Accepted Manuscript

Title: Epoxidation of limonene over low coordination Ti in Ti-SBA-16

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 PII:
 S0926-860X(17)30001-7

 DOI:
 http://dx.doi.org/doi:10.1016/j.apcata.2017.01.001

 Reference:
 APCATA 16112

To appear in: Applied Catalysis A: General

 Received date:
 15-11-2016

 Revised date:
 31-12-2016

 Accepted date:
 3-1-2017

Please cite this article as: Luc Charbonneau, Serge Kaliaguine, Epoxidation of limonene over low coordination Ti in Ti- SBA-16, Applied Catalysis A, General http://dx.doi.org/10.1016/j.apcata.2017.01.001

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Epoxidation of limonene over low coordination Ti in Ti- SBA-16

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Graphical abstract



Highlights

- New robust active, selective and reusable Ti-SBA-16 with high content of low coordination Ti
- Comparison 3D pore structure of Ti-SBA-16 with 2D Ti-SBA-15
- New mechanism for limonene epoxidation

Abstract

Epoxidation of limonene was studied over Ti-SBA-16 catalysts prepared using two different post grafting techniques. The first one consisted of an in-situ synthesis of a titanium acetylacetone (ACAC) precursor and the other one used directly TiO(ACAC)₂. Reaction conditions such as temperature, concentration of TBHP and solvent polarity were examined. The reaction should be carried out at 75°C in acetonitrile using a TBHP/limonene molar ratio of 11/6. The conversion of limonene reached 80% with a 1,2-limonene oxide selectivity of 79% for both impregnation methods using Ti-SBA-16 with a Ti/Si atomic ratio of 7.3%. Under the same conditions the 3D pore structure of SBA-16 support favors reactants and products mass transfer compared to the 2D pore structure of SBA-15. No differences in catalytic activity were observed as atomic ratio Ti/Si was varied from 5 to 13.4% in Ti-SBA-16. Repeated catalytic tests showed no change in activity over three process cycles.

Keywords: titanium catalysts, epoxidation, limonene, solvent effect

1. Introduction

The polymer industry is facing the new challenge of producing more green and renewable polymers. Corma et al underlined that natural products could be alternative sources to petroleum derived monomers [1]. Limonene is a low cost raw material easily obtained by extraction from citrus oil. The annual production of limonene reached 70 000 tons per year in 2013 [2, 3]. Limonene oxide is the epoxidation product of limonene. Limonene oxide based polycarbonates have been synthesised and have shown very promising properties [4, 5]. Homogeneous catalysis using molybdenum or trimethylrhenium complexes have shown high limonene conversion with high selectivity to the 1,2-limonene epoxide [6-8]. Homogeneous catalysts are however difficult to implement at industrial scale due to the need of separation from the reaction mixture and problematic reusability.

In the early seventies, Sheldon reported that titanium supported on silica can epoxidize olefins in the presence of a peroxide [9, 10]. Further studies of supported titanium have shown high olefin conversion and selectivity, as high as homogeneous molybdenum catalysts [11]. Sheldon thought that the activity of silica supported titanium is related to its Lewis acid character. Based on his homogeneous catalysis observations, it was believed that silica enhances the Lewis acid character of titanium which led to a higher activity than pure TiO₂. At this time, Sheldon was not aware of the importance of titanium coordination for catalytic activity.

Berube et al. developped a soft-templating titanium post-grafting impregnation on SBA-15 [12, 13]. This technique was shown to yield very active solid catalysts for the epoxidation of cyclohexene. Recently some attempts were made to epoxide limonene over Ti-SBA-15 but conversion and selectivity were still low [14-20]. One work describes the use of MCM-41supported Ti for limonene epoxidation. No catalyst stability was reported MCM-41 is known to be a thin walled not hydrothermally resistant mesostructured silica material. The various solids produced were compared as catalysts in the epoxidation reaction of limonene to limonene oxide [21]. In this work it was attempted to prepare low coordination Ti-SBA-16 by the technique of Bérubé et al. and

to improve on this preparation method by directly impregnating the support with a solution of titanium ACAC.

2.Experimental

2.1 Material Synthesis

SBA-16 synthesis is similar to the one reported by Kleitz et al. [22-24]. In a typical synthesis, 5.35g of F127 (BASF) was dissolved in a stirred solution containing 257.2 g water and 10.6 g concentrated hydrochloric acid (35-37%) at 45°C. When the F127 was dissolved, 16,1 g of n-butanol was added to the solution as a cosurfactant. Finaly 25.45 g of tetraethylorthosilicate (TEOS, 98%, Aldrich) was added to the mixture. The solution was agitated for 24 h. The resulting mixture was transferred to an autoclave to allow hydrothermal aging for 24 h at 140°C. The solution was thereafter cooled down to 5°C and the pH was adjusted to 10. For the preparation of Ti-SBA-16 by the method of Berube et al (method 1) a mixture of Ti(OPr)₄ (Alfa Aesar, 98%) and acetylacetonate (Aldrich,) with a molar ratio of 1/3 in anhydrous ethanol was then added to the suspension of SBA-16 in its mother solution [12, 13]. The solution was stirred for 2 h, filtered and washed with a 300 mL anhydrous ethanol to remove any un-grafted complexe. Finally, the material was dried for 24h at 100°C and calcined at 550°C (ramp of temperature: 2°C/min) for 3 h. A new simpler method (method 2) has been developed in this work. TiO(ACAC)₂ (Strem 98%,) was dissolved in 200 mL toluene at 45°C. SBA-16 was previously calcined at 550°C for 6 h, added to the solution and agitated for 2 h. The solid was filtered, washed with 300 mL of toluene and dried in oven at 100°C for 24 h. Finally, the sample was calcined at 550°C (ramp of temperature: 2°C/min) for 3 h. In order to avoid any confusion, the post grafting method is specified in parentheses; (1) for method 1 and (2) for method 2.

2.2 Characterization

Nitrogen adsorption-desorption isotherms were measured at -196 °C using an Autosorb-1C sorption analyzer. The pore size distributions and the cumulative surface area curves were determined using the nonlocal density functional theory (NLDFT) method 31 supplied with the Autosorb-11.55 software from Quantachrome Instruments. The kernel selected was N₂ sorption on silica at -196 °C assuming a cylindrical pore geometry and implementing the model of (metastable) NLDFT adsorption isotherms (adsorption branch).

Small angle X-ray scattering (SAXS) measurements were taken on a Nanostar U small angle X-ray scattering system (Bruker, Germany) using Cu K α radiation (40 kV, 35 mA). The *d*-spacing values were calculated by the formula $d=2\pi/q$. Prior to elemental analysis, the catalyst was digested in a mixture of 10% (V/V) hydrochloric acid and hydrofluoric acid 1% (V/V). Elemental analysis was performed in a Perkin-Elmer Atomic Absorption M1100B spectrometer. Titanium coordination was determined by diffuse reflectance UV-Vis on a Varian Cary 300 Bio with a scan rate of 200 nm per second.

2.3 Catalytic tests

The catalytic tests were performed in a 50 mL round bottom flask with 300 mg of catalyst, 10 mL of the appropriate solvent, 6.2 mmol of limonene and 11,2 mmol of TBHP in decane solution at 75°C for 24 h with an agitation at 500 rpm using a Fisher Scientific Thermoplate equipped with a thermocouple. The catalyst was separated from the solution by centrifugation. The reaction mixture was analyzed using a CP-3800 gas chromatograph (Varian Inc.) equipped with a flame ionization detector (FID), a Stabilwax column (30 m × 0.53 mm × 1 μ m) coupled with a 5 m guard column. The limonene conversion was determined using Equation 1

$$Conv(\%) = \frac{n_o(limonene) - n_f(limonene)}{n_o(limonene)} * 100$$
(1)

And the selectivity was calculated using Equation 2:

$$Sel(\%) = \frac{n_{epoxide}}{n_o(limonene) - n_f(limonene)} * 100$$
(2)

The reaction by-products were identified using a GC-MS ionic trap Thermo Instrument ITQ-900 Ultra Trace. The column used was a DB-5-MS ($30 \text{ m} \times 0.28 \text{ mm} \times 1 \text{ }\mu\text{m}$).

3. Results and discussion

3.1 Catalysts characterisation

3.1.1 BET Analysis

Titanium acetylacetonate (ACAC) complexes were favored over other titanium complexes in this study. The interests of using these compounds as Ti precursors to functionalize SBA-16 is the requirement of obtaining high dispersion and low coordination of the active Ti sites. Several catalysts were synthesized by method 1 with different Ti/Si ratios ranging from 5 and 13.4%. In this method, the amount of ACAC, temperature and pH of the solution are important parameters to control in order to produce a monomeric Ti(ACAC)₂(OPr)₂ [12, 13]. In reference [13] this synthesis method was used to prepare catalysts with Ti/Si ratios ranging from 0 to 13.4%. The epoxidation activity was shown to increase as theas the ratio was raised up to 5% which is the upper limit at which isolated tetracoordinated Ti species as produced. Above this value (5 to 13.4%) the activity was found to be constant but the materials showed increased stability. Due to this Ti/Si range of density of tetracoordinated Ti remained essentially constant but some high coordination (up to 5) Ti was also formed. The advantage of using the ACAC ligand for catalyst preparation by method 2 is its ability to isolate the central titanium atom on the silica support, allowing high dispersion. In both impregnation methods, the two titanium ACAC complexes react with the hydroxyls of the surface and are converted to titanium oxide surface species upon calcination. N₂ sorption isotherms of pure SBA-16

and Ti-SBA-16 materials were determined. As can be seen on Fig.1, all samples exhibit a type IV isotherm with an hysteresis loop, indicating the presence of well-defined mesopores in the structure.

Calcined Ti-SBA-16 mesporous catalysts displayed a relatively high surface area, large pore diameter and large pore volume (Table 1). The pore size was calculated by non linear DFT using adsorption branch. Table 1 shows that the surface area slightly decreases upon addition of higher titanium amount which still however preserves the mesotructure of the material. The impregnation with toluene TiO(ACAC)₂ (method 2) yielded higher pore volume and pore diameter than the one of materials prepared by method 1. It seems that this impregnation method results in a better dispersion compared to the in-situ formation of the titanium ACAC complex (method 1).

3.1.2 Small angle X-ray diffraction

The XRD patterns, represented on Fig.2, for the calcined Ti catalysts, exhibit a strong 110 reflection peak at 0.54° corresponding to the *Im3m* cubic geometry of SBA-16 [25]. As illustrated on Fig.2 the symmetry of mesoporous structure was essentially maintained after calcination of the grafted titanium material.

In this study the hydrothermal aging of SBA-16 was set to be at the high temperature of 140°C which enhances the formation of larger pores in order to favor the diffusion of the reactants. The catalytic activity of the epoxidation catalyst is mainly influenced by its accessibility of the reactants to the active sites. Low temperature hydrothermal aging could have resulted in high silanol density, mainly situated in the intrawall micropores allowing high amounts of grafted titanium [12, 26]. On the other hand, during calcination, the condensation of these silanols would have entrapped the active sites located in the micropores, blocking their accessibility for the reactants [12]. Materials,

prepared at high temperature hydrothermal aging, present therefore higher density of accessible active sites after calcination. This effect allows reaching higher catalytic activities[12].

3.1.3 DR-UV

To be active in epoxidation reaction, Ti(IV) must be in a tetrahedral coordination. Diffuse Reflectance UV–Visible (DR-UV-Vis) spectroscopy is a rapid and effective technique for revealing the state of titanium species in porous silica materials. In the range of 200-400 nm, the absorption of visible light is highly sensitive to the coordination of the titanium states and to the presence of TiO_2 clusters. Fig.3 shows the DR-UV-Vis spectra of Ti-SBA-16 obtained by impregnation with method 1, the in-situ titanium ACAC synthesis and impregnation method 2.

All catalysts, prepared by both impregnation methods, show a peak centered at 220 nm indicating that titanium is present in a tetrahedral coordination. For sample prepared by method 1 with Ti/Si atomic ratios between 5 to 13.4%, the adsorption signal at 220 nm does not increase which indicates that the amount of tetrahedral titanium reached a constant value. These results are similar to those obtained for Ti catalysts based on SBA-15 mesoporous silica [13]. Moreover, the adsorption spectrum is rather broad with secondary peak at 320-340 nm. This suggests that small TiO₂ clusters of pentacoordinated titanium species are formed which could be ascribed to the formation of Ti-O-Ti chemical bonds during the calcination process [27].

3.2 Catalytic performance

3.2.1 Effect of reaction temperature

The reaction of limonene with TBHP in the presence of Ti-SBA-16 catalysts may result in different epoxide isomers represented on Fig.4.

In general, the rate of epoxidation increases with increasing substitution of the olefin with alkyl groups, which is consistent with the electrophilic nature of the reagent [11]. Based on this observation, the major products will be of course 1,2-limonene oxide. 1,2-8,9-limonene dioxide would be produced by the double epoxidation of limonene.

Limonene oxide based polycarbonates are produced by reacting 1,2-limonene oxide with CO_2 [4, 5]. For industrial applications, it is crucial to obtain the highest possible yield of 1,2-limonene oxide. A series of catalytic tests were conducted using a catalyst prepared by method 1 with an atomic ratio of Ti/Si of 7.3% in the interest of establishing the optimal reaction parameters. First, the temperature effect on the conversion of limonene and selectivity toward 1,2-limonene oxide was studied and the results are summarized on Fig.5:

Fig.5 shows that a rise in temperature from 70°C to 75°C improves the conversion from 59% to 80% without affecting its selectivity. GC-MS analysis of the reaction medium was performed for the determination of the reaction by-products. Only 8,9-limonene oxide isomer as a secondary product was present in the reaction mixture. At 80°C, the selectivity for 1,2-limonene oxide decreases drastically from 81% to 51% which is explained by the thermal autodecomposition of tert-butyl hydroperoxide. At 45°C, TBHP is considered to be indefinitely stable. On the other hand, heating the reaction medium above this temperature favors the reaction of TBHP autodecomposition represented on Scheme 1[28, 29]:

The first step of this reaction consists of the homolytic cleavage of the peroxo group forming tert-butyl-O⁻ and a radical OH⁻. Tert-butyl-O⁻ then reacts with another tert-butyl hydroperoxide molecule which produces tert-butanol and tert-butyl-OO⁻ radical. The final step of this radical mechanism consists of the conversion of tert-butyl-OO⁻ radical into

molecular oxygen and tert-butyl-O. These radicals present in the reaction medium react with limonene and convert it into sub-products such as carvone, perillal and carveol. Even though these molecules are often considered as undesired products, they could be used in fragrance or perfume industries, and they also have real interest in polymer industries.

3.2.2 Effect of TBHP

Tert-butyl hydroperoxide in decane solution was favored over aqueous TBHP and hydrogen peroxide solutions in this work for several reasons. On the basis of their electrophilic properties, there should not be difference between TBHP and H₂O₂ in conjunction with metal catalysts epoxidation. TBHP is however far superior because of its stability and ease of manipulation [11, 28]. The aqueous TBHP solution reduces the conversion and selectivity since water molecules compete with the peroxide for adsorption on the actives sites [30, 31]. Moreover, the presence of water in both H₂O₂ and TBHP reduces the selectivity of epoxide, as when the latter is formed it is readily converted to the corresponding diol [32]. When TBHP was used in aqueous solution, the selectivity for the 1,2-limonene diol varied from 8 to 20% [15, 17, 33-35]. Even by changing the hydrophilic properties of silica to make it hydrophobic, the 1,2- limonene diol was still produced with a selectivity as low as 8% [33]. Only one reference reports limonene epoxidation over SBA-15 supported Ti using both H₂O₂ and TBHP in aqueous solution with apparent high selectivity to limonene oxide in contradiction with all other published works [36]. Finally, TBHP is more beneficial to the selective production of epoxide than H₂O₂. Transition state involving Ti–OOR and a cyclic alkene must be much bulkier than that related to the Ti-OOH and alkene. This characteristic significantly retards the reaction rate of cyclic alkenes with TBHP, further decreasing the possibility of acid-catalyzed secondary ring-opening reaction of epoxide molecules [37].

Sheldon has suggested that epoxidation of alkenes under homogeneous conditions should be performed at a high alkene/peroxide ratio to favor the selectivity for the epoxide and

avoid the competing radical reaction (scheme 1). On the other hand, under these conditions, the yield for epoxides is very low and becomes less significant for industrial needs [11]. It was later found that using 2 equivalents of anhydrous TBHP with 1 equivalent of olefin can yield as high as 90% of epoxide [11]. Different catalytic tests were performed with different amounts of TBHP in acetonitrile at 75°C, the optimal temperature determined in the previous section. The results are summarized on Fig.6.

The results in Fig.6 show that increasing the amount of TBHP from 2.75 to 8.25 mmol, increases the conversion up to 45% with a selectivity remaining as high as 95%. When the reaction was performed with 11 mmol of the TBHP, which corresponds to oxidizing agent-olefin molar ratio of nearly 2:1, the conversion drastically increases to nearly 80% as the selectivity for 1,2-limonene oxide has decreased to 81%. GC-MS analysis has shown that 8,9-limonene oxide was present but no 1,2-8,9 limonene diepoxide was detected in the reaction mixture. At 11 mmol of TBHP, it is then possible to conclude that the selectivity for monoepoxides is 100%. The selectivity for the 1,2-epoxide decreases from 81% to 54% when the reaction is carried out with 13.5 mmol of TBHP. At this TBHP content, the autodecomposition reaction (scheme 1) becomes more favorable and the OH⁻ radical formation becomes more important which decreases the selectivity toward the epoxide [28, 29].

3.2.3 Effect of solvent

The activity and selectivity of titanium catalysts for the epoxidation of alkenes is related to the nature and polarity of solvents. For example, acetonitrile exhibits higher conversion and selectivity when catalysts such as Ti-MWW and Ti-Beta are employed compared to TS-1 which was shown to be more active in methanol medium [38, 39]. However, methanol and acetonitrile has similar polarity and they only differ by their

protic/aprotic properties. Polar protic solvent, especially alcohols, can form complexes with the active center that help stabilizing the Ti-OOR with the formation of an hydrogen bond [38, 39]. On the other hand, like water, alcohols such as methanol are less interesting solvents due to their reaction with the epoxides which converts the later into ether-glycol by-products [32]. In this, study three different aprotic solvents, ranging from non-polar to highly polar, were used and compared. The results are displayed in Table 2.

Cyclohexane is the less interesting solvent. Its non-polar hydrophobic character does not allow good diffusion of the substrate from the reaction medium to the active sites. In the presence of titanosilicate materials, alkanes are known to be converted to alcohol by radical reactions [[40]]. The high conversion of limonene in the presence of cyclohexane is mostly related to the radical reaction from the tert-butyl hydroperoxide decomposition. Ethyl acetate yields interesting conversion and selectivity. Carniato et al obtained similar results by using TiO₂ on amorphous SiO₂ [16]. Acetonitrile, which has the highest polarity, is by far the first choice solvent for epoxidation of alkenes such as limonene using TiO₂/SiO₂ catalysts. This solvent was also found to be the first choice for cyclohexene epoxidation and has yielded the highest conversion and selectivity [33, 35, 37-39]. For epoxidation reaction, solvent molecules are believed to be stabilising agents of the Ti-OOR in order to maintain the complex and avoid decomposition of the peroxide. Corma has proposed that a coordination chemical bond is formed between the supported titanium peroxo complex with a lone electron pair of methanol. Then, a bond is formed between one oxygen of Ti-OOR and the hydrogen from OH functional group. This solvent-Ti-OOR structure helps stabilise the peroxo group and favors higher conversion [39]. The relation between methanol and TiOOR is represented on Scheme 2a. Acetonitrile possesses the ability to complex with transition metals with its C-N π electrons [41]. In this work, we propose that the coordination of acetonitrile with

supported titanium catalysts is similar to that of methanol. The complex between acetonitrile and the supported titanium active site is represented on Scheme 2 b.

Similar to the coordination bond between the π electrons of C-N and titanium, a Van der Waals interaction is formed between the electron poor nitrogen atom of acetonitrile and a lone electron pair from the Ti-OOR. This bond enables to stabilise the peroxo group and favors the conversion and selectivity for epoxides. Ethyl acetate does not possess the ability to complex with titanium by strong coordination bonding which implies that the conversion and selectivity is less with this solvent. Scheme 3, with the coordinating solvent molecule not being represented for sake of simplicity, shows our proposed mechanism for the epoxidation of limonene to limonene oxide.

The first step consists of the reaction between the supported titanium with TBHP which forms a Ti-peroxo complex, the source of oxygen for the formation of the epoxide. The Ti-O-Si chemical bond is broken and Ti-OOR and Si-OH are formed. Then limonene reacts with the catalyst to form the epoxide by a concerted mechanism. The final products of the reaction are limonene oxide isomers and tert-butanol. Finally, the Ti-OOR is regenerated by reaction of Ti-OH with a molecule of TBHP present in the liquid medium.

3.2.4 Effect of pore structure and titanium loading

In this work, a comparison of SBA-15 and SBA-16 was also performed under the optimal conditions determined in the previous section. A sample of Ti-SBA-15 was synthesised by method 1 with physicochemical properties similar to the SBA-16 sample with Ti/Si =7.3% shown in Table 1 (Ti/Si=8.2%, surface area of 637 m²/g, pore volume of 0.94 cm³/g and pore diameter of 8.4 nm) [13].

The conversion and selectivity reported in Table 3 show that in absence of catalyst, the reaction of epoxidation does not occur. It was found that Ti-SBA-16 gives higher conversion and selectivity compared to the Ti-SBA-15 catalyst. This is likely due to differences in the rate of deactivation by pore blockage by oligomerization of epoxide products. In general, the tridimensional cage structure of SBA- 16 allows a much more rapid diffusion of the products out of the catalyst particle than the straight cylindrical pore shape of SBA-15 [23, 24, 42, 43]. Carniato et al. using ethyl acetate solvent also found that the conversion of limonene is less important when SBA-15 is used compared to amorphous SiO₂ support [16]. The structure problems associated with the diffusion in SBA-15 have been described in the literature [44].

As reported in Table 4, the Ti-SBA-16 with 7.9 % prepared using method 2 (TiO(ACAC)₂) gives results in the epoxidation of limonene similar to those obtained with Ti-SBA-16 prepared by the post-grafting technique developed by Berube et al (method 1) [12]. This indicates that both materials with nearly the same amount of titanium possess the same catalytic activities even though method 2 is simpler and more easily controlled. Values of TBHP conversion and selectivity are obtained from GC traces are also shown in Table 4. The selectivity values are conservative estimates as some TBHP thermal decomposition may happened in the hot injector (260°C).

1,2-limonene oxide is obtained as a mixture of cis and trans isomers. Low molecular weight polylimonene carbonate may be produced by the reaction of CO_2 with a mixture of cis and trans 1,2-limonene oxide, but high molecular weight polycarbonate is only obtained from trans 1,2-limonene oxide [4, 5]. Table 5 shows the trans/cis ratio results obtained by GC-MS with the different catalysts.

For Ti catalysts prepared by method 1 with Ti/Si of 5.0 and 7.3%, the isomer ratio trans/cis does not seem to be affected. On the other hand, an increase of the trans isomers is observed when the atomic ratio is 13.4%. The post grafting technique (method 2) yielded higher trans/cis atomic ratio compared to the in-situ technique (method 1). It seems that the proportion of the trans/cis isomers is affected by the atomic Ti/Si ratio and that the source of ACAC also influences this proportion.

3.2.5 Catalysts stability

One important asset of heterogeneous catalysts is their reusability. It is shown on Fig.7 that the conversion and selectivity remained almost unchanged for three repeated cycles. Between cycles, the catalysts were removed from the liquid phase by centrifugation, dried in air and finally calcined in air at 550°C.

(a)

(b)

The loss of titanium by leaching after three catalytic cycle was around 5% for all catalysts impregnated by both methods except for Ti-SBA-16 with an atomic ratio of 13.4% which the leaching was less important and around 1.2%. One interesting comparison to make is the reusability of the Ti-SBA-16 (Ti/Si = 5.0%) compared to the Ti-SBA-15 (5.6%) by Berube et al for epoxidation of cyclohexene [13]. In our case conversion is nearly the same for the three cycles while for Berube the conversion drops by nearly 12%. The effect of the support structure is considered negligible. The only difference is that in this work TBHP in anhydrous solvent was used in comparison to Berube et al that used the aqueous THBP. The main advantage using TBHP in aqueous solution is that it is commercially available in high concentration of the oxidizing agent. On the other hand, besides the problems related to the epoxide yields mentioned in the previous section, the presence of water is affecting catalyst reusability. It is then believed

that the hydrolysis of the Ti-O-Si when the epoxidation reaction in the presence of water is more important than in anhydrous conditions. During the recalcination process, the water molecules adsorbed on Ti sites favor the formation of titanium clusters with higher Ti coordination structure, from tetrahedral toward octahedral, and then reduce the surface density of actives sites which induces the decay of the olefin conversion [31, 45, 46].

4. Conclusion:

In conclusion, this work reports the catalytic epoxidation reaction of limonene over Ti-SBA-16 catalysts. The 3D cage structure of SBA-16 was confirmed to favor the diffusion of the reactants to the active sites compared to the 2D pore structure of SBA-15. The epoxidation of limonene to limonene oxide was shown to be very sensitive to reaction parameters such as temperature and amount of the oxidizing agent. These needs to be appropriately controlled in order to avoid the autodecomposition of the TBHP which favors the radical reaction. In this work, it has been established that the high polarity solvents lead to higher limonene conversion and 1,2-epoxide selectivity. Acetonitrile is a far better solvent than ethyl acetate. Finally, the catalysts were shown to be stable over three catalytic tests in terms of both conversion or selectivity.

Acknowledgements:

Financial support from the Natural Sciences and Engineering Council of Canada (NSERC). We thank Professor D.Zhao and W. Shuai from Fudan University for the Small angles XRD measurements. We also thank Professor T.O. Do from Laval University for DR-UV measurements.

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Fig.1 N₂-Sorption isotherms for Ti-SBA-16 catalysts



Fig.2 Small angle X-ray diffraction patterns of Ti-SBA-16 catalysts



Fig.3 DR-UV of selected Ti-SBA-16 Catalysts



Fig.4 Epoxides from the epoxidation of limonene



Fig.5 Temperature effect on conversion of limonene and selectivity for 1,2-limonene oxide using Ti-SBA-16 Ti/Si = 7.3 %, 11 mmol of TBHP, 6 mmol of limonene in acetonitrile



Fig.6 Conversion and selectivity to 1,2-limonene oxide as a function of TBHP initial content using Ti-SBA-16-(1) Ti/Si = 7.3 %, at 75° C with 6 mmol of limonene in acetonitrile



Fig.7 Conversion of limonene a) and selectivity to 1,2-limonene oxide b) upon repeated catalytic tests



Scheme 1 Mechanism of TBHP decomposition



Scheme 2 Coordination of a) Methanol with supported titanium on silica according Corma et al.[39] and b) Proposed coordination structure of acetonitrile with Ti-SBA-16



Scheme 3 Proposed mechanism for the epoxidation of limonene to 1,2-limonene oxide

Catalyst	Ti/Si (%)	Surface (m²/g)	Pore diameter (nm)	Pore Volume (cm ³ /g)
SBA-16	-	693	12.6	0.82
Ti-SBA-16-(1)	5.0	608	11.6	0.71
Ti-SBA-16-(1)	7.3	600	11.4	0.68
Ti-SBA-16-(2)	7.9	635	11.7	0.78
Ti-SBA-16-(1)	13.4	582	11.2	0.60

 Table 1 Physical properties of the catalysts

Solvent	Relative polarity	Temperature ℃	Conversion (%)	1,2-limonene oxide Selectivity (%)	
Acetonitrile	0.460	75	80	82	
Ethyl Acetate	0.228	75	65	68	
Cyclohexane	0.006	75	58	5	
Reaction conditions: 6.2 mmol of limonene, 11 mmol of THBP in decane, 0.3 g of Ti-SBA-16-(1) (Ti/Si					
7.3%), 75°C, 10 mL of solvent, 24h					

Table 2 Relation of solvent dielectric constant with conversion and selectivity

Catalyst	Ti/Si (%)	Conversion (%)	1,2-limonene oxide Selectivity (%)	TBHP Conversion (%)	TBHP Selectivity (%)
No catalyst	0	47	3		
Ti-SBA-16-(1)	7.3	80	82	75	45
Ti-SBA-15	8.2	38	72	80	20

Table 3 - Marked Comparison of catalysts support in the epoxidation of limonene to limonene oxide

Reaction conditions: 6.2 mmol of limonene, 11 mmol of THBP in decane, 0.3 g of catalyst, 75°C,10 mL of acetonitrile, 24h

Catalyst	Ti/Si (%)	Conversion (%)	1,2-limonene oxide Selectivity (%)	TBHP Conversion (%)	TBHP Selectivity (%)
Ti-SBA-16-(1)	13.4	77	79	81	41
Ti-SBA-16-(1)	7.3	80	79	75	45
Ti-SBA-16-(2)	7.9	80	80	76	47
Ti-SBA-16-(1)	5.0	76	78	74	45

 Table 4 - Marked Effect of titanium loading on the epoxidation of limonene to 1,2-limonene oxide

Reaction conditions: 6.2 mmol of limonene, 11 mmol of THBP in decane, 0.3 g of Ti-SBA-16 catalyst, 75°C, 10 mL of acetonitrile, 24h

Catalyst	Ti/Si (%)	Ratio Trans/Cis		
Ti-SBA-16-(1)	13.4	2.00		
Ti-SBA-16-(1)	7.3	1.41		
Ti-SBA-16-(2)	7.9	1.71		
Ti-SBA-16-(1)	5.0	1.43		
Reaction conditions: 6.2 mmol of limonene, 11 mmol of THBP in decane, 0.3 g of Ti-SBA-16 catalyst 75° C 10 mL of acetonitrile 24h				

Table 5 Ratio of Trans/Cis 1,2-limonene Oxide Isomer