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Synthesis of TiSBA-15 with low HCl content as catalysts in cyclohexene epoxidation

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ABSTRACT

A series of TiSBA-15 mesoporous materials were synthesised by hydrothermal and wet impregnation method at low HCl content (pH 1.5) (Si/Ti 15 and 30). The calcined samples were characterized by N_2 adsorption, FT-IR, DRX, SEM and elementary chemical analysis by atomic absorption. The Ti-containing mesoporous materials showed good textural properties even for load of titanium up to 12% (w/w). FT-IR spectroscopy and elemental analysis provided that it is possible to know the amount of Ti (IV) incorporated into the SBA-15 framework. On our synthesis conditions a limit of 4% (w/w) was found. The catalysts were evaluated in the cyclohexene epoxidation with TBHP (tert-butyl hydroperoxide) as oxidant agent; the selectivity toward cyclohexene epoxide was 100%, and conversion was 50–70% depending on synthesis procedure. It is possible that part of the catalytic response is due to the chemical nature and reactivity of the Ti sources employed. The catalysts obtained by impregnation were more active than that obtained by hydrothermal synthesis for same load of titanium; we cannot discard that non-crystalline TiO_2 species co-exist with Ti (IV) isolated and contribute to catalytic activity.

1. Introduction

An important aspect in the development of new materials for application in large-scale catalytic processes is the control of the wastewaters generated during the synthesis of catalysts. Accordingly, successful efforts have been made aimed at obtaining silicate SBA-15 at less acidic pH conditions than usual [1,2]. The mesoporous molecular sieve SBA-15 [3] is usually synthesised on strongly acidic conditions (pH 0), which leads to high waste of mineral acids during processing. Due to their textural properties, high hydrothermal stability and well-ordered pore structure, the SBA-15 type materials prove to be interesting to incorporate metal ions with redox properties such as titanium, in order to be used as catalysts in selective oxidation reactions. The synthesis of mesoporous Ti-silicates began with Ti-MCM-41 [4], then Ti-HMS [5] and more recently Ti-SBA-15 [6–8], and it is carried out by inserting a titanium source during the hydrothermal synthesis of SBA-15 silicate, or by post-synthesis procedures. Recently [9], it was proposed the hydrothermal synthesis of Ti-doped mesoporous SBA-15 using ammonium fluoride to catalyze the hydrolysis and condensation of the silica precursor at low HCl content, however, the use of fluoride salts adds other pollutant (F^-) on the synthesis procedure; this is an important aspect to consider when a large-scale process is devised.

Selective oxidation reactions are central to many chemical processes on an industrial scale; epoxidation reagents require high oxygen content, preferably low-pollution such as hydro peroxides, using metal species that serve as a catalyst. With titanium species as catalyst, the epoxidation reaction takes place usually via peroxo intermediate, and it was established that the most active catalysts are those containing Ti (IV) isolated sites and accessible to substrate [10,11]. However, other authors show that dimers or nano clusters of Ti–O–Ti are catalytically active for epoxidation reactions [12,13], and that some factors such as accessibility to Ti species and particle size can influence the catalytic performance [6].

In this study we evaluated the catalytic behaviour of TiSBA-15 type solids obtained by hydrothermal synthesis at pH 1.5 and by wet impregnation of SBA-15 silica on the oxidation reaction of cyclohexene using TBHP as oxidant, in order to study the physicochemical properties of the synthesised materials and the effect that the preparation method has on the catalytic activity.

2. Experimental

For the hydrothermal synthesis of Ti-silicates, gels with two HCl content were prepared. The procedure followed in one case was as follows (based on the method reported by Zhao et al. [3] for purely siliceous SBA-15): surfactant TCP (Pluronic P-123 from Aldrich) was dissolved in distilled water and HCl (37% Merck) at 313 K (pH 0) with vigorous magnetic stirring. Tetraethoxysilane was added (TEOS 98%, Aldrich) as silicon source. After 1 h, titanium ethoxide

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(Eto) or isopropyl orthotitanate (Iso) (titanium sources) dissolved in ethanol to homogenize the organic and aqueous phases, were added dropwise to obtain gels with Si/Ti 15 y 30 ratios. The composition of the gel was: 1 SiO_2: 6 HCl: 0.0017 P123: x TiO_2: 144 H_2O, where x represents the amount of Ti in each case. The mixture remained stirring and heating for 48 h. After the hydrothermal treatment the solid product was filtered, washed with distilled water and dried for 12 h at 343 K. Calcinations were carried out at 793 K for 8 h under air flux with rate of 1 K/min in order to remove the surfactant. In other series, the P-123 surfactant was dissolved in distilled water and adjusting the pH at 1.5 with 3 M HCl solution at room temperature under magnetic stirring overnight, then adjusted the temperature to 313 K and remains under stirring for 48 h. The addition of silicon and titanium sources, as well as solid recovery treatments was similar to those used for the synthesis at pH 0. The composition of the synthesis gel was: 1 SiO_2: 0.06 HCl: 0.017 P123: x TiO_2: 74 H_2O. The procedure for impregnated materials (Ti/SBA-15) consisted of placing the calcined SBA-15 (following the procedure used for the hydrothermal synthesis without titanium) in a 25 mL flask to which a solution of Ti source in ethanol is added at the desired concentration in order to obtain Si/Ti 15 and 30. The mixture is placed in a rotary evaporator at 323 K under continuous stirring for 8 h and dried at 343 K for 12 h. The dry solid was calcined under air flux at 793 K for 8 h.

X-ray powder diffraction (XRD) patterns were collected on a Phillips diffractometer (Cu kα radiation). The silicon and titanium contents were obtained by atomic absorption in a Perkin–Elmer 2100. N_2 adsorption–desorption isotherms were measured at 77 K on a Micromeritic TriStar 3000 (previous degassing of the samples was performed at 593 K for 12 h). The specific surface area was calculated based on the BET model. Fourier transform infrared spectroscopy (FT-IR) in a Thermo Nicolet Omnic spectrometer, 1% sample wafers in dry KBr were prepared. Scanning electron microscopy (SEM) in a Phillips XL 30 was used to study the morphology and Ti location on the surface samples by energy-dispersive X-ray spectroscopy (EDX).

The oxidation reactions were carried out using tert-butyl hydroperoxide (TBHP 5 M in decane) as oxidant agent in a system at atmospheric pressure with magnetic stirring and a reflux condenser. The reaction flask immersed in a thermostatic bath containing 3 mL of cyclohexene, 5 mL of acetonitrile as solvent and 0.3 g of catalyst dried overnight, leading to reaction temperature (348 K) under stirring. In all cases the ratio oxidant to substrate (molar) was 1:2. Continually N_2 flow 15 mL/min through the reaction system to prevent the participation of O_2 from the air as oxidant. Samples were taken from the reaction mixture for 5 h and filtered before being analysed on a gas chromatograph Hewlett Packard model 5890 with FID detector, using N_2 as carrier gas. The identification of reaction products was carried out using known standards. The cyclohexene conversion was defined as cyclohexene conversion × 100/theoretically possible conversion (maximum amount of the oxygenated products that could be obtained if all TBHP was consumed).

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of calcined SBA-15 silicates. It is possible to observe an intense peak in $2\theta \sim 1^\circ$ and two less intense peaks in $2\theta = 1.5–3.5^\circ$, these patterns are characteristics of the hexagonal array of SBA-15. Note a shift in the position of the first diffraction peak for the solid synthesised at pH 1.5 (SBA-$15_{1.5}$) to lower diffraction angles with respect to synthesised at pH 0 (SBA-15_0). The unit cell parameter, assuming a hexagonal symmetry ($a_0 = 2d_{100}/\sqrt{3}$) was 9.58 nm for SBA-15_0 and 9.93 nm for SBA-$15_{1.5}$, that indicates there is a lattice expansion by varying the HCl content in synthesis gel. The XRD patterns obtained for Ti-SBA-15 and Ti/SBA-15 showed no significant changes compared to those obtained for pure silica. On the range 4–60° 2θ the samples presented a wide line at $2\theta = 22^\circ$ characteristic for amorphous silica, the diffraction peaks corresponding to TiO_2 phase were not observed in Ti-silicates samples (shown in supplementary material).

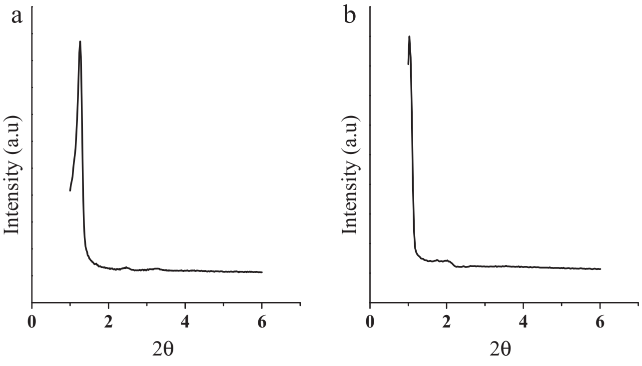

Fig. 1. X-ray diffraction patterns of SBA-15_0 (a) and SBA-$15_{1.5}$ (b).

The SBA-15 silicates exhibit a type IV isotherm, according to IUPAC classification. An increase of the adsorbed N_2 volume occurs at a relative pressure $P/P_0 \approx 0.6$ (Fig. 2). The sharpness of hysteresis indicates the uniformity of mesopores for both samples. The mesopores size distribution for SBA-$15_{1.5}$ is wider than the corresponding to SBA-15_0. The mesopore diameter measured by BJH method was 4.1 nm for SBA-15_0 and 4.9 nm for SBA-$15_{1.5}$ (as shown in the size mesopores distribution inserted in Fig. 2). The textural properties of SBA-15 and TiSBA-15 materials are summarized in Table 1. On SBA-15 materials may be noted that decreasing the amount of acid (pH 0 to 1.5), the specific surface area (S) remains around 700 m^2/g and microporosity in the silica wall increased for SBA-$15_{1.5}$ compared to the SBA-15_0 sample. Considering the structural and textural characteristics of the SBA-$15_{1.5}$, the synthesis procedure with low HCl content is proposed as alternative to reduce the volume of contaminating waste generated in the production of SBA-15 type silicate.

For Ti-SBA-15 materials, the analysis of textural properties in general, shows that there is a reduction on specific surface area, a decrease of microporosity and an increase in the mean pore diameter compared to SBA-15, as a consequence of the incorporation of Ti in the silica framework. Isomorphic substitution of Si by Ti atoms

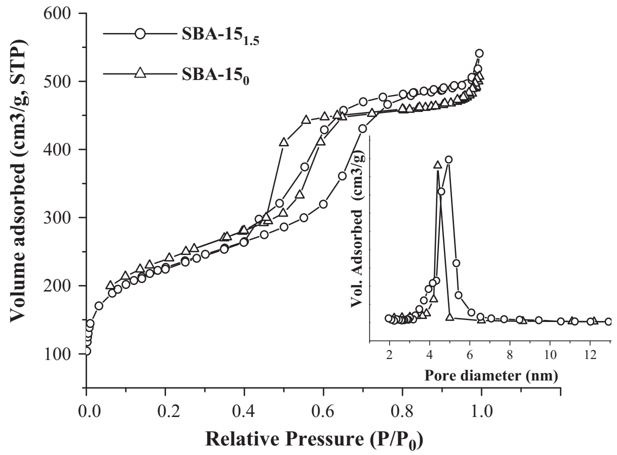

Fig. 2. Nitrogen adsorption/desorption isotherms and mesopore size distribution (BJH) for SBA-15_0 and SBA-$15_{1.5}$.

Table 1
Physico-chemical properties of the calcined samples.

Sample	pH	% Ti	Si/Ti[a]	$S_{(BET)}$[b] (m^2/g)	$Dp_{(BET)}$[c] (nm)	Vp[d] (cm^3/g)	Vμp[e] (cm^3/g)
SBA-15_0	0	0	∞	737	4.1	0.935	0.115
SBA-$15_{1.5}$	1.5	0	∞	772	4.3	0.828	0.149
Ti-SBA-15 (Eto)	1.5	6.9	30	537	4.6	0.572	0.056
Ti-SBA-15 (Eto)	0	0.2	30	694	4.8	0.564	0.063
Ti-SBA-15 (Iso)	1.5	2.0	30	548	4.6	0.576	0.067
Ti-SBA-15 (Iso)	0	0.9	30	670	4.7	0.560	0.068
Ti-SBA-15 (Eto)	1.5	12	15	726	4.6	0.518	0.057
Ti-SBA-15 (Iso)	1.5	11	15	716	4.4	0.456	0.038
Ti/SBA-15 (Iso)	1.5	11	15	617	4.5	0.464	0.069
Ti/SBA-15 (Eto)	1.5	11	15	553	3.5	0.458	0.046
Ti/SBA-15(Iso)	1.5	6	30	713	4.6	0.701	0.134
Ti/SBA-15 (Eto)	1.5	6	30	682	3.8	0.631	0.108

[a] Si/Ti nominal.
[b] S = Specific surface area.
[c] $Dp_{(BET)}$ = Mean pore diameter calculated by BET method.
[d] Vp = Total pore volume.
[e] μVp = Micropore volume.

produces the expansion of the framework, provided that the length of Ti–O bond compared to Si–O bond is higher. The higher content of titanium in weight is obtained when working with less acid gels; however, yield in the solid silicate formation is diminished. Conversely, at very low pH (excess H^+) silica condenses easily, improving the solid yield, but there was not structural titanium incorporation in this case. The results of characterization for Ti/SBA-15 solids show that specific surface areas, the mean pore diameter (Dp), total volume pore (Vp) and micropore volume (μVp), decrease with increasing titanium content in the solid (Table 1). This effect is more pronounced in samples synthesised with titanium ethoxide as Ti source. In this case, the microporous volume diminishes ~57% with the increment of titanium content; contributing to a reduction of the specific surface area from 682 to 553 m^2/g. Part of the Ti species can be found forming clusters that reduce the volume of microporous channels.

In Ti-silicates, the infrared band located at 962 cm^{-1} is attributed to the vibration of the Si–OH bond of the silanol groups at the defect sites in silica structure and also to vibration of the Ti–O–Si bonds, whereas the band located around 800 cm^{-1} is assigned to Si–O–Si vibrations. The integrated area ratio of infrared bands 962/800 cm^{-1}, allows to appreciate differences related to structural titanium incorporation into the mesoporous silica [14,15]; an increase of it can be taken as a strong indication of the presence of Ti atoms actually incorporated in the siliceous network. On the other hand, the absence of the band near to 550 cm^{-1} is indicative of the absence of titania phase (TiO_2). Fig. 3 shows the FT-IR spectra of Ti-SBA-15 and Ti/SBA-15 calcined samples, it can be noted a strong signal at 960 cm^{-1} and the absence of the characteristic band for titania phase (550 cm^{-1}) for all samples, indicating the presence of structural titanium species and the absence of anatasa crystalline phase. Fig. 4 shows the results obtained by analysing the ratio of intensities of the bands located at 962 cm^{-1} and 800 cm^{-1} for solids synthesised by hydrothermal procedure for both pH of synthesis (Table 1). It can be noticed a proportional relationship between the amount of titanium by weight in the solids and the ratio of the integrated areas of the FT-IR bands studied. We observe a nearly linear trend at 0–4% of Ti (w/w), similar to that reported for Ti-MCM-41 by Eimer et al. [14]. The region of the curve to content Ti < 4% seems to correspond to the presence of structural titanium in silicate, as it significantly modifies the signal at 800 cm^{-1}. For higher contents of titanium an almost constant ratio is noted, and the intensity of signals near to 800 cm^{-1} was less affected, that suggests the presence of TiO_2 superficial species, the band located at 550 cm^{-1} assigned to the Titania phase, however, has not been observed.

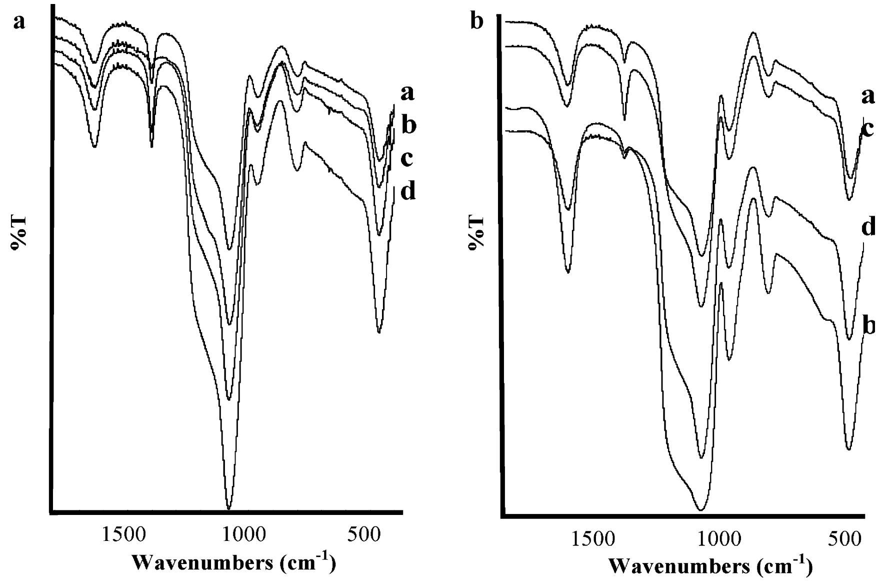

Fig. 3. FT-IR spectra of Ti-SBA-15 (a) and Ti/SBA-15 (b): (a) Eto. Si/Al 15, (b) Eto. Si/Al 30, (c) Iso. Si/Al 15, (d) Iso. Si/Al 30.

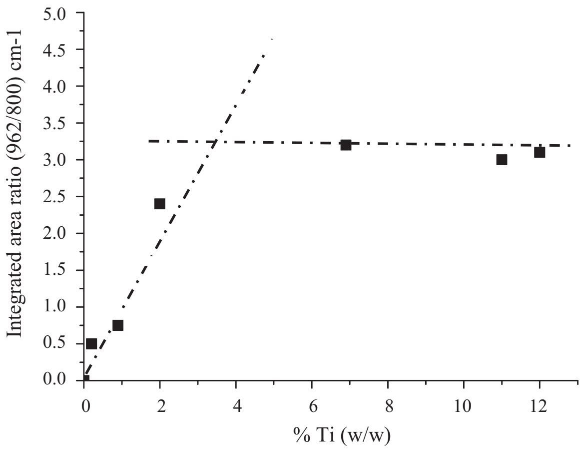

Fig. 4. Integrated area ratio 962/800 cm^{-1} FT-IR bands vs. load of titanium.

The Ti-silicates obtained by hydrothermal synthesis at pH 1.5, as well as those obtained by impregnation of SBA-15$_{1.5}$ silicate, were evaluated in the oxidation reaction of cyclohexene with TBHP. The oxidation of cyclohexene has been frequently used as test reaction for evaluating titanosilicates and TiO_2–SiO_2 mixed oxides [16–18]. When using TBHP as oxidant the reaction is highly selective and mostly gives cyclohexene epoxide with traces of glycol, cyclohexen-ol and cyclohexen-one. The results expressed on yield of cyclohexene epoxide are shown in Fig. 5. SBA-15 silicates were not active for oxidation. The only product of oxidation observed with our catalysts was cyclohexene epoxide (taken into account that % selectivity was 100%, yield of cyclohexene oxide = cyclohexene conversion), regardless of the synthesis procedure used. The level of cyclohexene yield does not correspond to the titanium content obtained by chemical analysis of the samples; it was expected that the epoxide yield owing to Ti content as the only factor responsible for the catalytic activity (Table 1) on Ti-SBA-15 samples obtained by hydrothermal synthesis should be Ti-SBA-15 (Eto) > Ti-SBA-15 (Iso), instead the result was: Ti-SBA-15 (Iso) (47 and 50%) > Ti-SBA-15 (Eto) (25 and 32%) for Si/Ti 30 y 15, respectively. The higher molecular volume of isopropyl orthotitanate, compared with titanium ethoxide, could contribute to the permanence of Ti species on the surface of the pores, inhibiting their migration into the silica walls in hydrothermal synthesis, allowing an easy access of the substrate into the active site. Moreover, as is known, one of the largest difficulties to incorporate heteroatoms as Ti or Al in SBA-15 is caused by difference in reactivity toward hydrolysis and condensation between silicon and heteroatom alcoxides. Titanium ethoxide, by its similar chemical nature to the source of silicon used (tetraethoxysilane) may integrate more effectively to the silica structure, following the hydrolysis and condensation occurring in the synthesis based on sol–gel method. Nevertheless, according to results of FT-IR spectroscopy, the TiSBA-15 catalysts with load of Ti > 4% should have a high proportion of non-structural Ti species, that leads to a diminished epoxidation activity for samples synthesised with titanium epoxide compared to those obtained using isopropyl orthotitanate as titanium source.

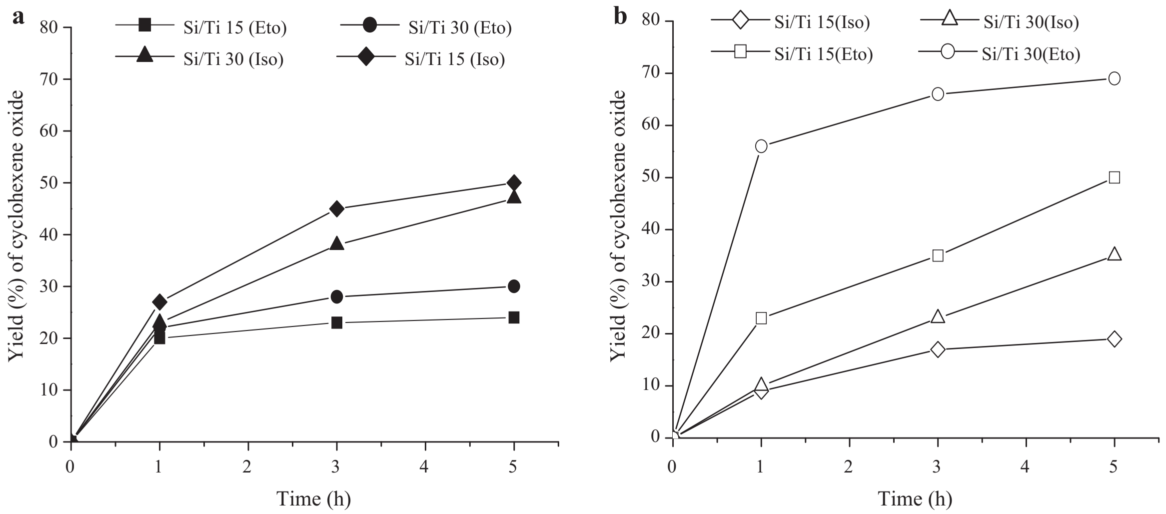

Fig. 5. Yield (%) of cyclohexene oxide vs. time (h) for Ti-SBA-15 (a) and Ti/SBA-15 (b).

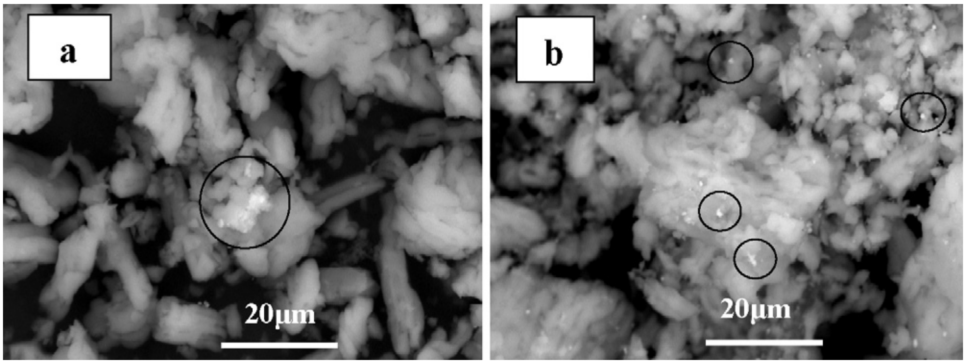

Fig. 6. SEM images for Ti/SBA-15 (Iso.) (a) and Ti/SBA-15 (Eto.) (b) Si/Ti 30.

For solids obtained by wet impregnation as for the previous series, the selectivity was 100% toward cyclohexene epoxide. Catalysts with titanium impregnated on mesoporous solids SBA-15 type could contain species-type TiO_2 crystalline anatase [19], not active for epoxidation reactions. An amount of work has been focused on the improvement of Ti/SBA-15 by post-synthetic procedures like grafting [6,12,20,21] and wet impregnation [19,22], with the purpose to obtain a highly dispersed Ti (IV) ions in tetrahedral coordination with application on epoxidation reactions. However, our results show that the epoxidation reaction with TBHP was more favored when Ti/SBA-15 was used as catalyst compared to its counterpart obtained by hydrothermal synthesis with similar Ti content (Ti/SBA-15 (Eto)). The high conversion of cyclohexene to epoxide, on the catalysts synthesised by wet impregnation suggests that part of Ti species on these solids is in tetrahedral coordination, however, SEM images show small conglomerated of Ti species (Fig. 6) on the external surface of SBA-$15_{1.5}$ silica, which are well dispersed and are smaller ($\sim$1 μm) when using titanium ethoxide as titanium source. Back scattered electrons of samples shows the Ti species as bright points, the elemental analysis by EDX indicated that the titanium species were heterogeneously distributed on surface samples. A better dispersion of conglomerated Ti species on silica surface enhances the performance of the catalysts in the epoxidation reaction.

The catalytic activity was diminished when the titanium content increased to both sources of metal, a possible explanation is that that dimeric Ti species or small oligomeric clusters are less active in epoxidation reactions than those with Ti isolated species [21]. The catalysts obtained by impregnation were more active than that obtained by hydrothermal synthesis for same load of titanium (see Fig. 5). We cannot discard that non crystalline TiO_2 (penta or hexacoordinated Ti species) co-existing with Ti (IV) isolated and contributes to catalytic activity. The active specie for cyclohexene epoxidation is not only the Ti (IV) isolated. Conversion of cyclohexene and epoxide selectivity obtained in this study were similar to those reported on mixed oxides TiO_2–SiO_2 and Ti-MCM-41 [14,15]. TiSBA-15 catalysts synthesised with low HCl content could be an alternative for use in selective oxidation reaction with alkyl hydroperoxides. We are currently conducting surface characterization studies to define the relative population of different titanium species found in our materials.

4. Conclusions

The synthesis of mesoporous TiSBA-15 type from synthesis gels with low content of HCl was effective and allows the production of solids with good structural and textural properties. The ratio of intensities of the FT-IR bands assigned to Si–O–Ti vibrations ($962\,cm^{-1}$) and Si–O–Si ($800\,cm^{-1}$) follows a linear trend with increasing titanium content in the calcined samples at Ti < 4% (w/w) after which the signals ratio has no apparent change, this can be interpreted as there is a limit of structural incorporation of up to 4% Ti by weight of SBA-15 silica under our synthesis conditions.

The oxidation reactions of cyclohexene with TBHP as oxidant were 100% selective toward the formation of epoxide. Conversion levels are attributable in part to the chemical nature and molecular size of the Ti source precursors, and the synthesis procedure, which are responsible for coordination and accessibility of the substrate to titanium sites.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cattod.2011.03.026.

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