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Ti-MCM-41 catalysts prepared by post-synthesis methods Limonene epoxidation with H_2O_2

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Abstract

Ti-MCM-41 catalysts were prepared incorporating Ti by post-synthesis methods: wetness and wet impregnation of MCM-41 mesoporous solid. The samples were characterized by XRD at low angle, UV–vis DRS, Raman spectroscopy, BET, ICP and colorimetry. The results were compared with those obtained for Ti-MCM-41 hydrotermically prepared. All catalysts were tested in the limonene epoxidation with H_2O_2. Three kinds of Ti sites were observed in post-synthesis catalysts which were different from that found in the hydrothermal Ti-MCM-41. These structural differences do not produce important changes in the catalytic activity, instead a slight decrease in the epoxide selectivity can be observed. The catalysts prepared by post-synthesis methods are promising in the limonene epoxidation with H_2O_2 since these methods are simple and reproducible.

Keywords: Ti-MCM-41; Limonene epoxidation; Post-synthesis methods

1. Introduction

The chemical industry is often associated with the damage of the environment and, at least in a number of cases, this cannot be denied. In order to improve chemical processes using clean technologies, the study of selective catalytic oxidation of organic compounds with innocuous oxidants for the environment requirements are in progress. In the particular case of the terpenes epoxidation in fine chemical industry, the present methods use peracids as oxidants. However, equivalent amounts of acid waste are produced with these reactants. Therefore, there is a strong necessity for a development of new epoxidation methods using safer oxidants and producing little waste. In this way, hydrogen peroxide seems to be an attractive option as oxidant since it is cheap, easily available and only produces H_2O as by-product. In relation with the nature of the catalysts, the heterogeneous ones are more adequate since they are easily separated from the product mixture and they can be recycled.

Among terpenes, the limonene epoxidation using H_2O_2 as oxidant has been carried out with different transition metal complexes supported on different solids. However, these catalysts have a poor stability and product yields, which leads to leaching during reaction and thus limits the recyclability [1,2].

Titanium has been widely used as catalyst for epoxidation reactions. In the last years, new solid materials that could be used as Ti support have been developed. Thus, the synthesis and characterization of different types of mesoporous solids, such as MCM-41 and SBA-15, have been reported by different authors [3–5]. These materials present a regular, hexagonal arrangement of uniform pores with diameters varying between 1.5 and 10 nm. In this way, some catalysts have been synthesized by grafting titanium on SBA-15, from $TiCl_4$ in gas phase. However, they also showed a very important Ti leaching with H_2O_2 [6].

The titanium incorporation in the framework of MCM-41 by hydrothermal methods was attained in order to use the peculiar textural properties of these solids, turning them in attractive catalysts to be used in epoxidation reactions of bulky molecules, with H_2O_2 or *tert*-butyl-hydroperoxide as oxidant agents [7–9]. Notwithstanding, the low reproducibility of the

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preparation methods of these solids and the Ti leaching from the framework of the MCM-41 appears as a problem to solve according to that reported by different authors [10,11]. In a previous work [12], we have found that under certain reaction conditions, no Ti leaching occurs during the limonene epoxidation with H_2O_2. Nevertheless, to find catalysts that allow to carry out the oxidation process with a minimum Ti leaching using H_2O_2 is still an interesting challenge. In this way, other preparation methods have been implemented. They consist in post-synthesis treatments, such as incipient wetness and wet impregnation of MCM-41 mesoporous solid previously synthesized [13–16].

Other authors [17,18] have shown that alumina itself is already active for the limonene epoxidation with H_2O_2. In spite of Al_2O_3 is the simplest catalyst compared with those above mentioned, to improve the selectivity to epoxides it is necessary to use a continuous azeotropic distillation in order to remove the water from the reaction mixture. The necessity to use anhydrous H_2O_2 is a disadvantage of this system.

Bearing in mind the previous discussion, the scope of the present work is to study the effect that the preparation method has on the location of titanium and its influence on the catalytic activity in the limonene epoxidation with H_2O_2. With this purpose MCM-41 catalysts modified with Ti were prepared using incipient wetness and wet impregnation methods which are the less studied in the bibliography. The solids were characterized and tested in limonene epoxidation reaction with H_2O_2. The characterization and activity results were compared with those obtained with a Ti-MCM-41 catalyst prepared by us using the more traditional method, hydrothermal synthesis. All catalysts were tested in such reaction conditions in which it was demonstrated that the hydrothermal solid does not show Ti ‘‘leaching’’.

2. Experimental

To obtain Ti-MCM-41 catalysts by post-synthetic techniques, MCM-41 synthesized according to the methodology proposed by Ryoo and Kim [4] was used as support. The mesoporous material was subjected to two different ways for titanium incorporation:

(a) Wetness impregnation: a volume of Ti-tertbutoxide (Ti (*t*-BuO)$_4$) (Sigma–Aldrich 99%) in isopropyl alcohol solution (IPA) (J.T.B. absolute, analytical quality) of the desired concentration equal to the MCM-41 pore volume was added, in order to obtain solids with Ti nominal loadings of 1, 2 and 3%, w/w.
(b) Wet impregnation: the support was suspended in a Ti(*t*-BuO)$_4$ in IPA solution. It was stirred during 5 h, and centrifuged during 15 min. The solid was separated and then washed with clean portions of IPA, until the turbidity appearance (TiO_2 formation) was not observed by adding a drop of water to the washing liquid.

Both impregnation methods were carried out in a glove box, in N_2 controlled atmosphere to avoid Ti(*t*-BuO)$_4$ hydrolysis.

In both cases the impregnated samples were dried in nitrogen atmosphere and then calcined in air stream (150 cm^3/min) according to the following thermal program: 3 h at 393 K; the temperature was increased to 823 K at 10 K/min, remaining at this value during 5 h.

The solids prepared by wetness impregnation were called WNI-1, WNI-2 and WNI-3 for nominal Ti contents of 1, 2 and 3% (w/w) respectively, and the solid prepared by wet impregnation was called WI.

Ti-MCM-41 catalyst prepared by hydrothermal synthesis, with a Ti content of 1.8% (w/w), was synthesized from tetraethyl-ortosilicate, cetyl-trimethyl-ammonium bromide and Ti-*tert*-butoxide, following the methodology described in ref [9]; this solid was called HT.

The samples were characterized by X-ray diffraction (XRD) at low angles, using Cu Kα radiation, diffuse reflectance spectroscopy (DRS) in the UV–vis range, specific surface area and pore radii distribution by N_2 adsorption (BET), inductively coupled plasma (ICP) and UV–vis spectrometry to determine the content of Ti (expressed like TiO_2). Raman spectra were adquired under room conditions using a Jasco TRS-600-SZ-P single monochromator spectrophotometer equipped with a coupled charge detector (CCD) cooled to about 150 K with liquid N_2. The excitation source was the line of 514.5 nm of a Spectra 9000 Photometrics Ar ion laser. The laser power, measured at the samples, was set at 80 mW and the exposition time was of 180 s.

The activity and selectivity measurements have been carried out in a glass batch reactor at 343 K equipped with refrigerant, thermometer and magnetically stirred. For a standard reaction, 50 mg of catalyst were added to a reaction mixture of 4.32 mmol of limonene (L), 2.7 g of acetonitrile (CH_3CN), used as solvent, and 1.17 mmol of H_2O_2 35%, w/w. The reactions were carried out in limonene excess since in a previous work we have found that in these conditions there is not titanium leaching [12]. Samples at different reaction times were obtained through a lateral tube of the reactor and were analyzed by GC using a capillary column (crosslinked methyl-silicone gum, 30 m × 0.53 mm × 2.65 μm film thickness) and quantified with FID detector. Reaction products were identified by GC–MS. The H_2O_2 conversion was measured by iodometric titration.

3. Results and discussion

3.1. Solids characterization

XRD patterns of all samples (Fig. 1), are characteristics of materials with hexagonal arrangement [4,9]. The MCM-41 and the samples prepared by post-synthesis methods display an intense peak in $2\theta = 2.1^\circ$, two broad and less intense peaks in $2\theta = 3.7^\circ$ and $2\theta = 4.3^\circ$ and a very weak signal in $2\theta = 5.7^\circ$ only in the samples obtained by wetness impregnation. The solid prepared by hydrothermal synthesis displays the main peak broadened, whereas two peaks less intense are not resolved. This result indicates that, in HT, a smaller structural regularity exists. In addition, the first peak appears shifted towards high angles suggesting a different pore diameter or wall thickness.

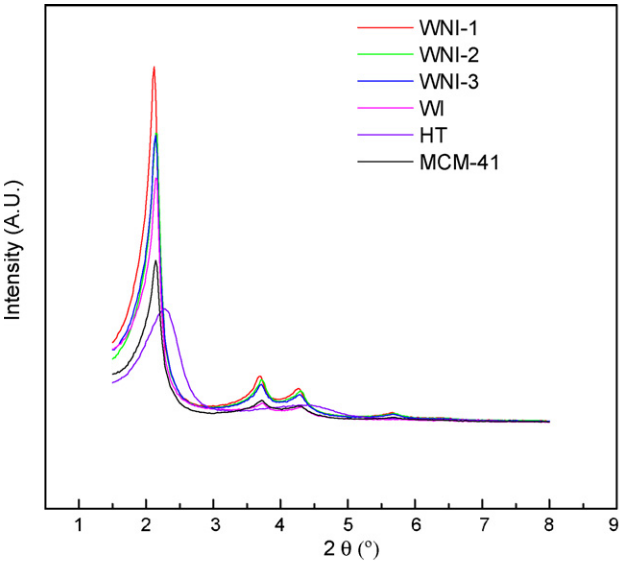


Fig. 1. XRD patterns of the catalysts.

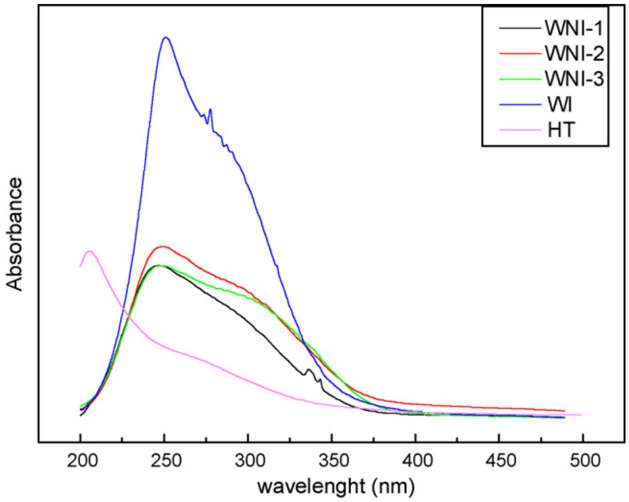


Fig. 2. DRS spectra of the catalysts.

Table 1 shows Ti content (determined by colorimetry) and BET results for all solids. The values of specific surface area are characteristics of mesoporosous MCM-41. A decrease in the specific surface area with the increase of the Ti content is observed for the post-synthesis samples, compared with the support. However, important changes in the pore diameter and wall thickness values were not observed. This would indicate that the Ti species would partially occlude the channels. Sample HT displays channels of equal diameter but with small wall thickness. This result, jointly with the lower structural regularity determined by XRD, would indicate a smaller structural stability of this solid.

Fig. 2 shows DRS spectra of the solids. In HT a strong transition around 205 nm and a shoulder at 258 nm, can be observed. In a previous work [12] the band at 205 nm was assigned to charge transfer transition (CT) from an ion O^{2-} to a Ti^{4+} ion located in the MCM-41 structure (closed sites) and the other band was assigned to open sites generated by the rupture of bridges Si–O–Ti of the closed sites, with the appearance of two OH groups, implying the insertion of a fifth oxygen atom to the first coordination sphere of titanium. The spectra of the samples obtained by wetness and wet impregnation methods are very different compared with HT. Considering that anatase displays a characteristic band centred at 330 nm [19] it would be useful to determine if this species is or not present in order to carry out a more accurate assignement of the titanium species present. With this purpose Raman spectroscopy was used since it is well known that this technique is extremely sensitive to the formation of crystalline TiO_2 anatase particles [20]. The most anatase intense peak (155 cm^{-1}) was not detected in any post-synthetic sample (Fig. 3), therefore, the crystalline TiO_2 (anatase) presence can be discarded. This result is in agreement with that obtained by Gao et al. [20] for TiO_2 supported on amorphous SiO_2. They found trace amount of crystalline anatase when the TiO_2 loading reaches 15%. The jointly use of DRS and Raman techniques allow us to conclude that in post-synthetic samples, Ti^{4+} ions are not located neither in isomorphic substitutional positions of the MCM-41 framework nor in anatase crystallites. In order to assign the possible Ti^{4+} ions locations, we fitted the DRS spectra with three Gaussian curves whose maxima can be observed in Table 2.

Table 1
Textural properties of the solids

Sample	%TiO_2 (w/w)	S_g(m^2/g)	D_p (nm)	WT (nm)
MCM-41	0	1167	2.9	1.9
WNI-1	0.8	969	2.8	2.0
WNI-2	1.8	926	2.9	1.9
WNI-3	2.9	930	2.9	1.9
WI	7.3	816	2.6	2.2
HT	1.8	1104	2.8	1.6

S_g: specific surface area; D_p: pore diameter; WT: wall thickness.

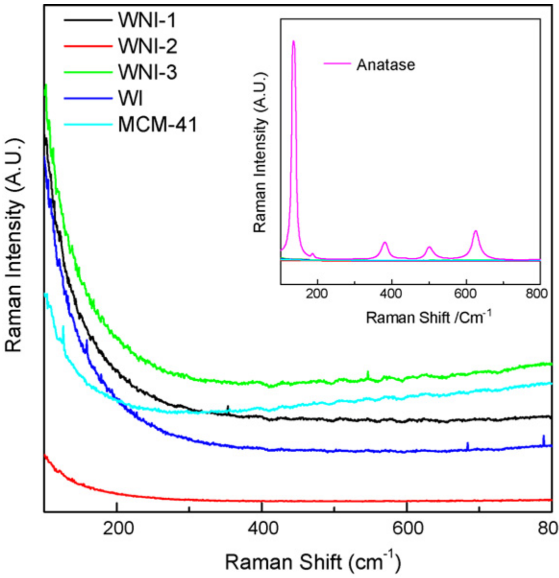


Fig. 3. Raman spectra of the catalysts. The insert shows the pure anatase raman spectrum and the catalysts spectra with the same Raman intensity scale for illustrative purposes.

Table 2
Wavelength maxima and relative areas of the DRS UV–vis spectra fitting

Sample	λ_1(nm)	(%)	λ_2(nm)	(%)	λ_3(nm)	(%)
WNI-1	240	25	269	29	297	46
WNI-2	241	21	263	21	300	58
WNI-3	241	23	265	19	304	58
WI	248	20	278	17	283	63

The fittings were carried out with Gaussian lines.

Gao et al. [20], showed that Ti species in isolated tetrahedrons adsorbed on the pores surface of the SiO_2 support, show a band at 210 nm; dimeric or unidirectional chains of tetrahedrons of TiO_4 generate a band in 246 nm; TiO_5 bidimensional clusters display an absorption at 256 nm and finally TiO_6 clusters absorb at 294 nm. According to this description, the band corresponding to isolated TiO_4 was not observed in our catalysts prepared by wetness or wet impregnation, instead the other three bands could be detected. Comparing the four samples, it can be seen that the Ti coordination increases when the Ti loading increases. Besides, it would be possible to conclude that in all samples the Ti ions are mainly inside small clusters of $(TiO_6)_n$ species, without forming anatase crystals. It is known that the presence of this compound in the catalyst is highly undesirable since it causes the H_2O_2 decomposition, diminishing the efficiency of this one for the oxidation reaction.

3.2. Activity and selectivity measurements

Previous to the activity and selectivity measurements of the catalysts, a blank experiment was carried out mixing the reactants in absence of catalyst. A limonene conversion (χ_L) of 1% was obtained. This value was subtracted in all experiments in order to evaluate only the catalytic behavior. Table 3 shows the values of χ_L, turnover frequency to epoxides (TOF), H_2O_2 conversion (χ_{H2O2}), H_2O_2 efficiency and reaction products distribution for all catalysts after 7 h of reaction. This time was selected since as it can be seen in Fig. 4, between 5 and 7 h of reaction time, all catalysts have reached a value of limonene conversion approximately constant. In each case it was corroborated by mass spectrometry, that the only obtained products are those listed in Table 3. On the other hand, the mass balance was verified making a balance of grams of carbon between the consumed limonene and the obtained products.

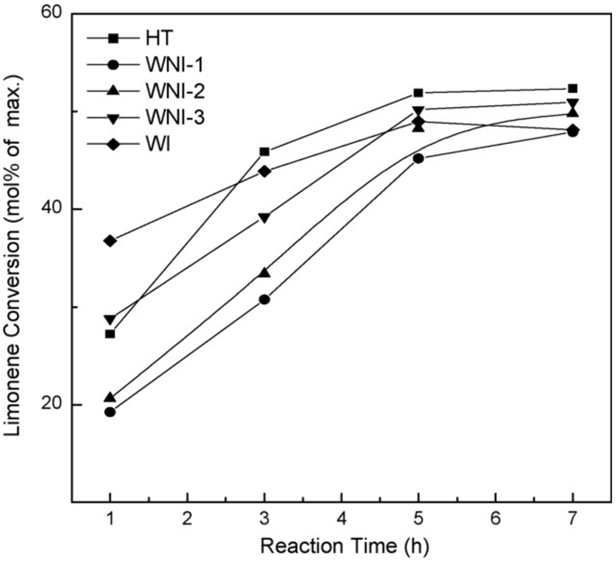


Fig. 4. Limonene conversion (as a percentage of the maximun possible conversion) vs. reaction time for all catalysts. Reaction conditions: $T = 343$ K, 4.32 mmol of limonene (L), 2.7 g of acetonitrile, 1.17 mmoles of H_2O_2 35% w/w and 50 mg of catalyst.

Considering that the limonene is in excess respect to H_2O_2, χ_L was calculated as a percentage of the maximum possible conversion, assuming complete conversion of H_2O_2 to oxygenated products. TOF to epoxides, is defined as the number of epoxides moles obtained by mol of Ti per hour (h^{-1}). It was assumed that all Ti atoms are exposed on the catalysts surface and all of them have the same activity. The H_2O_2 efficiency represents the percentage of this reagent that leads to oxygenated products of limonene. Finally, considering that the only products detected by GC–MS are those shown in Table 3 (no by-products were detected), the selectivity to an "i" product (S_i), is expressed as:

$$S_i = \frac{``i\text{''}\ product \cdot (moles)}{\sum_{i=1}^{n} ``i\text{''}\ product \cdot (moles)} \times 100.$$

Table 3
Activity and selectivity results of limonene epoxidation with H_2O_2 after 7 h of reaction

Catalyst	χ_L (% max.)	TOF (h^{-1})	χ_{H2O2}	Efficiency H_2O_2[a]	Selectivity (mol.%)[b]			
					Epoxides[c]	Carvone + Carveol	Diepoxide	Glycols
WNI-1	48	6.9	68	71	43	32	14	11
WNI-2	50	3.4	74	68	46	34	9	11
WNI-3	51	2.3	79	64	48	33	7	12
WI	48	0.9	81	59	50	31	5	14
HT	52	4.5	80	65	58	22	12	8

Reaction conditions: $T = 343$ K, 4.32 mmol of limonene (L), 2.7 g of acetonitrile, 1.17 mmol of H_2O_2 35% w/w and 50 mg of catalyst. χ_L (% max.): limonene conversion as a percentage of the maximum possible conversion. TOF (h^{-1}): turnover frecuency to epoxides. χ_{H2O2}: conversion of the oxidant determined by iodometric titration.

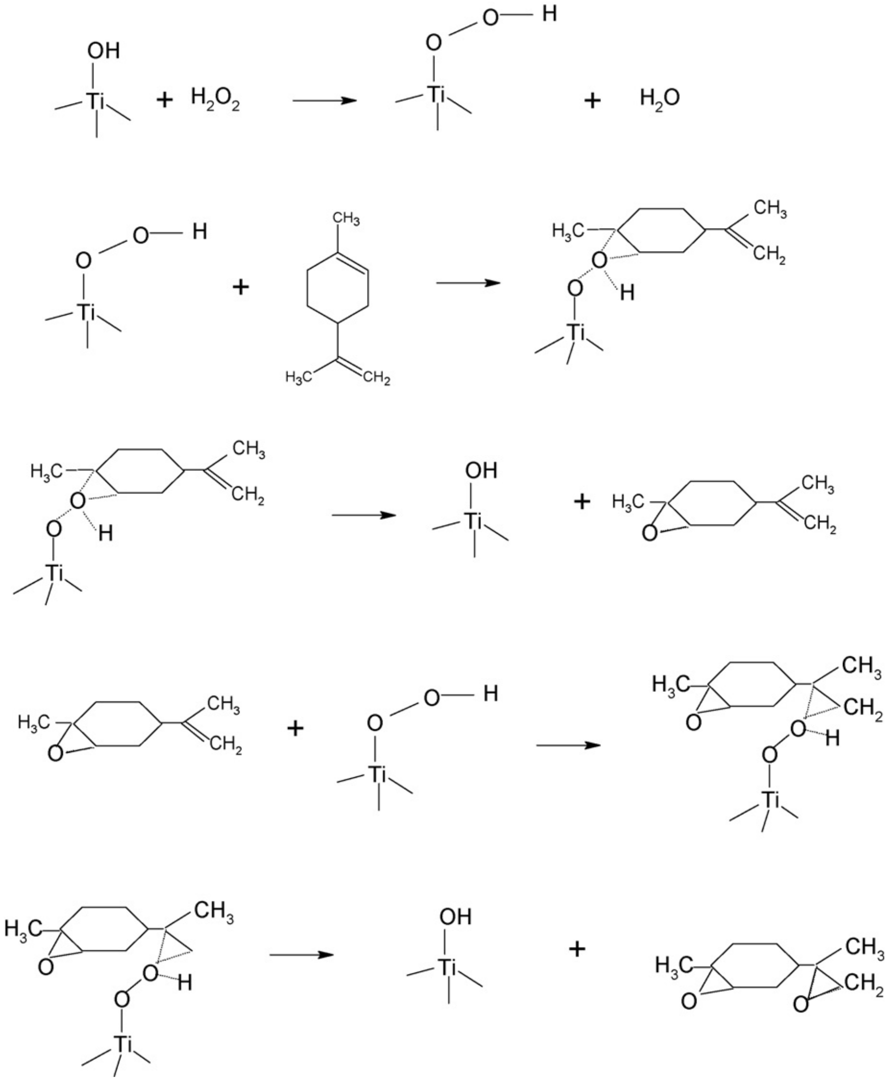
[a] H_2O_2 efficiency, percentage of H_2O_2 consumed to produce oxygenated products.

[b] Expressed as a percentage of the total formed products.

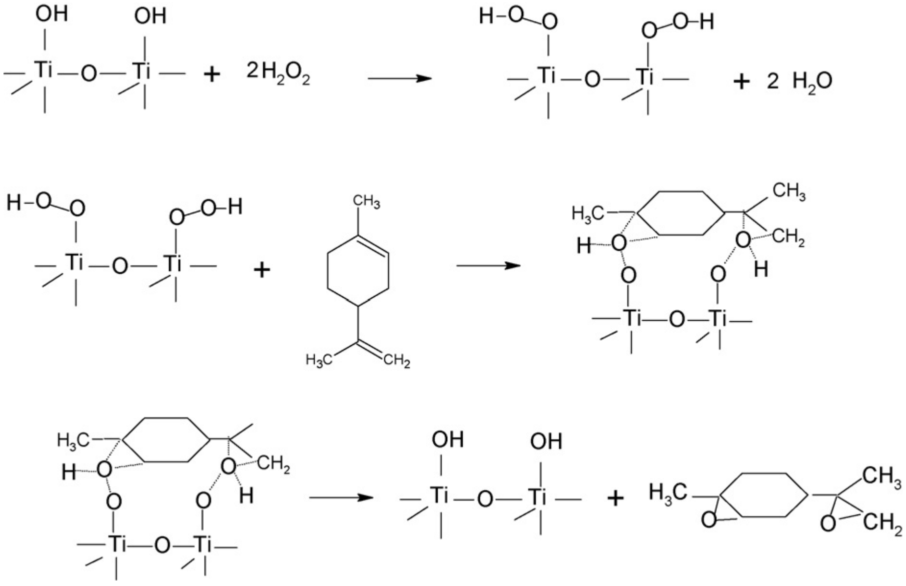
[c] 1,2 and 8,9 epoxylimonene.

The catalysts prepared by post-synthesis treatments show very similar values of limonene conversion. However, the H_2O_2 conversion increases as the content of Ti is increased up to 81% for WI catalyst, whereas the H_2O_2 efficiency follows an inverse relation. Finally, the TOF to epoxides shows an important decrease, about one order of magnitude from WNI-1 to WI. These results can be explained if it is assumed that Ti located in $(TiO_6)_n$ sites is inactive or less active for the selective oxidation of limonene and besides these sites show tendency to decompose the H_2O_2, since the relative population of these sites is the only one that increases from WNI-1 to WI (Table 2). The solid prepared by hydrothermal synthesis, shows values of χ_L, TOF to epoxides, χ_{H2O2} and H_2O_2 efficiency similar to WNI-2 catalyst. Both catalysts have the same Ti content (1.8% w/w). However, HT solid has Ti sites different from the ones of the post-synthetic samples. Therefore, the presence of Ti^{4+} sites replacing Si^{4+} ions in the MCM-41 framework, would not be necessary to produce the catalytic results mentioned above.

When Ti loading increases for post-synthetic samples, the selectivity results show that: the epoxides increase, the diepoxide diminishes and glycols and carvone + carveol remain approximately constant as it can be seen in Table 3. It can be considered that the diepoxide synthesis can follow two ways: a consecutive reaction where, first a double bond is epoxidized and then the other one, or a simultaneous epoxidation of both double bonds. The two mechanisms could occur on Ti^{4+} tetrahedral sites of dimeric or unidirectional chains and/or on pentacoordinated Ti (TiO_5). Besides, the relative population of tetrahedral sites remains nearly constant, whereas the pentacoordinated sites diminish from WNI-1 to WI. Taking into account the above considerations, if diepoxide production would occur on TiO_5 sites following Scheme 1, the epoxide percentage might diminish. However, epoxide percentage increases, therefore, the diepoxidation through Scheme 2 would occur on TiO_5 sites. Consequently, when TiO_5 population decreases, diepoxide production also diminishes.



Scheme 1. Proposed consecutive diepoxidation mechanism.



Scheme 2. Proposed simultaneous diepoxidation mechanism.

The greater selectivity to products of allylic oxidation (carveol and carvone) showed by these catalysts, can be explained by a radicalary mechanism [12], competitive with the formation of an active intermediate, peroxo-metal complex, showed in Schemes 1 and 2. The free-radicals ($OH^{\bullet}$) production would be favoured by Ti species with greater coordination number, TiO_5 and $(TiO_6)_n$ which are absent in HT.

On the other hand, HT catalyst shows the highest selectivity to epoxides and the lowest production of allylic oxidation (carvone + carveol) among all solids tested in this work. This result demonstrates that the isolated tetrahedral sites of Ti^{4+} in framework replacing positions of the MCM-41 are the most selective ones for the limonene epoxidation reaction when H_2O_2 is used as oxidant.

Finally, as it was mentioned above, Ti-MCM-41 can experiment Ti ‘‘leaching’’ when H_2O_2 is used as oxidant leading to a little activity in homogenous catalysis [21]. Bearing in mind that, the Ti^{4+} ions in HT are hardly strained in substitutional positions inside the SiO_2 lattice, the breaking of Ti bond and its extraction by H_2O_2 may be easy. However, in a previous work [12] we found the operative conditions to avoid Ti leaching in HT. In the present work we have used the same reaction conditions for post-synthesis catalysts and Ti leaching was not observed, considering the detection limits of the technique used (ICP). The assays were carried out in the liquid phase after 7 h of reaction for all catalysts. Taking into account that substitutional Ti^{4+} was not detected in post-synthesis catalysts, the Ti leaching absence is an expected result, since in these solids the Ti^{4+} ions are less strained.

4. Conclusions

In the present work different Ti-MCM-41 catalysts were prepared via post-synthesis (wetness and wet impregnation) methods. The solids showed a better long order hexagonal arrangement in comparison with a solid obtained by hydrothermal method. Using DRS and Raman spectroscopy, it was demonstrated that these solids present three types of Ti sites, which are different from that found in HT catalyst. These structural differences do not lead to significant changes in χ_L values, in limonene epoxidation with H_2O_2. However, the selectivity to epoxides appears diminished with an increase in the production of allylic oxygenated (carvone + carveol). These results indicate that the structural characteristics of the Ti^{4+} sites do not influence on the catalyst activity but they are important in order to define the solid selectivity.

Besides, the greater structural quality of post-synthesis mesoporous solids compared with HT, does not produce beneficial effects on the activity and/or selectivity in the limonene epoxidation with H_2O_2.

On the other hand, in the post-synthesis solids, Ti loadings higher than about 2% do not produce a χ_L increase and H_2O_2 efficiency is noticeable lower. Therefore, it is not recommended to surpass this loading. Finally, we think that the epoxide selectivity differences between HT and post-synthesis solids are compensated by the simplicity and reproducibility of the last preparation methodology.

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