amount of titanium in the tetrahedral framework of the mesoporous silica from 1 to 5 wt% unsilylated Ti-TUD-1 samples (Table 1) [28]. The results for the FTIR spectra verify the increase in the amount of Ti in the framework of the TUD-1 samples.

Fig. 1 compares the FTIR spectra of selected silylated and unsilylated Ti-TUD-1 samples. A schematic representation of the chemical reaction of HMDS with silanol groups of the mesoporous silica of Ti-TUD-1 is presented in Scheme 1, showing the changes in the types of bonding [2]. The different physical and chemical changes occurring on silylation of the Ti-TUD-1 samples are well reflected in the FTIR spectra. The ratio of $I_{960\ \mathrm{cm}^{-1}}/I_{1060\ \mathrm{cm}^{-1}}$ decreased on silylation, which can be explained by the decreased number of Si–OH groups. The FTIR spectra of unsilylated Ti-TUD-1 samples show an intense sharp band at 3743 cm^{-1} and a broad band at around 3555 cm^{-1} as a shoulder, which are assigned to stretching vibrations of isolated Si–O–H and to Si–O–H involved in hydrogen bonding, respectively [21,25,27]. A contribution of H–O–H stretching modes of physisorbed water to the 3555 cm^{-1} band also can be seen. The O–H stretching frequency of –Ti–OH groups also is expected in this region of the spectrum [40].

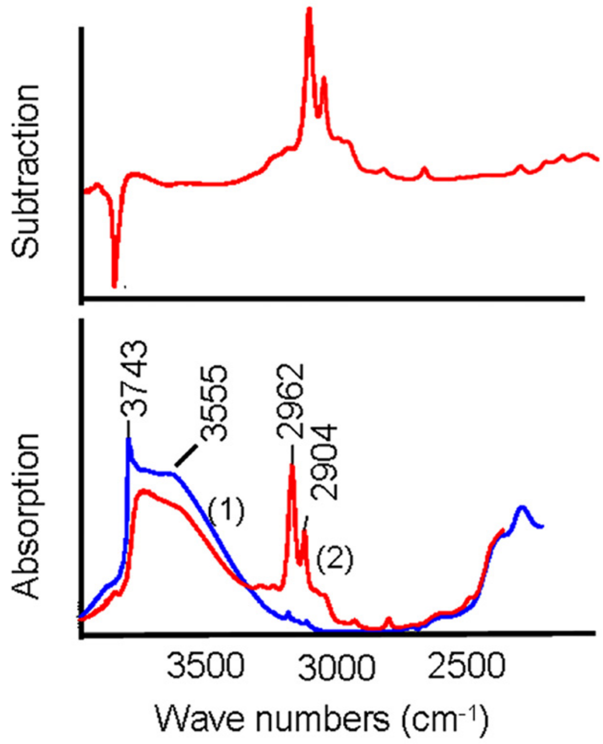
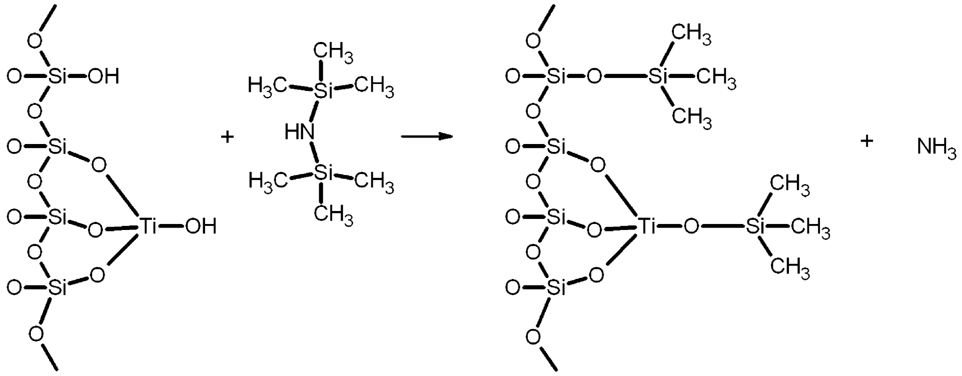


Fig. 1. (Bottom) FTIR spectra of Ti-TUD-1 samples (from 2500–4000 cm^{-1}) for unsilylated Ti-2.5 (1) and silylated Ti-2.5 S (2); (top) difference spectrum (2 − 1) emphasizing the changes upon silylation.

The intense, sharp band at 3743 cm^{-1} and the intensity of the broad feature at 3555 cm^{-1} were significantly reduced in the FTIR spectra of the silylated samples. This observation is in agreement with the decrease in the number of silanol groups (Si–OH) and increasing hydrophobicity of the surface. Furthermore, the intensity of the 960 cm^{-1} band in silylated samples was decreased considerably compared with unsilylated samples, as evident from the ratios of the $I_{960\ \mathrm{cm}^{-1}}/I_{1060\ \mathrm{cm}^{-1}}$ reported in Table 1. Finally, an important difference observed in the FTIR spectra of the silylated samples is the presence of the C–H stretching frequencies at 2962 cm^{-1} and 2904 cm^{-1}, which confirms the presence of trimethylsilyl groups on the silica surface [27].

3.1.3. *Weight loss of Ti-TUD-1 samples*

The amount of weight loss in the various samples was determined by TGA at 30–155 °C. The total weight loss is assumed to be a result of loss of water, and the values are considered a measure of the relative hydrophobic nature of the silylated and unsilylated Ti-TUD-1 samples: the more weight (water) loss, the less the hydrophobicity. The weight loss of the various samples is presented in Table 1. The samples were stored under atmospheric conditions, and they underwent no pretreatment before the TGA analysis. The weight loss of the unsilylated Ti-TUD-1 catalysts was around



Scheme 1. Schematic equation for the silylation of Ti-TUD-1 samples with hexamethyldisilazane (HMDS). Indicated is the concerted reaction of a Si–OH and a Brønsted acidic Ti–OH group with HMDS; obviously the reaction of two Si–OH groups or two Ti–OH groups with HMDS molecules is also feasible.

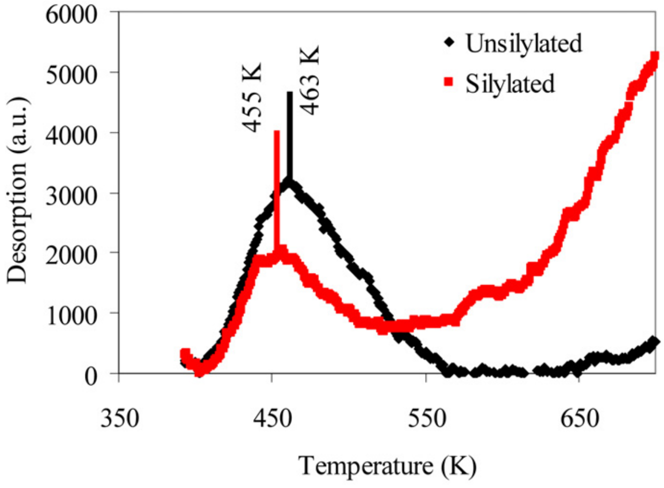


Fig. 2. NH_3-TPD of the samples Ti-2.5 and Ti-2.5S.

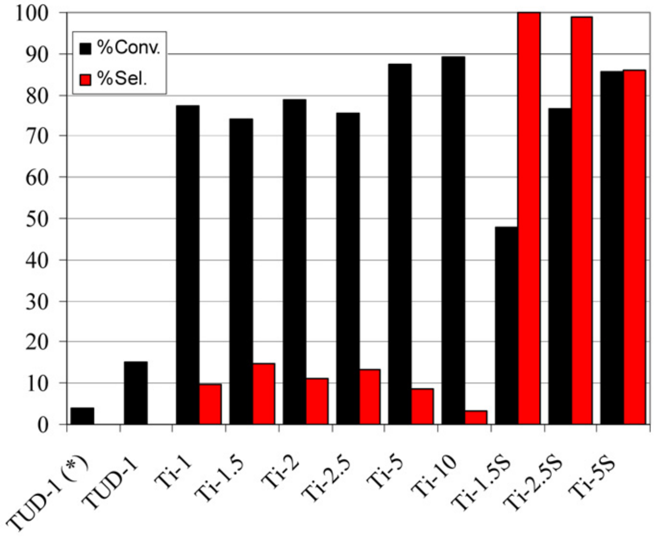


Fig. 3. Conversion of CHP and selectivity to 1,2-epoxy octane based on CHP in the epoxidation of 1-octene after 8 h catalyzed by various TUD-1 samples. TUD-1 (∗) is a dehydrated sample. Reaction conditions: 1-octene (10 mmol), CHP (3.33 mmol), catalyst = 50 mg, 60 °C, 250 rpm. %Conv. = % conversion of CHP, %Sel. = % selectivity to epoxide based on peroxide consumed.

10 wt%, some 25%–50% lower than that reported previously for Ti-MCM-41 [12,24–26], indicating significant hydrophobicity [34]. The weight loss decreased further on silylation of the Ti-TUD-1 samples (Table 1); the silylated samples showed weight losses in the range of only 2–4 wt%. Storage of the silylated samples for 1 day in ambient atmospheric conditions after the TGA analysis led to reabsorbance of water. This observation confirmed that the weight loss is only due to loss of water from the samples.

3.1.4. *Acidity of the silylated and unsilylated samples*

The acidity of Ti-TUD-1 samples was evaluated by ammonia temperature-programmed desorption (NH_3-TPD) measurements (Fig. 2). Two interesting observations arise from these acidity measurements. Less ammonia was desorbed from the silylated Ti-TUD-1 (0.042 mmol) than from the unsilylated Ti-TUD-1 (0.10 mmol), and the maximum temperature at which ammonia was desorbed was somewhat lower for the silylated Ti-TUD-1 (455 K) than for the unsilylated Ti-TUD-1 (463 K). The shift in temperature indicated this latter effect was predominant in the stronger acidic sites. These findings indicate that the acidity of the Ti-TUD-1 samples decreased on silylation. The desorption observed for the silylated sample starting from 550 K is due to the decomposition of the organic trimethylsilyl groups present on the surface.

Both Si–OH and Ti–OH groups would be expected to become silylated on reaction with HMDS. Based on the catalytic results described in Section 3.2.2, however, we can conclude that the a-selective decomposition of CHP is cause mainly by the stronger Brønsted acidic Ti–OH sites. Thus, the different acidity of the unsilylated and silylated TUD samples as observed in the NH_3-TPD measurements can be ascribed to the reduced number of Ti–OH groups.

3.2. *Epoxidation catalysis*

3.2.1. *Epoxidation of 1-octene with unsilylated Ti-TUD-1 samples*

Cumyl hydroperoxide (CHP, 80% in cumene) was used as an oxidant for the epoxidation of 1-octene with TUD-1 catalysts of differing Ti content at a substrate-to-oxidant molar ratio of 3:1. The results and a comparison with the parent TUD-1 catalyst are shown in Fig. 3. All catalysts gave low yields of epoxide (only 2%–4% yield of epoxide based on olefin) and exhibited poor selectivities to epoxide based on the amount of peroxide converted. Typically, 80% of the CHP was consumed after 8 h, with >90% being a-selective decomposition. Large amounts of phenol and acetone were found in the reaction mixtures, which are typical products of Brønsted acid-catalyzed decomposition of CHP. In fact, the commercial process for phenol (and acetone) production involves the sulfuric acid-catalyzed decomposition of CHP. The rapid and unselective decomposition of CHP can be attributed mainly to the Brønsted acidic Ti–OH sites in the silica/titania framework of Ti-TUD-1, because under comparable reaction conditions, the parent

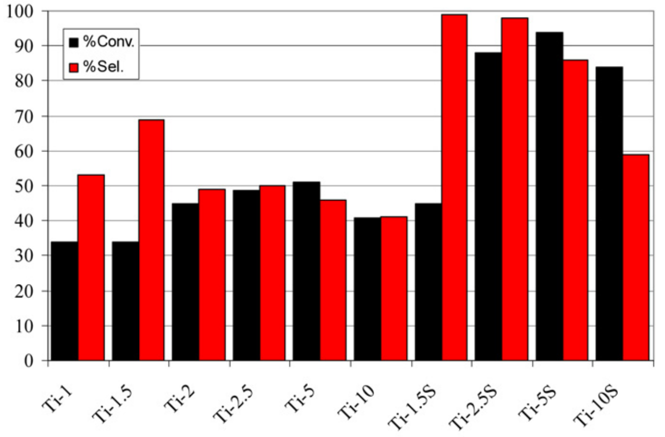


Fig. 4. Conversion of TBHP and selectivity to 1,2-epoxy octane based on TBHP in the epoxidation of 1-octene after 8 h catalyzed by various TUD-1 samples. Reaction conditions: 1-octene (10 mmol), TBHP (3.33 mmol), catalyst = 50 mg, 60 °C, 250 rpm. %Conv. = % conversion of TBHP, %Sel. = % selectivity to epoxide based on peroxide consumed.

Table 2
Epoxidation of 1-octene with TBHP (entries marked with * with CHP) using various Ti-TUD-1 samples.[a]

Entry	Catalyst	Yield of epoxide (%)	TON	%Conv.	%Sel.
1*,[b]	TUD-1	0	0	15	0
2	Ti-1.5S	14.8	130	52	85
3	2nd run	15.1	133		
4	Ti-2.5S	28.7	154	88	98
5	2nd run	25.2	135		
6*,[b]	Ti-2.5S	25.1	135	77	98
7*,[b]	2nd run	22.1	121		
8	Ti-5S	25.6	79	94	86
9	2nd run	24.6	76		
10*,[b]	Ti-5S	24.4	75	86	86
11	Ti-10S	16.5	25	84	59
12	2nd run	11.1	17		

[a] Reaction conditions: 1-octene (10 mmol), TBHP or CHP (entries 1, 6, 7 and 10) (3.33 mmol), catalyst = 50 mg, 60 °C, rpm = 250, 8 h. Max yield of epoxide is 33%. Turn over number in mol epoxide/mol Ti; %Conv. = conversion of peroxide (%); %Sel. = selectivity to epoxide based on converted peroxide (%).

[b] Oxidant is CHP.

TUD-1 catalyst exhibited only 5-15% a-selective decomposition of CHP. The formation of phenol in these reactions also was indicated by the typical brown color of oxidized polyphenolic products in the reaction solutions, and their presence was confirmed with GC and GC-MS analyses of the reaction mixtures.

When *t*-butyl hydroperoxide (TBHP, 66.4% in decane) was used as the oxidant in the epoxidation reaction with unsilylated TUD-1 samples, less TBHP was converted, but higher yields of epoxide were obtained (Fig. 4 and Table 2). Typically, after 8 h, 30–50% of TBHP was consumed, of which 40–70% ended up in the epoxide. The selectivity to the epoxide decreased in the order Ti-1.5 $>$ Ti-1 $>$ Ti-2 $\approx$ Ti-2.5 $>$ Ti-5 $>$ Ti-10. The lower selectivity of the high Ti-loaded sample can be explained by the facile heterolytic decomposition of alkyl hydroperoxide over TiO_2-containing Ti-TUD-1 samples. On the other hand, the peroxide conversion increased with the amount of Ti loading into the TUD-1 samples up to Ti-5. Overall, the use of unsilylated TUD-1 samples resulted in low selectivity to epoxide based on peroxide and relatively low epoxide yields even when TBHP was used as the oxidant. Nevertheless, products other than the epoxide were not found, and all of the catalysts gave practically 100% selectivity to the epoxide based on converted olefin. The TOF of 1-octene over Ti-1.5, defined as the number of moles of 1-octene converted per mole of titanium per hour, was calculated to be $\sim$40 h^{-1}, within the same order of magnitude as reported previously for the same catalyst in the TBHP-mediated cyclohexene oxidation [35].

The low selectivities based on peroxide when both CHP and TBHP were used as oxidants thus can be rationalized by the presence of protic mildly acidic sites (Si–OH, Ti–OH) in the mesoporous silica framework of Ti-TUD-1 samples, which are responsible for the acid-catalyzed decomposition of the organic hydroperoxides. The more facile heterolytic decomposition of CHP compared with TBHP is the reason for the very low selectivities obtained with CHP as the oxidant.

3.2.2. *Epoxidation of 1-octene with silylated Ti-TUD-1 samples*

With the aim of obtaining more selective catalysts for the epoxidation reaction, the Ti-TUD-1 samples were silylated using HMDS to remove –Si–OH and –Ti–OH sites, according the general reaction shown in Scheme 1. The silylated samples were used in the epoxidation of 1-octene with both CHP and TBHP as oxidant. As shown in Figs. 3 and 4, the silylated Ti-TUD-1 samples indeed exhibited spectacularly increased peroxide selectivities to the epoxide, which, particularly for CHP, is a significant improvement relative to the unsilylated catalysts (Fig. 3). In the case of TBHP, the activity of the catalyst for conversion to epoxide also was markedly improved with silylation; up to 90% of the oxidant was consumed after 8 h, with near-quantitative conversion into the epoxide. For CHP, however, the conversion of the oxidant tended to drop on silylation, particularly at low Ti loadings, although the selectivity was improved significantly. After 8 h, 50–80% of the CHP was converted, with $<$10% a-selective decomposition. The now colorless reaction mixtures confirmed the absence of phenolic products formed by acid-catalyzed heterolytic decomposition of CHP. Among the silylated TUD-1 samples, the selectivity to epoxide formation decreased in the order Ti-1.5S $\approx$ Ti-2.5S $>$ Ti-5S $>$ Ti-10S, whereas the greatest conversion of peroxide was achieved with Ti-5S.

These results again indicate the presence of a separate nanocrystalline TiO_2 phase in the higher Ti-content Ti-5S and Ti-10S samples, which is considered responsible for the lower peroxide selectivity to the epoxide compared with Ti-2.5S. The higher epoxide selectivity and yield enhancement is considered a consequence of the silylation of Ti-TUD-1 catalysts, through which most of the a-selective CHP decomposing Brønsted-acidic sites in the samples are eliminated. The increased hydrophobicity of the silylated Ti-MCM-41 samples, leading to enhanced concentration of the apolar olefin at the hydrophobic surface, has been suggested as the most likely cause of the higher activity for epoxidation with TBHP [12,26]; however, our results for the HMDS-treated TUD-1 samples with CHP as the oxidant suggest an additional factor—removal of the protic CHP decomposition sites—as the main reason for the high selectivity in epoxidation with CHP. For TBHP, both the increased hydrophobicity and the removal of acidic sites are suggested to lead to significantly enhanced activity and selectivity for epoxidation. The acidity of the protic Ti–OH groups, but not the Si–OH groups, in the unsilylated catalysts is suggested as the main reason for the unselective decomposition of peroxide, because the parent TUD-1 catalyst shows relatively less a-selective decomposition of alkyl hydroperoxides.

To the best of our knowledge, these are the highest selectivities to epoxide for 1-octene oxidation with metal-substituted mesoporous silica using CHP as the oxidant reported to date. Corma et al. reported similar activities after applying TBHP as the oxidant with silylated Ti-MCM-41 catalysts in their studies performed under different conditions [36].

3.2.3. *Effect of the addition of conventional base*

From the results of our characterization studies, we can conclude that the acidity of Ti-TUD-1 samples played a key role in the

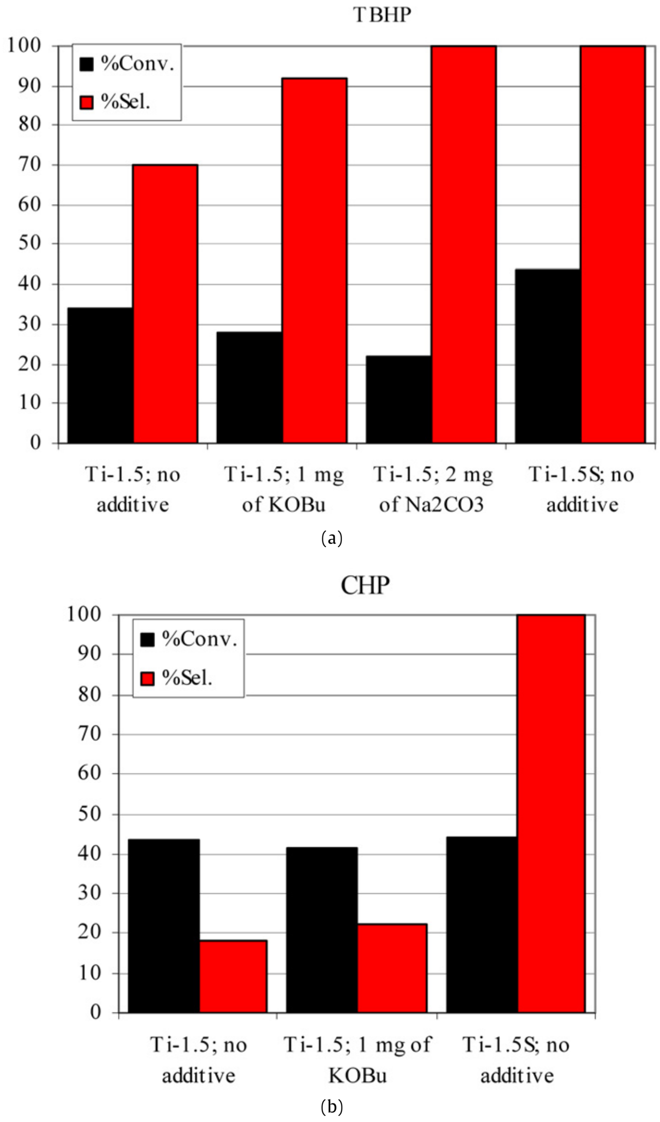


Fig. 5. Effect of base and silylation on the conversion of peroxide and selectivity to 1,2-epoxy octane based on peroxide in the epoxidation of 1-octene after 8 h. Reaction conditions: 1-octene (10 mmol), TBHP (a) or CHP (b) (3.33 mmol), catalyst = 50 mg, 60 °C, 250 rpm. %Conv. = % conversion of peroxide, %Sel. = % selectivity to epoxide based on peroxide consumed.

efficiency of peroxide utilization during the epoxidation reactions. Experiments also were performed by adding conventional bases, such as KO^{t}Bu and Na_2CO_3, to the epoxidation reaction mixtures using the unsilylated Ti-TUD-1 samples. Although the selectivity based on TBHP was significantly enhanced with the addition of these bases, a lower peroxide conversion with lower epoxide yields was observed (Fig. 5). In contrast, in epoxidation reactions with CHP as the oxidant, the selectivity based on peroxide did not significantly increase on the addition of a conventional base. This suggests that either the weakly acidic Ti–OH sites responsible for the decomposition of CHP survived neutralization by common bases or that the Lewis acidic Ti–O–alkali metal site was now responsible for decomposition of CHP under the applied conditions. We currently favor the latter explanation, because this suggests that the polarity of the active Ti-site is an important factor [i.e., Ti–O–$Si(CH_3)_3$ vs. Ti–O^-Na^+], in line with our conclusion that both surface hydrophobicity (i.e., a-polarity) and low acidity are important factors in selective epoxidation, particularly with such oxidants as CHP, for which decomposition is highly sensitive to these factors.

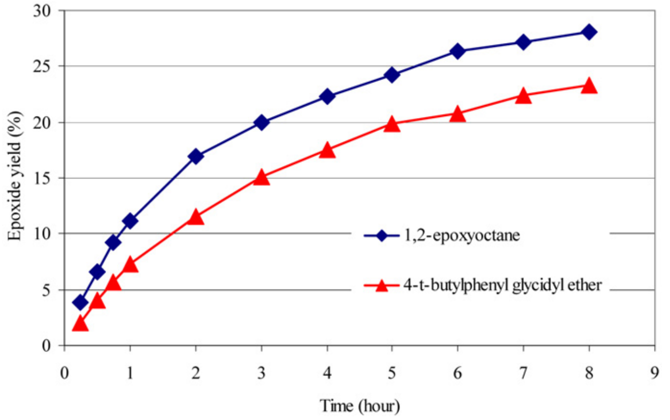


Fig. 6. Formation of epoxides in time in the epoxidation of 1-octene and *p-tert*-butylphenylallyl ether catalyzed by Ti-2.5S with TBHP. Reaction conditions: 1-octene (10 mmol), TBHP (3.33 mmol), or *p-tert*-butylphenylallyl ether (5 mmol), TBHP (1.67 mmol), catalyst = 50 mg, 60 °C, 250 rpm.

3.2.4. Epoxidation of *p-tert*-butylphenylallyl ether

Epoxidation of *p-tert*-butylphenylallyl ether was performed with the catalyst Ti-2.5S using TBHP as the oxidant. The results are compared with those for 1-octene epoxidation in Fig. 6. The use of Ti-2.5S in the epoxidation of *p-tert*-butylphenylallyl ether resulted in 87% selectivity to epoxide, lower than that found for 1-octene epoxidation. The product *p-tert*-butylphenylglycidyl ether was obtained at a 23% yield after 8 h, after which time the rate of the reaction was very low, resulting in a total epoxide yield of 29% after 21 h (maximum theoretical yield = 33%; olefin/peroxide = 3). Clearly, competition between epoxide production and the unselective heterolytic decomposition of the organic hydroperoxide depends on the relative rates of these reactions. When the olefin is relatively unreactive, the unselective decomposition of peroxide will be more dominant, as observed in the case of *p-tert*-butylphenylallyl ether. In this case, the product mixture was yellow and the catalyst became slightly brown, in contrast with the observations for 1-octene epoxidation. This coloration could be due to the formation of a small amount of phenolic oligomers through ring hydroxylation of the *p-tert*-butylphenylallyl ether during epoxidation. No soluble phenolic products were detected by GC analysis of the product mixtures, however.

3.2.5. Catalyst stability and reusability

Leaching of the heterogeneous catalyst (Ti-5S) was evaluated by filtering the hot solution after 30 min and following the epoxidation of 1-octene in the filtrate. After the catalyst was removed, no further epoxidation activity was observed, which rules out the possibility of leaching of active titanium species into the solution.

The reusability of the catalyst was investigated by performing catalytic epoxidation with spent catalyst in a second run. The results of the second run, presented in Table 2, show that catalyst activity was preserved after the first use, with similar turnover numbers seen for epoxide during the epoxidation of 1-octene. Catalyst deactivation was more pronounced in the epoxidation of *p-tert*-butylphenylallyl ether, however, likely due to the formation and precipitation of some heavy phenolic oxidation byproducts in the pores of the catalyst.

4. Conclusion

We found that silylated Ti-TUD-1 catalysts performed much better in 1-octene epoxidation than their unsilylated parent catalysts on the basis of epoxide formed per peroxide converted.

Our comparative study using TBHP and CHP as oxidants suggests that Brønsted acidic sites in the unsilylated catalysts were mainly responsible for the unselective decomposition of the organic hydroperoxides, particularly CHP. Our findings indicate that successful epoxidation of olefins with (organic) hydroperoxides as oxidants depends on both the hydrophobic nature of the catalyst surface as well as the presence (or absence) of Brønsted acid sites. This finding may also be relevant for controlling the olefin epoxidation selectivity with in situ generated H_2O_2 (from H_2 and O_2) over Au-supported materials [3]. Silylation by treatment with HMDS eliminated Brønsted acidic sites by converting protic acidic –Si–OH and Ti–OH surface species to trimethylsilyl capped analogous sites, $-Si-O-Si(CH_3)_3$ and $-Ti-O-Si(CH_3)_3$. Silylated Ti-TUD-1 samples with low Ti loadings showed excellent selectivity to epoxide based on peroxide conversion, even at a relatively low olefin-to-peroxide ratio of 3.

The silylated Ti-TUD-1 catalysts are quite active for the epoxidation of relatively electron-poor olefins, such as *p*-*tert*-butylphenylallyl ether. Our catalytic results for 1-octene epoxidation indicate that the silylated Ti-TUD-1 catalysts are similar to the existing Ti/SiO_2 catalysts in terms of the selectivity of epoxidation based on peroxide conversion. Regarding catalytic activity under identical conditions, the 1-octene epoxidation rate constants of optimized Ti/SiO_2 catalysts were double those of the Ti-2.5S-TUD-1 catalyst [41]. The relatively cheap synthetic methods for obtaining these catalysts may confer an advantage over existing processes, especially when used in combination with a recyclable oxidant, such as CHP.

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