Bifunctional properties of Al-TS-1 synthesized by wetness impregnation of amorphous Al_2O_3–TiO_2–SiO_2 solids prepared by the sol–gel method

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Ti-containing ZSM-5 (Al-TS-1) has been synthesized by wetness impregnation of amorphous Al_2O_3–TiO_2–SiO_2 solids with TPAOH solutions and subsequent crystallization under autogenous pressure at 170°C. The cogel containing aluminum, titanium and silicon oxides used as raw material has been prepared following a two-step (acid–base) sol–gel process which leads to the formation of Si–O–Ti and Si–O–Al bonds previously to the zeolite crystallization. X-ray diffraction (XRD) confirms the high crystallinity of TS-1 and Al-TS-1 obtained by this procedure whereas thermogravimetric analysis (TGA) of TPAOH-containing samples and n-C_6 adsorption measurements show the purity of the different samples. Fourier transformed infrared spectroscopy (FTIR) evidences the incorporation of Ti and NH_3 temperature programmed desorption confirms the acidic properties of Al-TS-1. Diffuse reflectance ultraviolet–visible spectroscopy (DR UV–VIS) shows that Ti atoms occupy tetrahedral positions in the Al-TS-1 and TS-1 lattices whereas bulk anastase and/or extraframework Ti species are not detected. ^{29}Si and ^{27}Al magic angle spinning nuclear magnetic resonance (MAS-NMR) spectroscopy indicate the presence of Al occupying tetrahedral positions in the Al-TS-1 framework. Therefore, the simultaneous incorporation of Ti and Al provides the Al-TS-1 samples with bifunctional properties showing high catalytic activity for n-hexane oxyfunctionalization with H_2O_2 and for alcohols etherification reactions. When it is compared to the conventional procedures of Al-TS-1 preparation by hydrothermal crystallization of a liquid gel, the method studied here is simpler, requires a lower reaction volume and proceeds with shorter synthesis time. In addition Al-TS-1 prepared through this alternative method exhibits better catalytic properties than the material synthesized following a recipe based on hydrothermal crystallization of a liquid gel.

Keywords: zeolite; Al-TS-1; sol–gel; bifunctional properties

1. Introduction

The discovery of crystalline titanium silicalite with a MFI structure, TS-1 [1], 13 years ago, has extended the use of molecular sieves in oxidation reactions, such as phenol hydroxylation [2,3], propene epoxidation [4], cyclohexanone ammoximation [5] and alkane oxyfunctionalization [6]. In all cases, high activities, selectivities and efficiency of H_2O_2 are obtained. As a consequence, several reactions catalyzed by TS-1 are at present in different stages of industrial application [7]. There have been several attempts to incorporate another ion along with Ti^{4+} to modify their catalytic properties. Coincorporation of titanium and trivalent metal ions such as Al^{3+}, Ga^{3+}, Fe^{3+} and B^{3+} in MFI and MEL structures has been reported recently [8–11]. These modified silicates are potentially active both in oxidation reactions, like titanium silicalites, and in acid-catalyzed reactions, like aluminosilicates, which may enlarge their use as catalysts in different processes. However, the presence of aluminum ions in aluminum–titanium–silicalites molecular sieves has been reported to be detrimental to the oxyfunctionalization of alkanes and to favour the direct H_2O_2 decomposition [10].

The most used methods in the literature for TS-1 [1] and Al-TS-1 [8–10] preparation are based on the hydrothermal crystallization of a liquid gel, obtained from respective alkoxides by basic hydrolysis with aqueous tetrapropylammonium hydroxide (TPAOH). The total absence of alkali metal cations is also an important requirement during the synthesis of this material in order to be catalytically active in oxidation reactions [12].

An alternative and simpler method for the synthesis of TS-1 has been studied and fine-tuned in our laboratory, based on the procedure initially developed by Padovan et al. [13], using as raw material amorphous SiO_2–TiO_2 solids prepared by the sol–gel process [14–16]. The use of the sol–gel route to prepare the raw SiO_2–TiO_2 solids has allowed us to obtain materials with high homogeneity and titanium dispersion, and to control their composition and properties. The TS-1 samples are synthesized from SiO_2–TiO_2 cogels prepared according to a two-step (acid–base) sol–gel process. The hydrolysis of the alkoxides is carried out in acid medium which leads to a slower and more controllable condensation of the titanium species avoiding TiO_2 precipitation. In the second step, the gelation of the solution to yield a polymeric solid is promoted by TPAOH addition which accelerates the condensation reactions once Ti–O–Si bonds have been formed. The TS-1 synthesis takes place by thermal treatment at autogenous pressure of the

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SiO_2–TiO_2 cogel, previously dried and wetness impregnated with the template solution.

In this work, we have used this method to incorporate simultaneously Al and Ti in the MFI framework, using as raw material Al_2O_3–TiO_2–SiO_2 cogels where Ti–O–Si and Al–O–Si bonds have been formed previously to zeolite crystallization. In the preparation of multicomponent silicates prepared following the sol–gel route [17], the sequential addition of the different alkoxides in the reverse order of their respective reactivities (least reactive precursor first) with a partial hydrolysis step after each addition is widely accepted as one of the most convenient procedures. The idea is that the newly added, unhydrolyzed alkoxides will condense with partially hydrolyzed sites of the polymeric species formed by the preceding hydrolysis steps (heterocondensation).

The Al-TS-1 synthesized following the method described in this work has been compared to TS-1 [14–16], and Al-TS-1 prepared by hydrothermal crystallization of a liquid gel [8–10].

2. Experimental

2.1. Sample preparation

2.1.1. Al-TS-1 (w.i.)

The Al_2O_3–TiO_2–SiO_2 solid used as raw material for the Al-TS-1 synthesis was prepared following the next two-step sol–gel process:

– *Step (1). Acid hydrolysis–condensation.* Tetraethyl orthosilicate (TEOS, Alfa) is first hydrolyzed at room temperature with 0.2 M HCl aqueous solution for 45 min (H_2O/TEOS mole ratio = 7.23). Aluminum isopropoxide (AIP, Aldrich) dissolved in isopropyl alcohol (AIP/isopropyl alcohol mass ratio = 0.039) is then added dropwise. This mixture is stirred for 45 min before adding to it a 20 wt% aqueous solution of TPAOH (Alfa) to increase the pH of the solution (1.5 g of aqueous solution), with additional stirring at 0°C during 20 min. Then, a solution of titanium tetrabutoxide in isopropyl alcohol (TNBT/isopropyl alcohol mass ratio = 0.17) is added slowly and hydrolyzed at 0°C. The clear mixture obtained is stirred for additional 20 min.

– *Step (2). Basic gelation.* The final solution of step 1 is converted into a solid cogel by dropwise addition of 20 wt% aqueous TPAOH (Alfa) at room temperature (0.8 g per 1 g of SiO_2). The content in alkali metals of this reagent was $Na^+ < 20$ ppm and $K^+ < 2$ ppm. Thereafter, the cogel is dried overnight at 110°C in order to remove alcohols and water and it is crushed to give a powdered material.

Al-TS-1 (w.i.) was synthesized by thermal treatment of the wetness impregnated cogel with aqueous TPAOH solution. The Al_2O_3–TiO_2–SiO_2 cogel was prepared with $SiO_2/TiO_2 = 40$ and $SiO_2/Al_2O_3 = 160$ molar ratios and the wetness impregnation point was reached by addition of 1.6 g of 20 wt% TPAOH aqueous solution per 1 g of dried cogel. After impregnation, the incipient wet Al_2O_3–TiO_2–SiO_2 cogel is charged into Teflon-lined autoclaves and crystallized under autogenous pressure and static conditions at 170°C for 24 h. The crystalline product of the synthesis is separated by centrifugation, washed several times with distilled water, dried overnight at 110°C and finally calcined in air at 550°C for 7 h.

2.1.2. Al-TS-1 (conv.)

A conventional Al-TS-1 sample was synthesized by hydrothermal crystallization of a liquid gel according to the guidelines of procedures described in previous works [8,10]. The synthesis was as follows: 14 g TPAOH (20 wt% aqueous solution, Alfa) was added dropwise at 0°C under stirring to a mixture containing 8 g tetraethyl orthosilicate (TEOS, Alfa) and 0.327 g titanium butoxide (TNBT, Alfa) in 6 g isopropyl alcohol. This clear mixture was stirred for an additional 30 min. Then, a solution of 0.098 g aluminum isopropoxide (AIP, Alfa) in 5 g isopropyl alcohol was added dropwise to the above mixture. Finally, 13.2 g double-distilled water was added slowly and the solution was stirred for 3 h at 70°C in order to remove the alcohol.

The clear mixture obtained is charged into Teflon-lined autoclaves and crystallized under autogenous pressure and static conditions at 170°C for 72 h. The crystalline product of the synthesis is separated by centrifugation, washed several times with distilled water, dried overnight at 110°C and finally calcined in air at 550°C for 7 h.

2.1.3. TS-1

TS-1 was synthesized using as raw material amorphous SiO_2–TiO_2 solids prepared by the sol–gel process [14–16]. The amorphous solid is prepared omitting the AIP addition and the neutralization step while the rest of the procedure is analogous to that of Al-TS-1 sample.

2.2. Characterization

Chemical analyses were performed by X-ray fluorescence (XRF) with a Philips PW 1480 spectrometer. X-ray diffraction (XRD) patterns were collected with a Philips X'PERT diffractometer with Cu Kα radiation. Crystallinity was determined from the peak area between $2\theta = 22°$ and 25° using a highly crystalline TS-1 sample as reference. Fourier transform IR (FTIR) spectra were recorded by means of a Nicolet 510P spectrophotometer using the KBr wafer technique. Diffuse reflectance UV–VIS spectra (DR UV–VIS) were obtained under ambient conditions on a Cary-1 spectrophotometer equipped with a diffuse reflectance accessory.

Ammonia temperature programmed desorption (TPD) was carried out with a Micromeritics TPD/TPR

Table 1
Synthesis conditions and molar gel composition of Al-TS-1 samples and TS-1

Sample	SiO_2	TiO_2	Al_2O_3	H_2O	TPAOH[a]	t_s (days)	T (°C)	Y_s[b] (%)
Al-TS-1 (w.i.)	40	1	0.25	216.2	7.44	1	170	95
Al-TS-1 (conv.)	40	1	0.25	1412.0	14.36	3	170	84
TS-1	40	1	0	216.2	6.69	1	170	95

[a] Both TPAOH added during the preparation of the raw cogel and during the subsequent synthesis included.
[b] Yield of the synthesis: amount of calcined sample, referred to the SiO_2 present in the starting mixture.

2900. The samples were first outgassed by thermal treatment, from ambient temperature to 560°C with a heating rate of 15°C/min in a He stream (80 ml/min). After cooling at 200°C, the sample is saturated with a NH_3 stream and consequently treated with a He stream (80 ml/min) for 90 min. Finally, the temperature is increased to 560°C with a heating rate of 15°C/min while recording NH_3 desorption.

Morphology and size of the crystallites were determined from scanning electronic microscopy (SEM) images taken with a Jeol JSM-6400 microscope. Thermogravimetric analyses (TGA) were performed with an MK2 thermobalance (C.I. Electronics) with a heating rate of 5°C/min and flowing 100 ml/min of a mixture of air and helium (air/He molar ratio = 1). The temperature was increased between 25 and 700°C and thereafter kept at 700°C for 1 h. The same instrument was used for the *n*-hexane adsorption measurements at 25°C and $P/P_0 = 0.2$, 0.4, 0.5. The samples were first outgassed by treatment at 400°C for 4 h in a He stream. After cooling at 25°C, He with different *n*-hexane partial pressures was contacted with the sample, 2 h being allowed for equilibration prior to the measurement of the weight increase in each point.

High resolution ^{29}Si and ^{27}Al magic angle spinning nuclear magnetic resonance (MAS-NMR) spectra of powdered samples were recorded at 79.49 and 104.26 MHz, respectively, in a Bruker spectrometer model MSL-400 equipped with a Fourier transform unit. The spinning frequency was 4000 cps and a time interval of 5 s between successive accumulations was selected. Measurements were conducted at room temperature with tetramethyl silane (TMS) and $[Al(H_2O)_6]^{3+}$ as external standard references, with accumulations amounted to 2000 and 400 FIDs respectively.

The catalytic tests of *n*-hexane oxyfunctionalization were carried out in magnetically stirred teflon lined autoclaves at 100°C for 1 h under autogenous pressure. Aqueous H_2O_2 (30 wt% Panreac) was used as oxidant and methanol as solvent ($H_2O_2/n\text{-}C_6$ molar ratio = 1.176, $n\text{-}C_6$/methanol mass ratio = 0.276 and $n\text{-}C_6$/catalyst mass ratio = 12). The H_2O_2 concentration after reaction was evaluated by iodometric titration. The catalytic test for *t*-butanol and methanol etherification to yield methyl *t*-butyl ether (MTBE) was carried out in stirred autoclaves at 100°C for 2 h under autogenous pressure (*t*-butanol/methanol mass ratio = 0.1, *t*-butanol/catalyst mass ratio = 2.5). All the reaction products were analyzed by gas chromatography (Varian 3400) on a capillary column, V1 methyl-silicone (60 m × 0.02 mm).

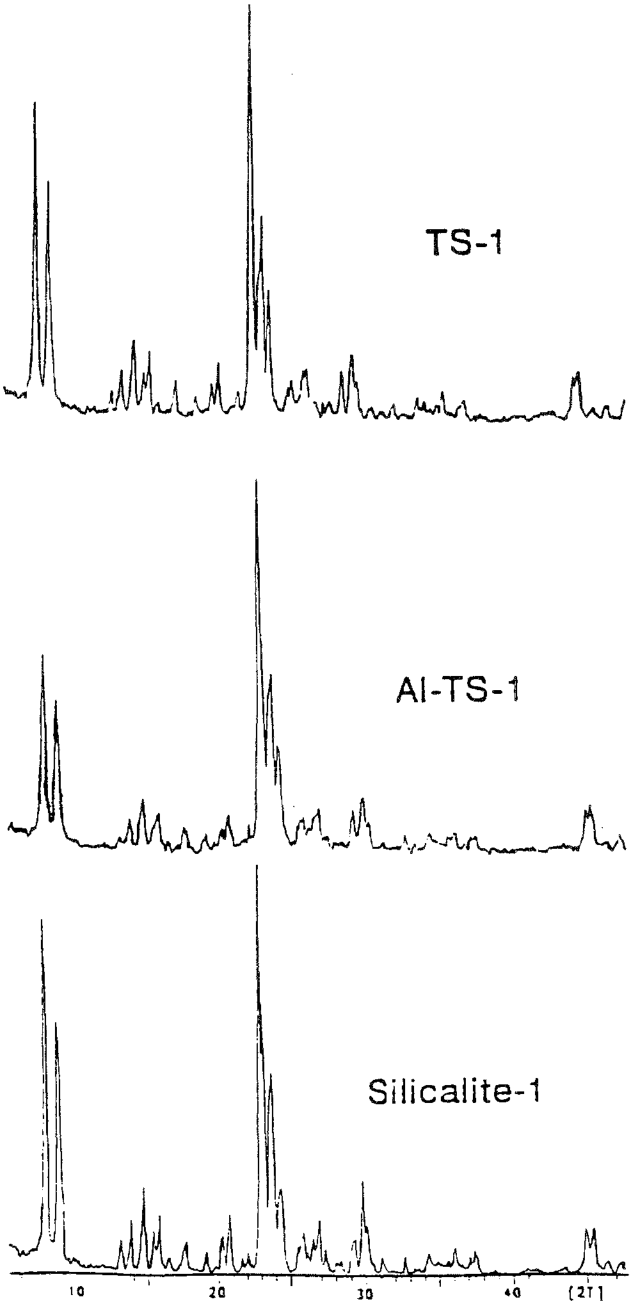

Fig. 1. XRD patterns of TS-1, Al-TS-1 (w.i.) and silicalite-1.

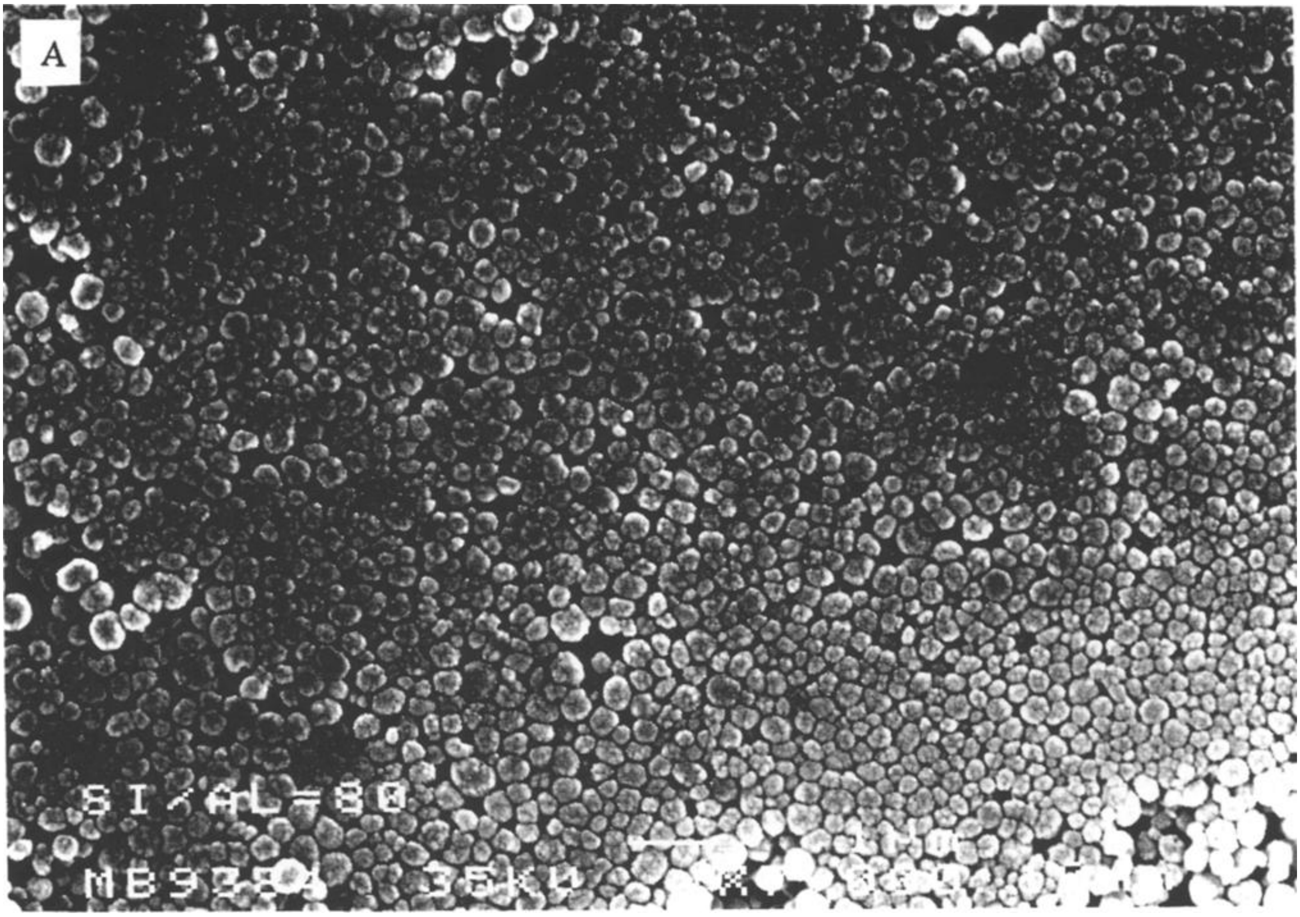

Fig. 2. SEM image of the Al-TS-1 (w.i.) sample. (A) X7000, (B) X30000.

3. Results and discussion

3.1. Al-TS-1 (w.i.) and TS-1 samples

Al-TS-1 (w.i.) and TS-1 were prepared according to the sol–gel method developed in our laboratory [14–16]. Both starting cogels previously described were impregnated with the same quantity of TPAOH solution (1.6 g of 20 wt% aqueous solution/1 g of dried cogel). The synthesis conditions and the molar gel composition of Al-TS-1 (w.i.) and TS-1 are given and compared in table 1.

Both synthesis processes lead to materials with MFI structure and high crystallinity as concluded from XRD measurements. The TS-1 sample shows clearly orthorhombic symmetry in contrast with silicalite-1 which shows monoclinic symmetry, whereas the Al-TS-1 symmetry can be considered a transition between orthorhombic and monoclinic (see fig. 1) as it corresponds to a silicalite containing Ti (orthorhombic) and Al (monoclinic). Although the morphology of both samples is quite similar (cuboid shape), the crystal size of the Al-TS-1 (w.i.) sample is in the range 0.4–0.5 μm, whereas the TS-1 crystal sizes are in between 0.7 and 1.1 μm (see fig. 2). The purity of these samples is confirmed by TGA. Thus, in the differential curves of Al-TS-1 (w.i.) and TS-1 thermogravimetric analyses (figs. 3a and 3b), a single peak is observed due to thermal decomposition of the TPA^+ ions occluded in the zeolite pores. The difference of peak temperature observed in both samples, 400°C for Al-TS-1 (w.i.) and 384°C for TS-1, could be attributed to the stronger interaction of Al atoms with the TPA^+ ions in the former. The weight loss associated with this peak for Al-TS-1 (w.i.) and TS-1 was 13.8 and 13.7% respectively (referred to the final sample weight), in good agreement with the theoretical content of four TPA^+ molecules per unit cell corresponding to pure MFI structure material. Similarly, the *n*-hexane adsorption capacity at $P/P_0 = 0.5$ of the Al-TS-1 (w.i.) and TS-1 samples was found to be 12.2 and 12.4% respectively, which agrees fairly well with the values reported in the literature [18,19], supporting the absence of amorphous material in the zeolite channels.

The chemical analysis performed by XRF shown in table 2 indicates that the Ti content in Al-TS-1 (w.i.) is lower than in TS-1 sample and in both cases this content is lower than that corresponding to the raw cogel, whereas Al content in Al-TS-1 (w.i.) is similar to the raw cogel. The presence of Al in the raw cogel lowers the incorporation of Ti in the zeolitic framework, probably

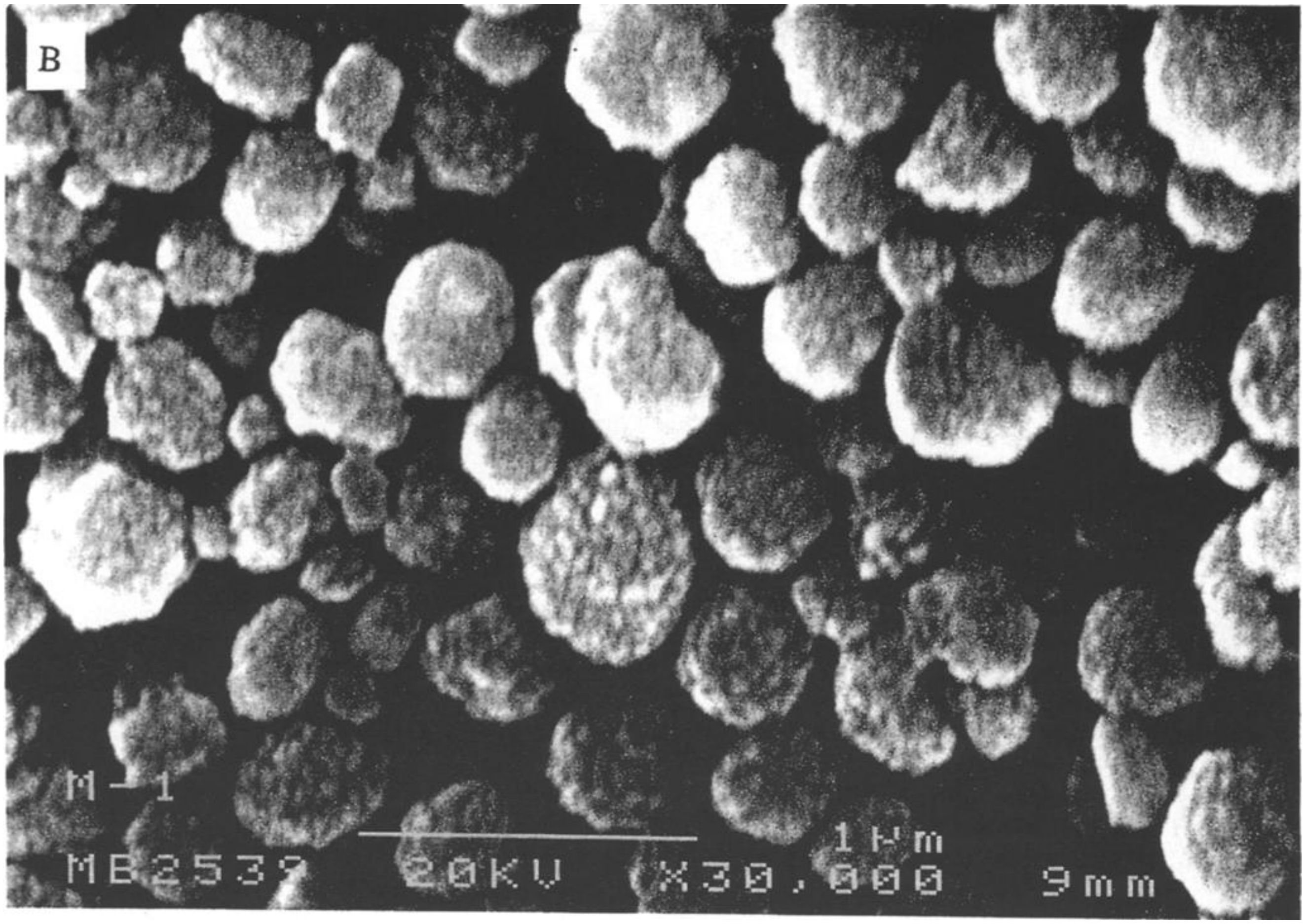

Fig. 2. Continued.

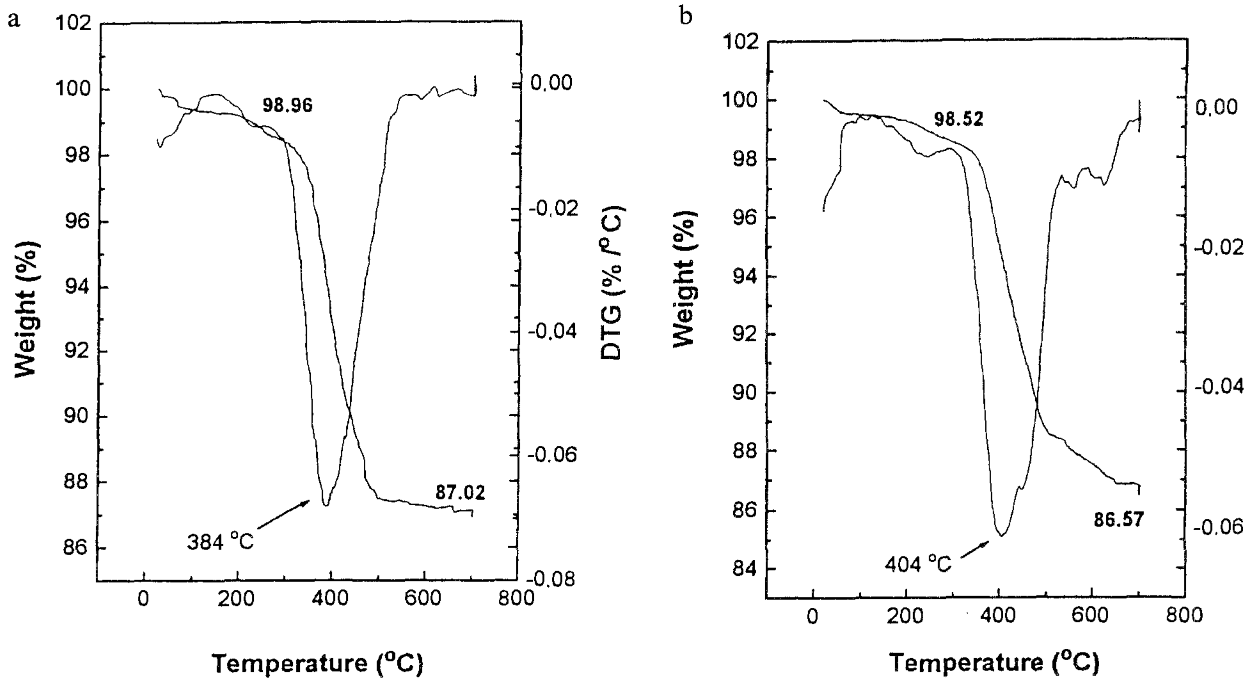

Fig. 3. Thermogravimetric analysis: (a) TS-1, (b) Al-TS-1 (w.i.).

Table 2
Molar sample composition and properties of Al-TS-1 samples, TS-1 and H-ZSM5

Sample	SiO_2	TiO_2	Al_2O_3	I_{960}/I_{800} [a]	D_c (μm)	TPD [b]
Al-TS-1 (w.i.)	76	1	0.48	1.36	0.4–0.5	0.17
Al-TS-1 (conv.)	48	1	0.30	1.37	0.2–0.4	0.15
TS-1	49	1	0	1.80	0.7–1.1	0
H-ZSM5	60	0	1	–	0.1–0.2	0.45

[a] Ratio between the intensities, in absorbance units, of the 960 and 800 cm^{-1} IR bands.
[b] NH_3 adsorption capacity in mmol NH_3/g.

due to a competitive effect of both elements [8]. Thus, the crystallites must be carefully separated and washed with distilled water after the synthesis in order to avoid the possible deposition of soluble species of Ti, Si and/or Al, that could lead to the presence of amorphous phases in the final materials.

The IR spectrum of Al-TS-1 (w.i.) shows a band at 960 cm^{-1} related to the stretching vibration of Si–O bonds adjacent to framework Ti atoms [20] (fig. 4). The relative intensity of this band I_{960}/I_{800} correlates well with the Ti content into the zeolite framework [19]. As can be seen in table 2, the ratio between the intensities of the 960 and 800 cm^{-1} IR bands is higher for TS-1 than Al-TS-1 (w.i.), which suggests a higher degree of Ti incorporation in the TS-1 sample in fair agreement with the chemical analysis performed by XRF. Fig. 5 shows the DR UV–VIS spectra of the TS-1 and Al-TS-1 (w.i.) samples and of the corresponding cogels. In both cases, absorption around 330 nm is detected neither in the samples nor in the cogels, showing the absence of bulk TiO_2 phases [21]. The narrow band corresponding to the Al-TS-1 (w.i.) and TS-1 samples is centered around 205 nm, confirming that the Ti atoms occupy tetrahedral positions in the zeolite framework [21]. In contrast, the spectrum of the cogels presents a wider band shifted to a higher wavelength. This suggests that in the starting amorphous solid, besides tetrahedrally coordinated Ti atoms, other Ti species are present, which disappear after the synthesis to give the more homogeneous Ti environment present in the crystalline zeolitic materials.

TS-1 exhibits a negligible strong NH_3 adsorption capacity whereas Al-TS-1 (w.i.) shows a capacity proportional to the aluminum content (see table 2) in close agreement with the theoretical Al content (0.20 Al mmol/g). The solid-state ^{29}Si and ^{27}Al MAS-NMR spectroscopic results of calcined Al-TS-1 (w.i.) and the corresponding cogel can be seen in figs. 6 and 7. The ^{29}Si spectrum of the Al-TS-1 (w.i.) sample shows an intense peak around −112 ppm and a small peak around −104 ppm. These peaks are attributed to Si bonded with 0 Al (Q_4) and 1 Al (Q_3), respectively [22], suggesting the presence of Al in tetrahedral positions in the zeolite framework. Additionally, the resolution does not allow the definition of a peak around −116 ppm although it is

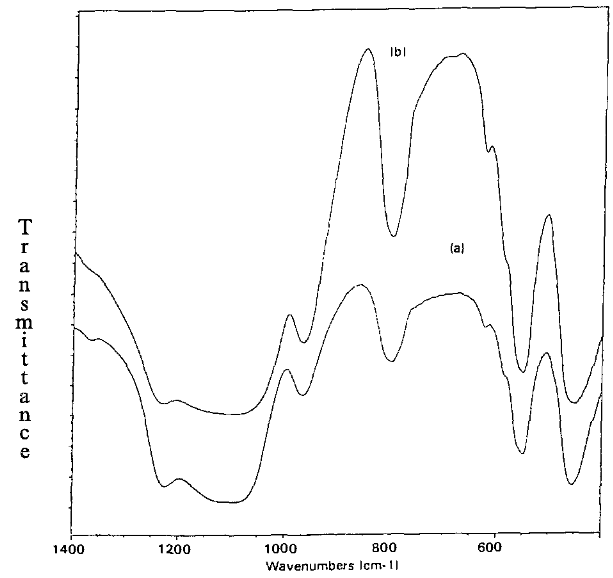

Fig. 4. IR spectra: (a) Al-TS-1 (w.i.), (b) TS-1.

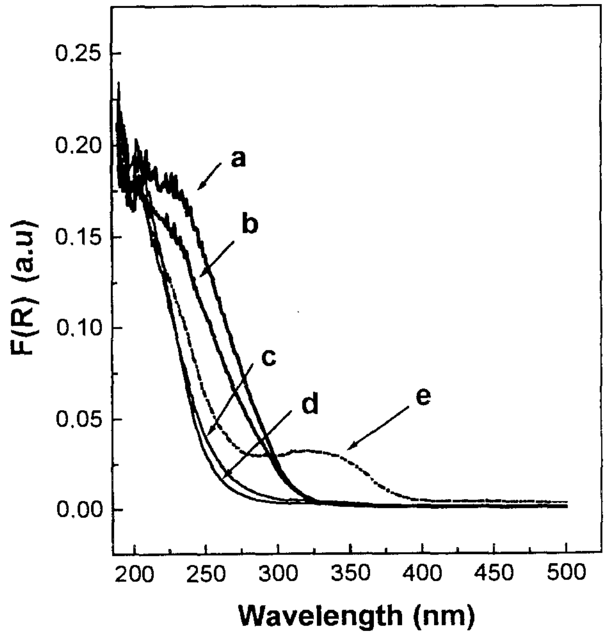

Fig. 5. DR UV–VIS spectra of zeolite samples and the corresponding uncalcined cogels: (a) Al-TS-1 cogel, (b) TS-1 cogel, (c) Al-TS-1 (w.i.), (d) TS-1 and (e) Al-TS-1 (conv.).

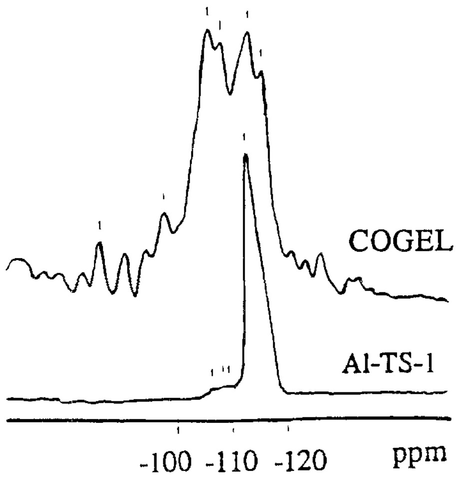

Fig. 6. ^{29}Si MAS-NMR spectra of the Al-TS-1 (w.i.) sample and the corresponding uncalcined cogel.

clearly shown as a shoulder of the main peak at -112 ppm which has been ascribed to Si–O–Ti bonds, the peak intensity increasing with Ti content in zeolite [19]. The ^{29}Si NMR spectrum of the cogel presents several broad peaks which suggests that in the initial cogel exists a high variety of environments according to the wide band found in DR UV–VIS spectra of the cogels. The ^{27}Al NMR spectrum of the cogel and the spectrum corresponding to the zeolite sample show a peak at 52 and 54 ppm respectively, due to Al atoms in tetrahedral positions [AlO_2^-] [23]. Besides, the large linewidth observed in ^{27}Al cogel NMR spectra is indicative of a broad distribution of environments as it was seen with ^{29}Si NMR spectra. Moreover, the absence of a peak around 0 ppm shows that octahedral Al species are not present in the two samples. Therefore, from both ^{27}Si and ^{29}Al NMR measurements, it can be concluded that Al atoms are located in tetrahedral environments in the starting Al_2O_3–TiO_2–SiO_2 cogel and in the Al-TS-1 (w.i.) sample.

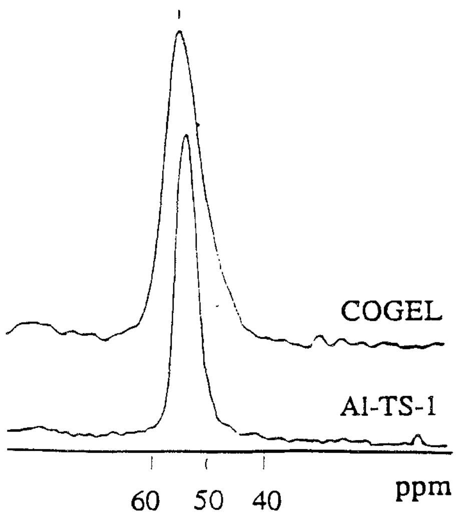

Fig. 7. ^{27}Al MAS-NMR spectra of the Al-TS-1 (w.i.) sample and the corresponding uncalcined cogel.

The results obtained with Al-TS-1 (w.i.) and TS-1 in the catalytic experiments of n-C_6 oxidation with H_2O_2 are given in table 3. Both samples exhibit a high activity for the conversion of n-C_6 into a mixture of 2- and 3-hexanols and hexanones with similar H_2O_2 selectivity, nearly 100%. The oxidation centers, related mainly with Ti sites capable to form the real active species (titanium peroxo complexes) [24] in Al-TS-1 (w.i.) are catalytically active for n-C_6 oxidation with high efficiency as in TS-1, but these sites in Al-TS-1 (w.i.) seem to be more active than in TS-1, since, as shown in table 3, the oxidation activity for both samples is similar although the TS-1 sample presents 50% more Ti than the Al-TS-1 (w.i.) sample. In order to determine the possible contribution of Al atoms to this oxidation activity, a sample of H-ZSM5, with a Si/Al molar ratio of 30 and similar crystal size (0.1–0.2 μm), has been synthesized and used in the n-hexane oxidation test. As shown in table 3, the hydrogen peroxide decomposition is clearly enhanced although there is certain conversion in this oxidation reaction, probably catalyzed by the Al atoms present in H-ZSM5. Even assuming that the oxidation activity of Al atoms located in Al-TS-1 is similar to that of Al in H-ZSM5, the n-hexane oxidation conversion of Al-TS-1 is still high for the Ti content of this sample in comparison with the TS-1 sample.

Noteworthy is the negligible H_2O_2 decomposition with the Al-TS-1 (w.i.) sample which is in contrast with the conclusions reported in a previous paper [10], where the H_2O_2 decomposition was attributed mainly to the Brønsted acid sites. A possible explanation of this disagreement could lay on the differences between the preparation methods and the lower Si/Ti and Si/Al molar ratios present in Al-TS-1 sample used in the previous reference. Another fact to have in mind is the excellent role of methanol as solvent in comparison to other ones used for alkane oxidation [14–16].

The presence of Al atoms in the zeolite framework of Al-TS-1 provides acid properties to this material as shown in table 3. The Al-TS-1 (w.i.) sample exhibits a high activity for the etherification of methanol and t-butanol into MTBE with a high selectivity (nearly 100%), which is related to its capacity of strong NH_3 adsorption and the presence of Brønsted acid sites. However, the TS-1 sample does not present any activity for this reaction as it was expected from its negligible capacity of strong NH_3 adsorption. The comparison with the H-ZSM5 sample shows again an acid activity above the expected one in the etherification reaction, since the Al content of the Al-TS-1 (w.i.) sample is almost half of the content in the H-ZSM5 sample. The high values of t-butanol conversion obtained in the experiments of table 3 could lead to erroneous conclusions, but the differences seem quali-

Table 3
Catalytic properties of Al-TS-1, TS-1 and H-ZSM5 samples

Sample	*n*-hexane oxidation[a]			Alcohols etherification[b]	
	n-hexane conversion (%)	H_2O_2 conversion (%)	H_2O_2 selectivity[c] (%)	*t*-butanol conversion (%)	MTBE selectivity[d] (%)
Al-TS-1 (w.i.)	65	85	96	75	97
Al-TS-1 (conv.)	55	73	96	71	91
TS-1	64	86	100	0	0
H-ZSM5	15.5	68.7	24.7	94	99

[a] Reaction conditions: $T = 100°C$, $t = 1$ h. Composition of the reaction mixture: $H_2O_2/n\text{-}C_6$ mole ratio = 1.176, $n\text{-}C_6$/methanol mass ratio = 0.276 and $n\text{-}C_6$/catalyst mass ratio = 12.

[b] Reaction conditions: $T = 100°C$, $t = 2$ h. Composition of the reaction mixture: *t*-butanol/methanol mass ratio = 0.1, *t*-butanol/catalyst mass ratio = 2.5.

[c] Selectivity defined as: (mol hexanol + 2 * mol hexanones obtained)/mol H_2O_2 converted.

[d] Selectivity defined as: (mol MTBE obtained/mol *t*-butanol converted).

tatively to indicate higher activities of the Brønsted acid sites present in Al-TS-1 (w.i.) with respect to those in H-ZSM5.

3.2. Comparison with conventional method

Ti-containing ZSM-5 zeolite (Al-TS-1) has been prepared according to the guidelines of the conventional methods described in refs. [8,10] for comparison. The molar gel composition and crystallization conditions corresponding to the synthesis of conventional Al-TS-1 (conv.) are given and compared with those of the Al-TS-1 (w.i.) sample prepared by wetness impregnation of amorphous Al_2O_3–TiO_2–SiO_2 cogels as given in table 1. The main advantages of the synthesis method followed in this work with respect to the conventional synthesis are the lower amount of TPAOH used to obtain the zeolite, the lower volume occupied by the initial mixture in the synthesis reactor and the shorter synthesis time. Besides, the yield of the synthesis is higher for the Al-TS-1 (w.i.). Additionally, the acid medium, present in the first step of the sol–gel method during the preparation of the raw cogel, does not allow the fast condensation of Ti species in solution, thus avoiding the formation of a very stable TiO_2 phase which could not be incorporated to the zeolite lattice during the synthesis. Finally, the conventional method is more complicated and laborious than the method studied in this work.

Both samples show MFI structure and high crystallinity as concluded from XRD measurements. These samples, as shown previously in fig. 1, exhibit a transition symmetry between orthorhombic (TS-1) and monoclinic (calcined H-ZSM5 and silicalite-1) due to the presence of Al and Ti atoms in tetrahedral positions of the zeolite framework. The crystal size of the samples determined by SEM is around 0.4–0.5 μm for the Al-TS-1 (w.i.) sample, whereas the conventional sample exhibits a somewhat lower crystal size, 0.2–0.4 μm.

The chemical analyses performed by XRF are shown in table 2. The Ti content of the conventional sample presents a higher value, near to that corresponding to the initial gel composition. The Si/Al molar ratio is very close (around 80) in both samples and similar to the raw material (liquid gel and amorphous cogel). Again, in the synthesis procedure developed in this work there is clearly competition between Al and Ti to be incorporated into the zeolitic framework, whereas this fact is not observed, at least from the chemical analysis data, in the conventional synthesis of Al-TS-1.

A good correlation has been found between the Ti content in the framework and the relative intensity of the 960 cm^{-1} IR band [19]. As can be seen in table 2, the relative intensity I_{960}/I_{800} is very similar for both samples, which suggests similar degree of Ti incorporation into the crystalline structure which is in contrast with the chemical analysis data. Fig. 5 shows the DR UV–VIS spectra of Al-TS-1 samples. In the sample synthesized by wetness impregnation of amorphous Al_2O_3–TiO_2–SiO_2 cogel, absorption around 330 nm is not detected, but the zeolite synthesized following the recipe of the conventional method presents an important absorption around this wavelength, showing the presence of bulk TiO_2 phases, which means that an important amount of Ti is not incorporated effectively into the zeolite framework. Since there was no macroscopic evidence of TiO_2 formation during the liquid gel preparation, the appearance of this undesirable species takes place during the zeolite formation under the synthesis conditions. TPD analysis shows a nearly similar NH_3 adsorption capacity and acid strength for both samples (table 2).

The results obtained with the Al-TS-1 samples in the catalytic experiments of $n\text{-}C_6$ oxidation with H_2O_2 and methanol/*t*-butanol etherification are given in table 3. The sample synthesized by the conventional method shows a lower oxidation activity but with H_2O_2 selectivity near 100%. This activity decrease is also observed for the etherification reaction. A possible explanation for this experimental feature is related to the location of the extraframework TiO_2 species inside the zeolitic pores hindering the access to a part of the active oxidation sites. This pore blockage is also in agreement with the lower n-C_6 adsorption capacity shown by this sample (11%) in comparison with the corresponding to Al-TS-1 (w.i.) sample (12.2%).

Following the results obtained by DR UV–VIS spectra, also a lower H_2O_2 selectivity should be expected towards the oxygenated products in the conventional sample due to decomposition of the oxidant by the extraframework TiO_2 [24]. However, the experimental data show a decrease in n-hexane and H_2O_2 conversion without significant change in the H_2O_2 selectivity . This feature could be supported by the use of methanol and its excellent role as solvent for alkane oxidation in comparison with other solvents [14–16]. Additionally, recently a relative low peroxide decomposition has been reported over titania obtained by a sol–gel procedure for the epoxidation of cyclohexene [25].

4. Conclusions

Al-TS-1 can be synthesized from amorphous Al_2O_3–TiO_2–SiO_2 solids by wetness impregnation with TPAOH solution followed by crystallization under autogenous pressure. XRD shows that the material obtained in this way is highly crystalline. DR UV–VIS results confirm the presence of the Ti atoms in tetrahedral positions of the zeolite framework whereas anatase and/or extraframework Ti species are not detected. ^{29}Si and ^{27}Al MAS-NMR spectroscopy confirm the presence of the Al atoms in tetrahedral coordination corresponding to the zeolite lattice. The method described in this work allows Ti and Al atoms to be effectively and simultaneously incorporated into tetrahedral positions of the MFI framework.

Not all the Ti present in the raw Al_2O_3–TiO_2–SiO_2 cogel is incorporated into the zeolite as it occcurs in the synthesis of TS-1 by a similar procedure. However, in Al-TS-1 the Ti incorporation degree is much lower than in TS-1, probably due to a competitive effect with Al species, which are incorporated almost totally into the framework during the synthesis.

Al-TS-1 has a symmetry lattice between orthorhombic and monoclinic, depending on the Ti and Al content which also determines the equilibrium between the acid and oxidant properties and the hydrophobic or hydrophilic character. Additionally, the Ti sites in Al-TS-1 framework seem to be catalytically more active for oxidation reactions than Ti sites in TS-1. On the other hand, the Brønsted acid sites in Al-TS-1 do not provide peroxide decomposition in the reaction conditions studied (methanol as solvent) and seem to be catalytically more active in the etherification reaction than the acid sites present in H-ZSM5.

Compared to the conventional method of Al-TS-1 synthesis, the procedure studied here is simpler, requires a smaller volume of reaction mixture and shorter synthesis times and proceeds with higher synthesis yield. The Al-TS-1 obtained by wetness impregnation of amorphous Al_2O_3–TiO_2–SiO_2 cogels exhibits better catalytic properties than Al-TS-1 synthesized according to the conventional method, since the latter leads to the formation of extraframework TiO_2. The great advantage of the alternative method of synthesis described in this work is based on the previous formation of the Al–O–Si and Ti–O–Si bonds in the cogels before zeolite crystallization, avoiding the extraframework TiO_2 formation during the synthesis, which is clearly shown in the tetrahedral environment of Al and Ti in these solids, as it was determined by MAS-NMR and DR UV–VIS analysis respectively.

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