XANES-PCA analysis of Ti-species in MCM-41 mesoporous silica synthesized by different method

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ABSTRACT

MCM-41 mesoporous silica was prepared with Ti incorporated in the structure by two different ways: hydrothermal and atmospheric pressure by sol–gel method. To evaluate each synthesis, these materials were in situ investigated through X-ray absorption fine structure (XAFS) spectroscopy in different stages of the synthesis. X-ray absorption structure at the near edge region (XANES) gives the coordination of Ti and the relative concentration of Ti-species present in the mesoporous materials, obtained by different synthesis. The Principal Component Analysis (PCA) of XANES spectra indicate that mesoporous silica modified by Ti synthesized by hydrothermal method has species with majority of Ti tetrahedrally coordinated. This coordination is increased up to six when the sample is hydrated. In the case of the sol–gel synthesis, Ti-sites have higher mean coordination, independently from the degree of hydration.

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1. Introduction

Recently, the synthesis and characterization of different types of mesoporous silicates, such as MCM-41, MCM-48 [1–3] and HMS [4] have been reported. These materials consist of a regular array of uniform one- or three-dimensional pores with diameters varying between 1.5 and 10 nm. In addition, MCM-41 mesoporous materials have shown high performance for the chemical exploration of intra-crystal inclusion [5]. Its main applications as catalysts are focused to the catalysis area of big substrates, absorption phenomena, separation and formation of new complex materials [6–8]. The structure of the silicate can be modified by partial substitution of elements such as Al, Ti, V, Sb, Fe or Pd. The substitution with titanium is particularly interesting, because it has shown great efficiency in the organics substrate oxidation [9–13]. As the size of the pores is bigger than in the zeolitic materials, systems such as Ti-MCM-41 are considered appropriate for substrate oxidation of great size molecules, usually used in fine chemistry. The titanium-silicalite catalysts such as TS-1, TS-2, Ti-Beta, Ti-MCM-41 and Ti-MCM-48 have been applied in the processes of hydroxylation of aromatic compounds, epoxidation of unsaturated compounds by hydrogen peroxide, oxidation of alkenes, alcohols and ketones [14]. They have been tested in the processes of epoxidation by hydrogen peroxide because they show high selectivity (including stereoselectivity) and permit performing the processes in mild temperatures and under atmospheric pressure. Moreover, very often the reactions lead to high conversion of hydrogen peroxide and the unsaturated compound [15]. Moreover, the Ti-MCM-41 catalyst has been used in the processes of oxidation and epoxidation of various organic compounds, e.g. oxidation of d-glucose, propylamine, propylene, epoxidation of crotyl alcohol, terpineol and terpinen-4-ol [16]. In these processes, this catalyst shows high selectivity. From among the other catalysts of this type, TS-1, TS-2, Ti-Beta, the Ti-MCM-41 catalyst is distinguished by having channels of greater diameter, showing smaller diffusion effects of the reagents and products, and offering the possibility of oxidation of large volume molecules of organic compounds. The best catalytic performance of this catalyst was observed in the oxidation of branched and cyclic alcohols. Otherwise, Ti containing-MCM-41 and other transition metal ions showed high activity for photocatalytic oxidation of organics and water splitting [17–19]. Titania loaded Cr-MCM-41 exhibited reasonable activity for photocatalytic organic elimination under visible light [20–24].

Some years ago, we have obtained successfully the vitamin K3 by selective oxidation of 2-methyl naphthalene over Ti-MCM-41 [25]. 2-Methyl-1,4-naphtoquinone, used therapeutically under the name of Menadione or vitamin K3, has more ant bleeding activity of the natural vitamin K1 or K2.

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Is important to determine the coordination of Ti and the relative concentration of Ti-species present in the mesoporous. A higher Ti loading gives rise to a lower titanium dispersion degree and the presence of titanium sites in higher coordination numbers and having Ti–O–Ti bonds [26,27]. Therefore, high titanium concentration in the mesopores leads to a quicker saturation of titanium species and to the consequent formation Ti–O–Ti linkages, which reduces their catalytic activity not only per active centre but also in absolute terms, partially helped by the corresponding decrease in surface area.

In this contribution, the Ti-MCM-41 catalysts were prepared by hydrothermal and sol–gel synthesis [28,29]. In order to study the nature of Ti-sites according to the different synthesis processes, samples in different preparation stages were investigated through XAFS (X-ray absorption fine structure) spectroscopy at the Ti-K-edge (4966 eV).

X-ray absorption near edge structures (XANES) represent electronic transition from an inner level to the outer unoccupied levels caused by X-ray absorption, thus giving information on the local electronic structure and coordination environment around an absorbing atom. Thus, XANES Ti-K-edge can probe the coordination state of Ti in a qualitative manner by comparison of shape and/or intensity of pre-edge XANES region with reference Ti-compounds. Different Ti coordination is distinguishable due to the presence of a pre-edge peaks corresponding to (Ti)$3d$/(O)$2p$ mixing [30] of electronic levels. The height of the pre-edge peak increases sequentially from $^{+6}$Ti to $^{+5}$Ti to $^{+4}$Ti due to the decreasing of the centre-symmetry as the coordination changes from octahedral to square pyramidal to tetrahedral, respectively. The energy of the pre-edge peak decreases in the same order. Pre-edge peak energies for $^{+6}$Ti show a large variation because $^{+6}$Ti can have regular or distorted octahedral coordination, which have higher or lower pre-edge peak energies respectively. In other words, when the number of oxygen atoms increases in the Ti-neighborhood, a peak shifting towards higher energies and a diminishing of its relative intensities can be seen at that region. Thus, the degree of p–d hybridization of the electronic levels of O and Ti is related with the site-geometry of the Ti atom.

Therefore, Ti-K-edge XANES is a decisively established method to investigate Ti coordination in a wide kind of materials [30–34], even at MCM-41 mesoporous ones [35,36], but further methodology have to be added to clearly separate different contributions to XANES spectra due to coexistence of different Ti-surroundings in the same catalyst. With this purpose, Principal Component Analysis [37] (PCA) was employed to determine the number of reference model spectra needed to reproduce the experimental data. In general, this analysis can be applied when the variable under study, like absorbance in a set of XANES spectra [38–41], can be represented mathematically as a linear sum of minimum set of uncorrelated components (factors), if the number of spectra is larger than that of the components. An important property of this method lies in the fact that every factor makes a maximum contribution to the sum of the variances of the variable. Thus, it allows reducing a large set of data to a controllable set of basis functions (spectra).

In this work, XANES experimental data combined with PCA analysis of those spectra obtained for Ti-species in Ti-MCM-41 mesoporous silica are presented. The use of this methodology allows establishing the number and nature of Ti-species, according to the different synthesis method employed to obtain Ti-species grafted in the mesoporous of MCM-41 materials in a quantitative based way.

Is important to remark that the reaction conditions employed for the hydrothermal synthesis, as well as the sol–gel synthesis were performed with the objective to obtain more than one Titanium species (NN = 4–6), in order to corroborate the goodness of the characterization techniques and the chosen strategies.

2. Experimental

2.1. Samples preparation

MCM-41 catalysts were prepared with Ti incorporated in the framework of the mesoporous material by hydrothermal synthesis (H-Ti-MCM-41) following original procedure [25]. Furthermore, a second sample was prepared by sol–gel (S-Ti-MCM-41) using the following reactants: tetraethylortosilicate (TEOS), as a source of silicon, tetraisopropylortotitanate as a source of Ti, dodecyltrimethyl-ammonium bromide as template agent. Xerogels of SiO_2/TiO_2 were used as a starting material, according to the following steps:

Step a: The TEOS was hydrolyzed with HCl during 1 h and then added to a Ti solution in methanol at 0 °C. The solution obtained was shaken during 20 min.
Step b: The final solution of *step a* is turned into a gel by addition of the template agent at room temperature. To obtain an adequate pH, a 20% tetraethylortosilicate hydroxide (TEAOH) solution was added, and the final pH reached was 12. The obtained xerogel was heated at 60 °C during 2 h and then was dried at 110 °C during 12 h.
Step c: The xerogel obtained in *step b*, was soaked with an adequate solution of template agent by incipient impregnation. SiO_2/TiO_2 gel was washed in distilled water and was dried at 110 °C. The template agent was removed by warming by TPD method (programmed thermal desorption) at 1 °C/min from 100 °C to 500 °C in nitrogen atmosphere (20 ml/min) and later in air (20 ml/min) up to 500 °C during 12 h.

For better identification of the samples, the criterion for labels is the following: letter H or S between parentheses after Ti identifies samples obtained by hydrothermal or sol–gel synthesis, respectively. After MCM between parentheses appears the indication D or H for dehydrated or hydrated samples, and the letters O or N according to the removal procedure of the template (in presence of oxygen or nitrogen atmosphere, respectively). Finally, letter P means *partially hydrated* and T means *with template*.

Thus, for the case of the catalyst prepared by hydrothermal synthesis, two samples were prepared in different stages: before the elimination of the organic steering used as template agent (Ti(H)-MCM(T)) and after its elimination (Ti(H)-MCM(O or N)). The elimination of the template agent was done by two different ways: (a) in inert atmosphere of N_2 (Ti(H)-MCM(N)) and (b) in oxidant atmosphere of O_2 (Ti-MCM(O)). Catalyst prepared by sol–gel synthesis was denoted as Ti(S)-MCM.

In order to characterize the catalysts in anhydride conditions, all the samples (in powder) were dehydrated by calcination in N_2 flow (30 ml/min). Sample Ti(H)-MCM(TH) was treated at 140 °C during 4 h to obtain the sample Ti(H)-MCM(TD). Finally, samples Ti(H)-MCM(NH), Ti(H)-MCM(OH) and Ti(S)-MCM(H) were treated at 550 °C during 9 h to obtain the dehydrated samples Ti(H)-MCM(OD), Ti(H)-MCM(ND) and Ti(S)-MCM(D), respectively. To avoid catalyst hydration, special cells containing a calcination camera, with an entrance and an exit for N_2 flow were designed.

2.2. Experimental set-up and data reduction

2.2.1. XANES

The Ti-K-XANES experiments were performed at the XAS1 beamline of the LNLS (Laboratorio Nacional do Luz Síncrotron, Campinas, São Paulo, Brazil). It is provided with a monochromator with a double crystal of Si (1 1 1) and a vertical opening of slits of 0.5 mm, obtaining an estimated resolution of 0.8 eV [42]. The harmonic contamination of the beam was lower than 1%, the beam energy was 1.37 MeV [43]. All the samples were measured
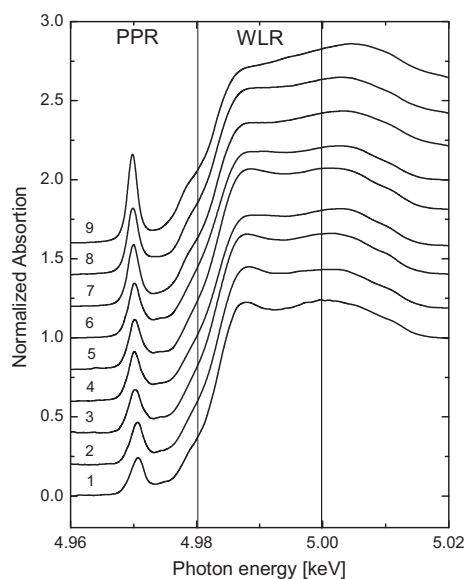
Fig. 1. XANES spectra of all the samples from nine to one: Ti(H)-MCM(ND), Ti(H)-MCM(OD), Ti(H)-MCM(TP), Ti(S)-MCM(D), Ti(H)-MCM(OP), Ti(S)-MCM(H), Ti(H)-MCM(OH), Ti(H)-MCM(NH) and Ti(H)-MCM(TH). Differences between different spectra are evidenced in the pre-peak region (PPR) and in the white line region (WLR).

in a transmission way using ionization chambers filled with air at room temperature and atmospheric pressure. The energy calibration was monitored measuring simultaneously a thin film of metallic Ti, together with each of the samples, through a third ionization chamber.

Catalysts were measured in a sample holder hermetically sealed, with Kapton windows, in order to hold pre-treated materials in desired conditions (see samples preparation) for its further XANES characterization.

2.2.2. Data reduction

The mathematical handling of XANES spectra consist in two fundamental and simple steps: the calibration of the energy scale and the normalization of the absorbance, being both mandatory to extract valuable information. The energy-scale calibration was reached by measurement of a reference of Ti-foil located between the second and the third ionization chamber, being the sample positioned between the first and the second ones. The edge position of the metallic Ti-reference was fixed at 4966 eV, considering the first zero of the second derivative of the spectrum. The XANES spectra analysis was performed by pre-edge background subtraction followed by normalization procedures described in the literature [44,45].

Experimental XANES spectra (Fig. 1) were analyzed with a program developed by Fernández-García [44–46] using factorial analysis of its most important components (Principal Component Analysis – PCA [37]). PCA assumes that the variable (absorbance of a set of XANES spectra) can be mathematically represented by a lineal combination of independent components known as factors or eigenvectors [29]. Thus, a typical situation where this method is really useful is in the reduction of a big set of data to obtain a handy group of basic functions (absorbance components). To determine which factors correspond to the signal and which ones to the statistic noise or error of low frequencies for the subtraction of the background and energy calibration, a F-test [47] is applied on the variance associated to kth factor and the sum of the variances of the group of auto values related to that noise. The kth factor is accepted as a principal component (signal), when the significant level of F-test, %SL [48], is lower than any reference test
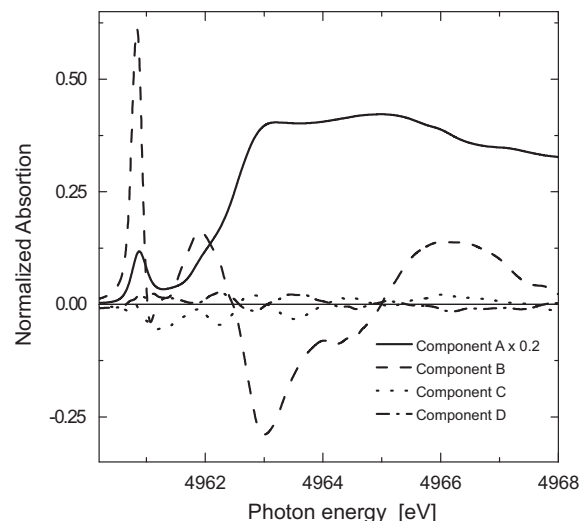

Fig. 2. Abstract components of absorbance, obtained from experimental XANES spectra of catalysts using PCA. Components A and B represent principal components of the set of data corresponding to Ti-species present in the MCM-41 while C and D reproduce the noise of the experimental data (see text in Section 3).

level. According to Fernández-García et al. [48], the test level can be considered as 5%. The reason between reduced auto values $R(r)$ [47,49] and the empiric function IND [50] were also used to extract the main components from the noise (Fig. 2). The reader interested in the specific application fundaments of this method on XANES analysis can review several and complete references [51,52].

3. Results and discussion

As mentioned in the introduction, electronic transitions evidenced by Ti-K-XANES experiments are a powerful probe to analyze the Ti-coordination. Fig. 1 clearly shows the variation in both position and intensity of the spectra in the pre-peak region (see PPR in Fig. 1) as well as in the white line region (see WLR in Fig. 1). Qualitatively, according to these results, the average coordination value for Ti in each sample (considering all the Ti-species present in each sample) is: Ti(NN) = 4 < Ti(H)-MCM(ND) < Ti(H)-MCM(OD) < Ti(H)-MCM(TP) < Ti(S)-MCM(D) < Ti(H)-MCM(OP) < Ti(S)-MCM(H) < Ti(H)-MCM(OH) < Ti(H)-MCM(NH) < Ti(H)-MCM(TH)) < Ti(NN) = 6.

This qualitative analysis indicates that depending on the sample preparation and after treatment, the Ti electronic structure is modified. To correlate this electronic modification with the Ti environment distortion we try to model the set of spectra using spectra of reference compounds with different coordination and symmetries around the Ti atoms. This approach does not give a reliable reproduction of the set of spectra. This lack of reproduction could be attributed to the high number of possible distortion that is not possible to find in the reference samples but are present in the set of samples under investigation. For this reason, PCA was performed to quantify the coordination of Ti in each sample, i.e. the number and amount of the different Ti-species in each sample according to their coordination number.

3.1. Determination of total number of Ti-species

Fig. 2 shows the four principal abstract components determined by PCA. From the same figure, it is also possible to recognize that just the first two components (A and B in Fig. 2) contribute to the signal, since from third component (see C and D in Fig. 2) the contribution is in between the level of the noise. Strictly, according to the parameters of the PCA, the values % SL and $R(r)$ reported in

Table 1
PCA parameters obtained for each abstract component. All the XANES spectra were included for this analysis.

Factor no.	Eigenvalue	$R(r)$	IND	Variance	%SL
1	5.96E+02	1.17E+03	7.85E−04	99.92	0
2	4.33E−01	1.10E+01	3.68E−04	0.073	0.41
3	3.25E−02	6.10E+00	3.06E−04	0.005	6.04
4	4.23E−03	9.13E−01	4.67E−04	0.001	35.56
5	3.44E−03	1.70E+00	7.56E−04	0.001	30.48

Table 2
PCA parameters obtained for each abstract component. Data corresponding to S-Ti-MCM41 samples were excluded for this analysis.

Factor no.	Eigenvalue	$R(r)$	IND	Variance	%SL
1	1.04E+03	4.39E+02	3.76E−04	99.781	0
2	2.15E+00	2.15E+01	1.14E−04	0.207	0
3	8.99E−02	3.59E+00	8.28E−05	0.008	1.27
4	2.23E−02	2.60E+00	7.44E−05	0.002	6.08
5	7.57E−03	1.15E+00	7.93E−05	0.001	16.33
6	5.72E−03	1.57E+00	7.90E−05	0.001	11.34

Table 1 indicates the presence of three pure species in all the group of studied samples of Ti-MCM-41. On the other hand, the behavior of IND could mislead to the existence of a fourth component. As it is discussed by Maschmeyer et al. [36], this occurs because the empiric function IND was defined for systems where source of noise is mainly statistic, witch is not our case. Besides this statistic component of noise, there is another one owing the process of background subtraction and energy calibration (Fig. 2). In agreement with criteria employed in reference for this type of situation [50], we can safely use %SL and $R(r)$ as the best parameters to define the number of principal components. Fixing the test level value at 5% and observing the behavior of $R(r)$, we can establish the number of principal components in three. A new PCA, excluding now the corresponding XANES spectrum of S-Ti-MCM-41 (Ti(S)-MCM(H) and Ti(S)-MCM(D)) sample, we obtained the results showed in Table 2. Following the analysis presented below, we can establish that the number of main components for this group is two.

3.2. Structure determination of Ti-species

According to the previous section, the number of components of the complete group of samples (hydrothermal synthesized samples and by sol–gel method in different grades of hydration) determined by PCA is three. As it was mentioned in Section 2.2.2, such components have not "explicit" physical meaning (i.e. they do not necessary represent real species) (Fig. 2). In order to transform these abstract components to spectra with physical meaning (the real spectra of pure species), Iterative Transformation Factor Analysis (ITFA) [38] algorithm was used. The results of this statistic test are shown in Fig. 3, where each individual real component (components 1, 2 and 3) exhibits a distinguishable pattern, in particular the component number one, because of the high of the pre-peak, it seems to be the responsible for the 4-folded component of Ti. The other two components represent Ti-species with higher coordination. Fig. 4 shows the position (energy) and height (intensity) of the pre-peak for pure species or principal components obtained from ITFA and reference compounds.

In addition, Fig. 5 shows a detailed description of the concentration of pure components in each sample. The contribution of the three principal components to the spectra of each sample can be represented in a three-dimensional Cartesian plot. This plot is generated by considering as the base axes to first and third components and as height the second of the principal component.

The composition of each spectrum as a linear combination of the pure components appears in Table 3. In Fig. 5, it is possible to iden-
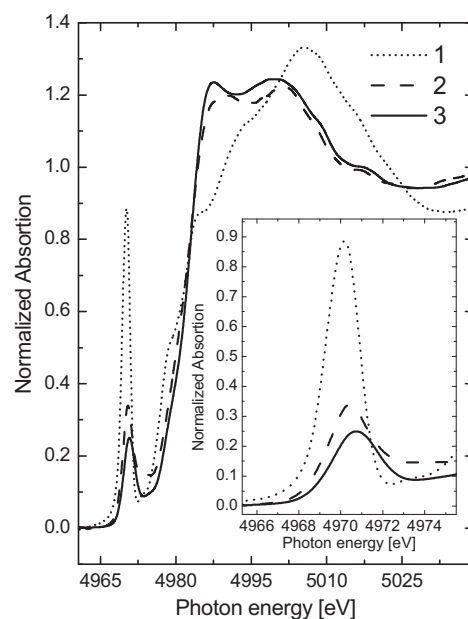

Fig. 3. the three pure and real components (1, 2 and 3) of absorbance obtained by Iterative Transformation Factor Analysis (ITFA) considering the total set of XANES data shown in Fig. 1. The inset shows the detail of the pre-peak region.
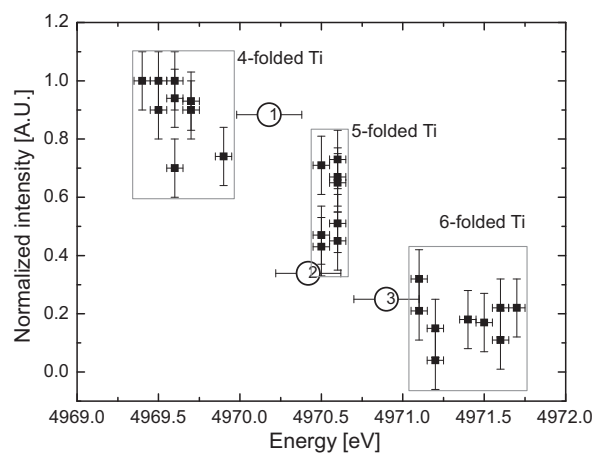

Fig. 4. Energy position and height of the prepeak (normalized according to Ba_2TiO_4 reference compound) for Ti oxides [30] and the three pure species in the catalyst obtained from ITFA.
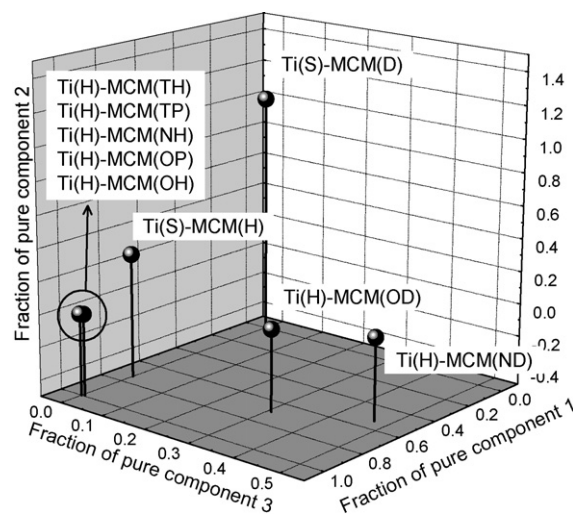

Fig. 5. Representation of the relative concentration of the pure species obtained by ITFA (shown in Fig. 3) in each sample.

Table 3
Pure component concentration obtained by ITFA (see Fig. 3) for each sample. Relative error for concentration is about 10%.

Sample	Comp. 1 [%]	Comp. 2 [%]	Comp. 3 [%]
Ti(H)-MCM(TH)	3	0	97
Ti(H)-MCM(ND)	55	0	45
Ti(H)-MCM(NH)	2	0	98
Ti(S)-MCM(H)	12	11	77
Ti-MCM(OH)	7	0	93
Ti(S)-MCM(D)	13	35	52
Ti(H)-MCM(TD)	26	0	74
Ti(H)-MCM(OD)	28	0	72
Ti(H)-MCM(OP)	11	0	89

tify different regions: samples Ti(H)-MCM(TH), Ti(H)-MCM(TP), Ti(H)-MCM(NH), Ti(H)-MCM(OH) and Ti(H)-MCM(OP). This set is almost located in the same place, indicating that they have almost the same Ti-species composition, with the absence of pure 5-folded Ti-species (component number 2 obtained by ITFA). In the same plane we can also find Ti(S)-MCM(H) and Ti(S)-MCM(D) samples. In particular, the first set of samples can be reproduced just by component 3 (the pure specie with highest Ti-coordination). The rest of the samples, i.e. Ti(H)-MCM(OD) and Ti(H)-MCM(ND) are the only ones with the presence of pure 4-folded Ti (and with lower concentration of pure Ti-species with NN = 6).

According to PCA (see Fig. 5 and Table 3), for all cases, the relative concentration of the 6-folded Ti-species grows as much as the grade of hydration of the samples increases. Dehydrated sample obtained by hydrothermal synthesis (Ti (H)-MCM(ND)), has the greater concentration of tetrahedral environment (component 1) for Ti sites.

In summary, according to the results shown in Fig. 5, Ti atoms have different average coordination in different catalyst. In the case of the synthesized catalysts by hydrothermal synthesis in anhydride conditions, Ti is almost located in a tetra-coordinated chemical environment when the template is eliminated in inert atmosphere (N_2). In the hydrated samples an increase in the average number of the oxygen near neighbors is observed.

4. Conclusions

A complete and very precise determination about the kind and concentration of each Ti-species in different Ti-MCM-41 catalysts were obtained by in situ and ex situ Ti-K-XANES study in combination with PCA and ITFA study.

The dehydrated Ti-MCM-41 catalyst obtained by hydrothermal synthesis has the majority of the species (about 55% in Ti(H)-MCM(ND) and 28% in Ti(H)-MCM(OD)) with Ti tetrahedral-coordinated, being this concentration lower when Ti-MCM-41 is obtained (and dehydrated) by sol–gel method (around 13%). The coordination of Ti in samples obtained by hydrothermal or sol–gel synthesis is increased closely to six when the samples are hydrated (being even higher for hydrothermal synthesis method). The presence of the template in the samples does not affect the Ti-coordination when the template is removed in presence of nitrogen. In the case of the sol–gel synthesis, Ti-sites have higher average coordination than Ti-species obtained by hydrothermal one, independently of the degree of hydration.

Acknowledgements

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