Available online at www.sciencedirect.com

SCIENCE DIRECT®

Catalysis Today 107–108 (2005) 397–403

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Ti-MCM-41 silylation: Development of a simple methodology for its estimation
Silylation effect on the activity and selectivity in the limonene oxidation with H_2O_2

María Virginia Cagnoli [a,*], Sandra Graciela Casuscelli [b], Ana María Alvarez [a], José Fernando Bengoa [a], Norma Graciela Gallegos [a], Mónica Elsie Crivello [b], Eduardo Renato Herrero [b], Sergio Gustavo Marchetti [a]

[a] *CINDECA, Fac. Cs. Exactas, Fac. Ingeniería, U.N.L.P., CICBA, CONICET. Calle 47 No 257, 1900 La Plata, Argentina*
[b] *CITeQ, Facultad Regional Córdoba, U.T.N., CC.36, 5016 Córdoba, Argentina*

Available online 18 August 2005

Abstract

Ti-MCM-41 was prepared and characterized. The isomorphical substitution of Si^{4+} by Ti^{4+} and the presence of mesoporous hexagonal structure were verified. The solid was silylated with increasing quantities of hexamethyldisilazane. This process did not change the structural properties of the solid. Using themogravimetric analysis, the optimal quantity of the silylant agent to neutralize the superficial silanols was evaluated. The non-silylated and the silylated solids (with the optimal quantity) were tested in the limonene oxidation with hydrogen peroxide. The silylated solid showed a greater hydrogen peroxide efficiency and a higher activity and selectivity in the limonene epoxidation, compared with the non-silylated one. These effects are attributed to the higher hydrophobic character of the solid surface, produced by the silanols neutralization.

Keywords: Ti-MCM-41; Silylation; Limonene oxidation; Silanols funcionalization

1. Introduction

The Ti incorporation inside the framework of the hexagonal mesoporous solid named MCM-41 was successfully carried out in 1994 for the first time [1,2]. The obtained results showed that this solid was an active catalyst when it was used in the oxidation of big molecules like α-terpineol and nor-bornene using H_2O_2 or *tert*-butyl-hydroperoxide as oxidant agents.

Several authors have found that the Ti ions can be extracted from the MCM-41 structure (leaching) when the catalyst is used with hydrogen peroxide as oxidant agent [3–5]. Besides, these catalysts show a lower activity in the oxidation reactions when H_2O_2 is used instead of *tert*-butyl-hydroperoxide. This behavior has been attributed to the higher hydrophilic character of the mesoporous solid pores. In order to solve this problem, the catalyst silylation was carried out to regulate the hydrophylicity degree. An important improvement in the activity was found, when these solids were used in cyclohexene, hexane and 2-penten-1-ol oxidation with H_2O_2 [6].

Different techniques have been used to evaluate qualitatively the silytation process [7,8]. However, the quantitative determination of the silylation efficiency is important to establish the optimum hydrophobicity/hydrophilicity ratio. Tatsumi et al. [6] have determine the concentration of surface silanol groups by NMR measurements in silylated Ti-MCM-41. On the other hand, Jentys et al. [9] have measured the concentration and type of hydroxyl groups in MCM-41 by adsorption of pyridine followed by IR spectroscopy. Taking into account the above

---

* Corresponding author.
E-mail address: mavic@quimica.unlp.edu.ar (M.V. Cagnoli).

0920-5861/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2005.07.034

description, a sophisticated and/or indirect method is necessary to determine the efficiency of the silylation process.

Considering these results, the aim of the present work is to develop a simple method for the quantitative estimation of the silylation degree of a Ti-MCM-41 catalyst. It was also evaluated the effect that silylation produces on the activity and the selectivity in the limonene oxidation reaction with hydrogen peroxide. Terpenes are widely distributed in nature and their epoxides often serve as starting materials for the synthesis of fragrances, flavors and therapeutically active substances [10]. In this way, one can design the required product by taking advantage of the highly reactive oxirane ring (epoxides) and choosing the right conditions to promote reactions, such as isomerization, condensation and nucleophilic substitution [11]. One of these terpenes is the limonene, extracted from citrus oil. The limonene oxidation is interesting because it contains an internal tri-substituted and an isolated terminal C=C bond that afford the 8,9-epoxide and/or 1,2-epoxide, respectively. Both are high added values products obtained from a reactant of relatively low cost.

2. Experimental

The Ti-MCM-41 catalyst (named Sil0), with 1.8% (w/w) of Ti content (expressed as TiO_2 and determined by inductive-coupled plasma (ICP)), was obtained following the methodology described in Ref. [12], schematized in Fig. 1.

The solid was characterized by X-ray diffraction (XRD) in a low angles range, using Cu Kα radiation, diffuse reflectance spectroscopy (DRS) in the UV–vis range, specific surface area and pores radii distribution by N_2 adsorption (BET), thermogravimetric analysis (TGA) and infrared spectroscopy (IR).

The silylation with hexamethyl-disilazane (HMDS) in toluene was carried out following the methodology schematized in Fig. 2.

Five silylations with 2, 1, 0.5, 0.2 and 0.08 ml of HMDS (9.48, 4.74, 2.37, 0.95 and 0.38 mmol, respectively) were performed. The obtained solids were called: Sil2, Sil1, Sil05, Sil02 and Sil008, respectively. They were characterized by XRD, BET, IR and TGA.

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), 65.85 mmol 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 [13]. Samples at different reaction times were obtained through a lateral tube of the reactor and were analyzed by GC using a capillary column (cross-linked methyl-silicone gum, 30 m × 0.53

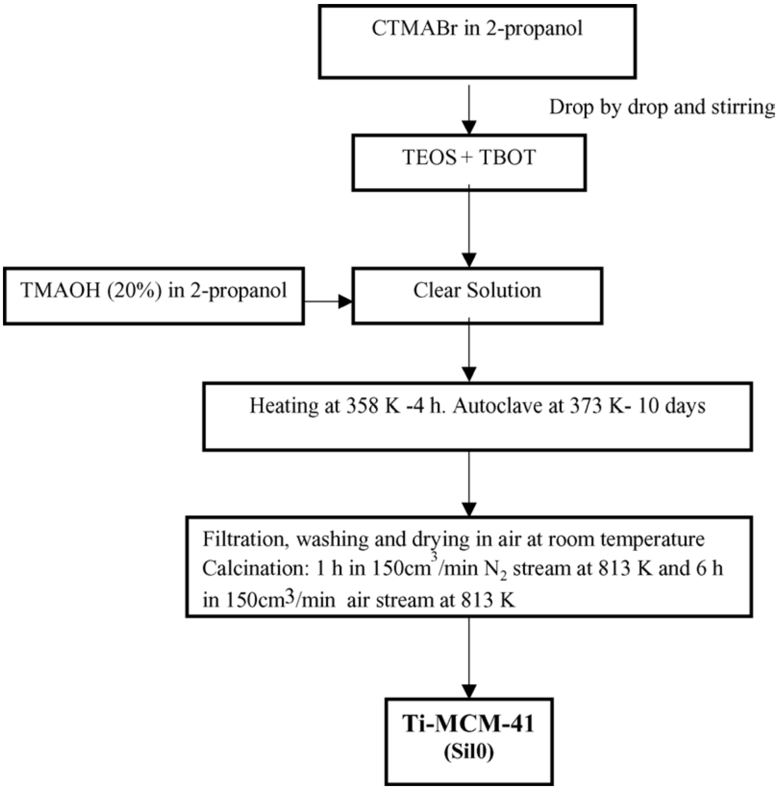

Fig. 1. Ti-MCM-41 synthesis scheme (CTMABr: cethylthrimethyl ammonium bromide, TEOS: tetraethylorthosilicate, TBOT: titanium tetrabutoxide, TMAOH: tetramethylamonium hydroxide).

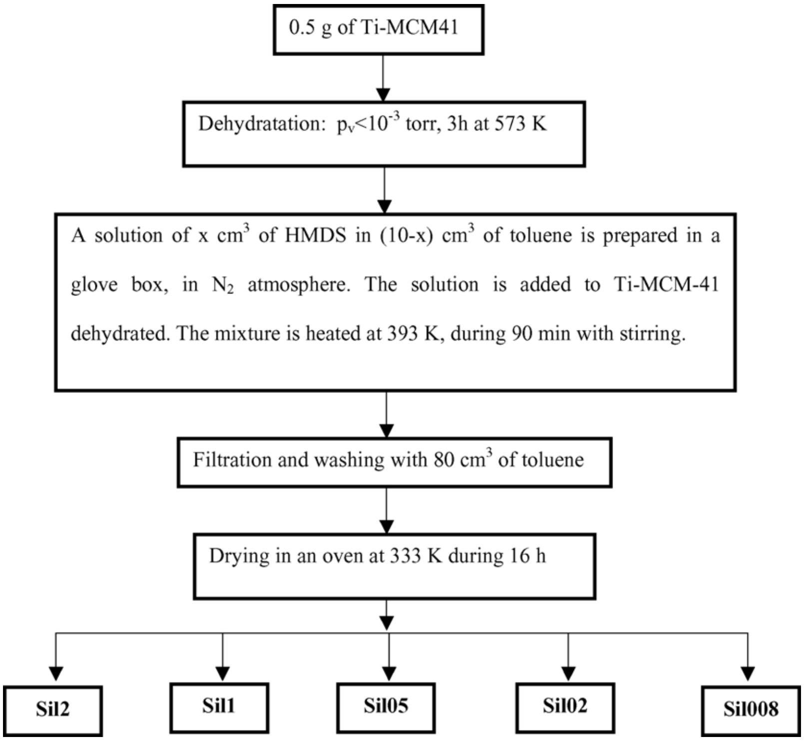

Fig. 2. Silylation procedure scheme.

mm × 2.65 μm film thickness). Reaction products were identified by GC–MS with FID detector. The H_2O_2 conversion was measured by iodometric titration. The limonene conversion (mol% of max) was calculated as the ratio of limonene conversion to theoretically possible conversion that is the maximum amount of the oxygenated products that could be obtained if all $H_2O_2$was became product. The selectivity is expressed as (product *i* (moles)/$\sum$ product *i* (moles)) × 100.

3. Results

3.1. Characterization of non-silylated sample (Sil0)

The X-ray diffraction pattern of Sil0 (Fig. 3), shows an intense peak at $2\theta = 2.3^\circ$ and a broad and less intense peak at $2\theta = 4.4^\circ$. This diagram is characteristic of a material with a hexagonal ordering [12]. However, the presence of only one broad peak between 2° and 7° implies a decrease of the spatial regularity compared with that typical structure of MCM-41.

The BET results are also typical of Ti-MCM-41 and they are shown in Table 1.

Fig. 4 displays the DRS spectrum of the Sil0 sample. There is a strong transition around 205 nm and a shoulder at about 258 nm. The spectrum was fitted using two Lorentzian functions. The parameters (position, full line-width at half-height and area) were not held fixed in fitting. These bands were assigned to charge transfer transition (CT) from O^{2-} ion to a Ti^{4+} ion ($O^{2-} \rightarrow Ti^{4+}$) located in the MCM-41 structure like in TS-1 system. This comparison is possible, since in both solids some of the Si^{4+} ions of silica framework have been substituted by Ti^{4+} ions. According with Lamberti et al. [14] we have demonstrated [15] the existence of two different framework Ti^{4+} sites in the TS-1: perfect ‘‘closed’’ and defective ‘‘open’’ sites. The ‘‘closed’’ sites structure can be expressed by $Ti(OSi)_4$, while the ‘‘open’’ sites are generated by the rupture of a Si–O–Ti bridge of a ‘‘closed’’ site with the appearance of two OH groups, implying the

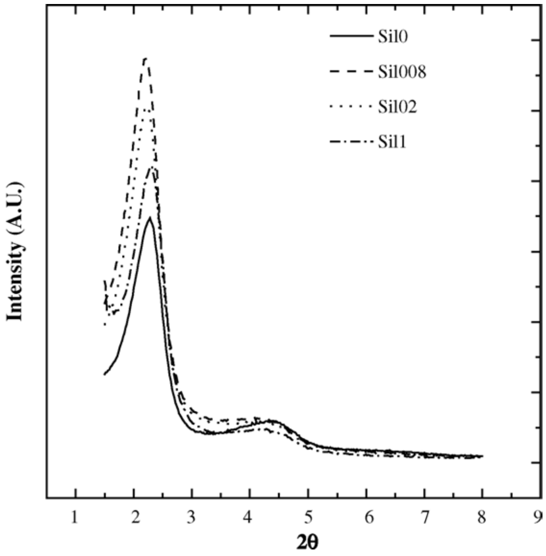

Fig. 3. XRD patterns of the samples.

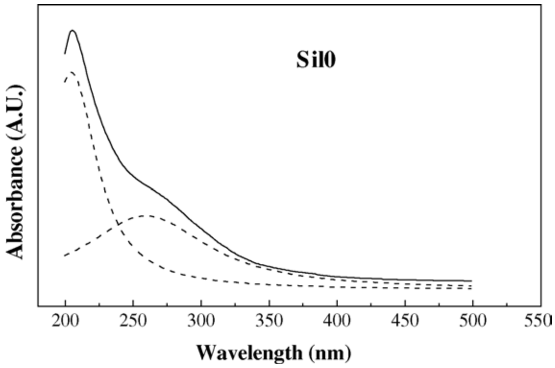

Fig. 4. DRS spectrum of Sil0.

insertion of a fifth oxygen atom in the first coordination sphere of Ti. Rhee and Lee [16] also have demonstrated that Ti replaces Si in the MCM-41 framework and its coordination environment was similar to that of TS-1. In this way, the 205 nm band was assigned to ‘‘closed’’ sites and the 258 nm band to ‘‘open’’ sites. It is important to remark the anatase absence in the solid since there is no band at 330 nm [17]. Its presence would produce the H_2O_2 decomposition decreasing the oxidant amount in the reaction environment.

The IR spectrum of Sil0 (Fig. 5) shows the presence of a band at about 960 cm^{-1} characteristic of materials containing Si, in which some Si^{4+} ions are substituted by Ti^{4+} ions [1].

The TGA analysis of the solid (Figs. 6 and 7) showed a weight loss in two steps. The first one between 303 and 373 K assigned to the surface water molecules elimination, and the second one between 523 and 623 K corresponding to the irreversible loss of water associated to the silanol groups.

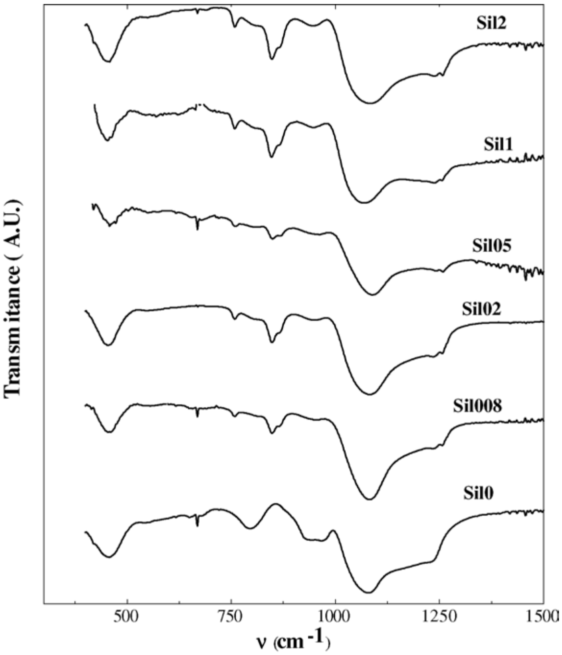

Fig. 5. IR spectra of the samples.

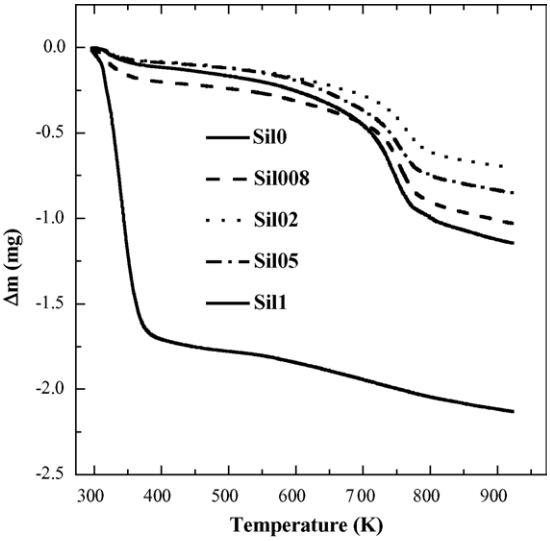

Fig. 6. TGA diagrams of the samples.

The solid dehydroxylation is not significant in this system since the water elimination by this process represents only 2% of the total water loss.

3.2. Characterization of the silylated samples

The XRD patterns of the silylated samples (Fig. 3) indicate that the ordered hexagonal mesoporous structure has not been modified during the silylation procedure.

Table 1 shows the BET results of the silylated samples. It can be seen a slight decrease of the specific surface areas and the pore diameters. However, a narrow unimodal distribution of channels has been maintained.

The IR spectra of the silylated samples (Fig. 5) display the appearance of new bands indicating that the silylation process has taken place appropriately. In this way, the new bands present increasing intensities with the increase of the

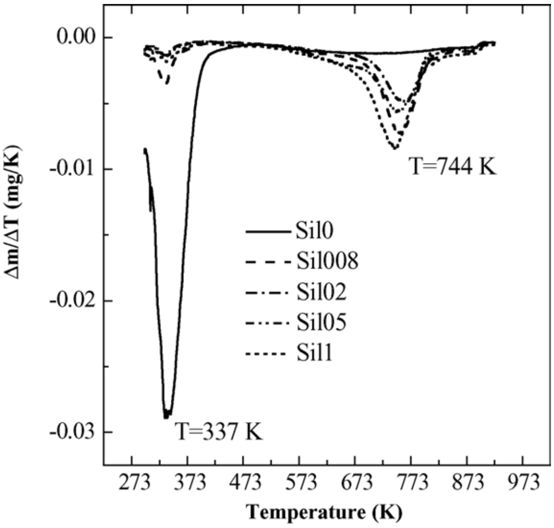

Fig. 7. Derivative curves of TGA diagrams of the samples.

Table 1
Textural properties of the solids

Sample	S_g (m^2/g)	D_p (nm)
Sil0	1104	2.8
Sil008	893	2.2
Sil02	854	2.2
Sil05	994	2.4
Sil2	994	2.3

S_g: specific surface area; D_p: pore diameter.

incorporated silylant agent. These bands were assigned to: Si–C bond "stretching" at 750 cm^{-1}, CH_3 groups "rocking" at 870 cm^{-1} and Si–CH_3 bond "stretching" at 1260 cm^{-1} [18].

3.3. Quantitative analysis of silylation process

The characterization results allow us to conclude that the silylation process has effectively occurred preserving the Ti-MCM-41 structure. Therefore, it becomes necessary to determine the quantity of silylant agent that has reacted with the surface. Then, the minimum concentration of silylant reactive to neutralize the total superficial silanol groups can be obtained.

With this purpose, the TGA of the samples after silylation were carried out in 20 cm^3/min of air stream, heating from room temperature up to 923 K, at a heating rate of 10 K/min. Fig. 6 shows the TGA results and in Fig. 7, the corresponding derivative curves can be observed.

The Sil0 sample has lost a 12.27% of weight, corresponding to the water loss, while the silylated samples lose a little quantity of water. This behavior indicates a poor capacity for water adsorption in the last ones. Besides, a temperature shift to lower values than 337 K, at the highest water loss rate, can be observed. This implies that the silylated samples present a weak adsorption capacity of water. On the other hand, these samples show other peak at 744 K assigned to the organic material "burnt".

In Fig. 8, the quantity of water loss and the amount of organic material "burnt" are represented as a function of the quantity of silylant agent added. It can be seen that a value between 0.08 and 0.2 ml of HMDS seems to be enough for the total surface silylation of the 500 mg of Ti-MCM-41. For greater quantities of HMDS, the water eliminated and the organic material "burnt" remained constant.

In Sil0, the amount of weight loss is not zero at 744 K, but that is attributed to the dehydroxylation above mentioned and not to the organic material loss.

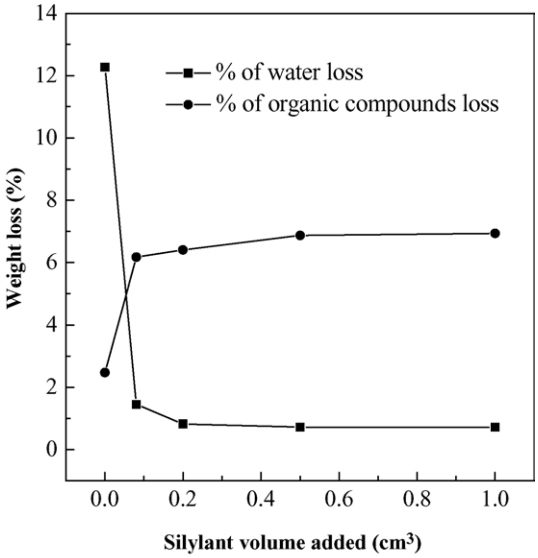

Fig. 8. Water and organic material loss vs. silylant agent amount.

Comparing Sil008 and Sil1, an increase of 92% of silylant mass was used, however the difference of organic material loss in "burnt" is of only 11%. Therefore, the silylant excess was eliminated in the washing step.

The reaction between the Ti-MCM-41 silanol groups with HMDS produce NH_3 according to the scheme shown in Fig. 9. During the TGA analysis, the methyl groups are "burnt" at 744 K (Fig. 7). In order to estimate the silylation percentage we propose a possible Ti-MCM-41 "burnt" mechanism (Fig. 10). From this model, when 1 HMDS mol is "burnt", a weight loss of 24 g might be produced. Analyzing the weight loss of samples with the lower and the highest silylant agent content: Sil1 and Sil008, and bearing in mind that: (a) one three-methyl-silyle group occupies 0.476 nm^2 surface [19] and (b) that for each HMDS molecule two $SiMe_3$ groups are fixed, in Sil1, 1656 m^2/g of surface area would be covered and in Sil008, 1474 m^2/g. Comparing these results with the S_g of Sil0 (Table 1), the proposed "burnt" mechanism seems to be reasonable. It can be note that the silylant agent amount added in Sil008 is enough to cover the total surface area.

Assuming that 0.08 ml of HMDS (0.38 mmol/500 mg of solid) is the enough quantity to neutralize the total silanol groups, from the silylation stoichiometry, a value of 1.5 mmol of OH^-/g was obtained. This result is comparable with that obtained by Jentys et al. [9] of 0.8 mmol of OH^-/g

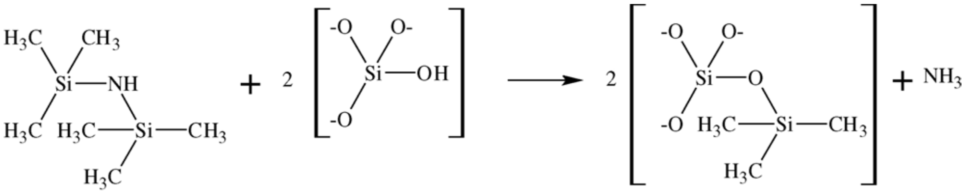

Fig. 9. Silylation scheme with HMDS.

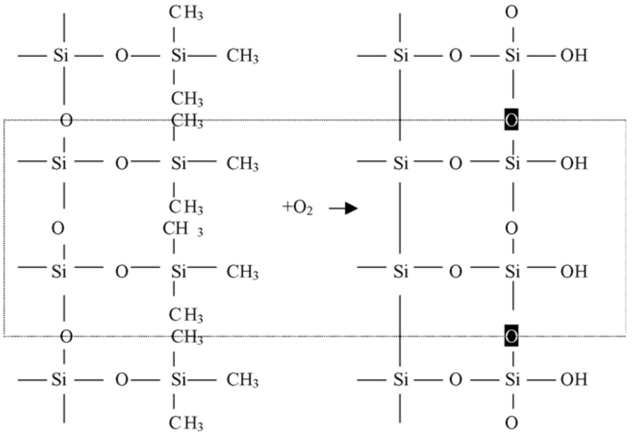

Fig. 10. Schematic representation of the silylated Ti-MCM-41 " burnt". From the two oxygens marked, in black, in the scheme, it was considered half of each one for the weight loss calculus.

for MCM-41. The difference can be attributed to the Ti^{4+} presence in our samples that would produce a different hydroxyls concentration at the surface. Notwithstanding, both values are in the same order.

3.4. Activity and selectivity measurements

The catalytic activity experiments were carried out using Sil0 and Sil008. A blank experiment was carried out mixing the reactants in absence of catalyst. A limonene conversion of 1% was obtained. This value was subtracted in all experiments, in order to evaluate only the catalyst behavior.

Tables 2 and 3 show the activity and product distribution, obtained from the catalytic analysis of the reaction with Sil0 and Sil008 at different reaction times. It can be seen that Sil008 is about 50% more active. It is important to note that, although the difference of selectivities towards to epoxides (1,2 and 8,9 epoxy-limonene) between both catalysts is small along the reaction time, Sil0 shows a tendency to decrease this selectivity when the limonene conversion increases. Instead, in Sil008 the selectivity remains nearly constant (Fig. 11). Consequently, the yield (conversion × selectivity) to epoxilimonene is notably increased by silylation (about 75% at 7 h). Carvone, carveol and the corresponding diepoxi product were also obtained, but in low concentration.

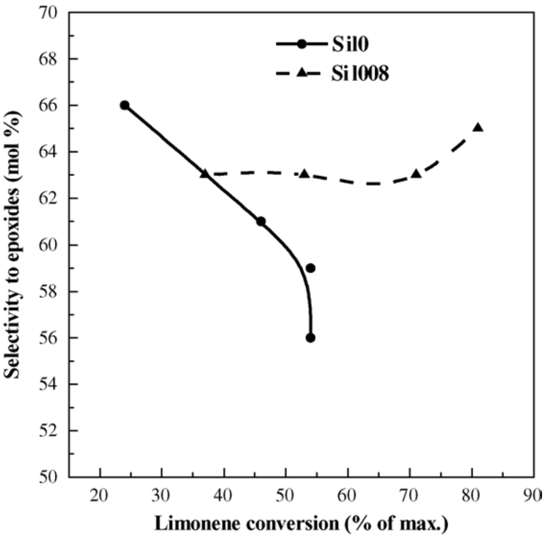

Fig. 11. Selectivity towards epoxides vs. limonene conversion.

Table 2
Activity and selectivity results for Sil0

t (h)	Conversion			Selectivity (mol%)[a]				
	% of máx.	H_2O_2[b]	H_2O_2[c]	Epoxide[d]	Carvone	Carveol	Diepoxi	Glycols
1	24	46	53	66	10	8	9	7
3	46	64	72	61	12	11	10	6
5	54	69	78	59	10	10	14	7
7	54	71	75	56	12	10	14	8

[a] Expressed as a percentage of the total formed products.
[b] Conversion of the oxidant determined by iodometric titration.
[c] Efficiency of the oxidant determined by iodometric titration.
[d] 1,2 and 8,9 epoxylimonene.

Table 3
Activity and selectivity results for Sil008

t (h)	Conversion			Selectivity (mol%)[a]				
	% of máx.	H_2O_2[b]	H_2O_2[c]	Epoxide[d]	Carvone	Carveol	Diepoxi	Glycols
1	37	40	92	63	13	9	10	5
3	53	65	82	63	12	10	10	5
5	71	78	91	63	12	10	10	5
7	81	82	98	65	13	9	8	5

[a] Expressed as a percentage of the total formed products.
[b] Conversion of the oxidant determined by iodometric titration.
[c] Efficiency of the oxidant determined by iodometric titration.
[d] 1,2 and 8,9 epoxylimonene.

The silanol groups neutralization turns the surface more hydrophobic. Therefore, the hydroperoxide is consumed in the oxidation reaction more efficiently in Sil008 than in Sil0. Besides, the greater selectivity to epoxides of Sil008 is also due to the lower free silanol groups number at the surface. This avoids the opening of the oxirane rings that generates glycols, decreasing the selectivity and deactivating the catalyst.

4. Conclusions

The Ti-MCM-41 silylation can be carried out without loss of the structural properties of the mesoporous solid, decreasing the hydrophilic character of its channels.

In this paper, it has been developed a simple method based on TGA experiments to evaluate the necessary amount of silylant agent to neutralize the total silanol groups belonging to the original Ti-MCM-41.

The silylated catalyst presents a higher efficiency in the hydroperoxide use and a higher activity in limonene epoxidation reaction compared with the catalyst without treatment. Besides, this catalyst shows a tendency to lose selectivity towards epoxides when the limonene conversion increases. The silylation avoids this problem. These positive effects are attributed to the higher hydrophobic character due to the lower concentration of silanol groups at the surface.

The results obtained show that this kind of synthesized material can be successfully used in the epoxidation of ‘‘bulky’’ olefins molecules using hydroperoxide as oxidant agent.

Acknowledgments

The authors acknowledge the support for this work to the Consejo Nacional de Investigaciones Científicas y Técnicas, Comisión de Investigaciones Científicas de la Provincia de Buenos Aires, Universidad Nacional de La Plata and Universidad Tecnológica Nacional, Facultad Regional Córdoba and Agencia Nacional de Promoción Científica y Tecnológica (PICT N°14-08456).

References

[1] A. Corma, M.T. Navarro, J. Pérez-Pariente, J. Chem. Soc. Chem. Commun. (1994) 147.
[2] A. Corma, M.T. Navarro, J. Pérez-Pariente, Stud. Surf. Sci. Catal. 84 (1994) 69.
[3] A. Corma, Top. Catal. 4 (1997) 249.
[4] L.Y. Chen, J.A. Chuah, S. Jaenicke, Catal. Lett. 50 (1998) 107.
[5] R.A. Sheldon, Stud. Surf. Sci. Catal. 110 (1997) 151.
[6] T. Tatsumi, K.A. Koyano, N. Igarashi, Chem. Commun. (1998) 325.
[7] M.B. D'Amore, S. Schwarz, Chem. Commun. (1999) 121.
[8] M.L. Peña, V. Dellarocca, F. Rey, A. Corma, S. Coluccia, L. Marchese, Micropor. Mesopor. Mater. 44–45 (2001) 345.
[9] A. Jentys, K. Kleestorfer, H. Vinek, Micropor. Mesopor. Mater. 27 (1999) 321.
[10] K. Bauer, D. Garbe, H. Surburg, Common Fragance and Flavor Materials: Preparation, Properties and Uses, Wiley, New York, 1997
[11] M. Sasidharan, P. Wu, T. Tatsumi, J. Catal. 209 (2002) 260.
[12] K.A. Koyano, T. Tatsumi, Micropor. Mater. 10 (1997) 259.
[13] M.V. Cagnoli, S.G. Casuscelli, A.M. Alvarez, J.F. Bengoa, N.G. Gallegos, M.E. Crivello, C.F. Pérez, E.R. Herrero, S.G. Marchetti, Appl. Catal. A: Gen. 287 (2005) 227.
[14] C. Lamberti, S. Bordiga, D. Arduino, A. Zechina, F. Geobaldo, G. Spanó, F. Genoni, G. Petrini, A. Carati, F. Villain, G. Vlaic, J. Phys. Chem. B 102 (1998) 6382.
[15] N.G. Gallegos, A.M. Alvarez, J.F. Bengoa, M.V. Cagnoli, S.G. Marchetti, A.A. Yeramian, Stud. Surf. Sci. Catal. 135 (2001) 349.
[16] C.H. Rhee, J.S. Lee, Catal. Today 38 (1997) 213.
[17] P. Wu, T. Tatsumi, T. Komatsu, T.P. Yashima, J. Phys. Chem. B 105 (2001) 2897.
[18] C. Beck, T. Mallat, T. Bürgi, A. Barker, J. Catal. 204 (2001) 428.
[19] A. Corma, M. Domine, J.A. Gaona, J.L. Jordá, M.T. Navarro, F. Rey, J. Pérez-Pariente, J. Tsuji, B. McCulloch, L.T. Nemeth, Chem. Comm. (1998) 2211.