Incorporation of Ti(III) into the $\text{AlPO}_4\text{-5}$ framework by direct synthesis

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ABSTRACT. This work focuses on the synthesis and characterization of a conceptually innovative series of TAPO materials, particularly centered in the AFI-structured TAPO-5. Unlike the conventional TAPOs, the so-called Ti(III)APO-5 are prepared by using Ti(III) sources. This strategy aims to avoid the presence of both Ti-O-Al and Ti-O-Ti bonds in TAPOs, undesired for catalytic purposes. The thermodynamic stability of this oxidation state of Ti in water and in the presence of air is low, but the preparation of the gel and the filling of the autoclaves under N_2 atmosphere allowed Ti to maintain its 3+ oxidation state in a considerable proportion in the hydrothermally-crystallized solids. The materials were characterized by powder XRD, ICP chemical analysis, SEM, DR-UV-visible spectroscopy, TGA and ^{31}P and ^{27}Al MAS NMR. DR-UV-visible spectroscopy certified the presence of Ti(III) in both tetrahedral and octahedral environments in the as-made samples before being exposed to air, whereas ^{31}P MAS NMR

indicated the vicinity of Ti in the second coordination sphere of P in the already oxidized sample. Although once dried and calcined in air Ti(III) is entirely oxidized to Ti(IV), Ti(III)APO-5 materials present key singularities against conventional TAPO-5. Thus, apart from the presence of Ti(OP)₄ environments, the charge transfer transition detected by DR-UV-vis appears at lower wavelength, whereas both TGA and ²⁷Al NMR indicates a peculiar hydration of the as-prepared samples, which is unprecedented in conventional TAPO-5. Based on these characterization features, the possible nature of the Ti centers generated by this synthesis approach is discussed.

KEYWORDS. TAPO-5, Ti(III) sources, Ti(OP)₄ environments, water retention, isomorphous substitution mechanisms.

1. INTRODUCTION

The isomorphous substitution of elements in suitable oxidation state and able to be accommodated in tetrahedral coordination into the framework of zeolite materials is a convenient procedure to render active and often also selective microporous catalysts. In the particular case of titanium, its incorporation as Ti(IV) in the framework of zeolite silica polymorphs of structures such as the medium-pore MFI [1] or the large-pore Beta [2] led to active catalysts able to oxidize a number of interesting organic substrates under mild conditions by using peroxides as oxidation agents [3].

Prompted by the successful preparation of these Ti-containing catalysts based on a silica framework, approaches to the incorporation of this element into microporous crystalline aluminophosphates (AlPOs) were also attempted [4-6]. As a result of this research effort, a

number of AlPO_4 -type structures containing titanium have been produced along the years, including the large pore TAPO-5 [7] and TAPO-36 [8]; the medium-pore TAPO-11 [7], TAPO-41 [9] and TAPO-31 [10]; the small-pore TAPO-34 [11], and even the extra-large-pore materials Ti-VPI-5 [12] and TAPO-8 [13].

Although some of these materials has been shown to be active in the selective oxidation of different organic molecules in liquid phase by using hydrogen peroxide aqueous solution as oxidant [14, 15], the analysis of the results already published for different TAPO catalysts allow to conclude that their activity is, in general, much lower than that corresponding to titanium substituted silica zeolites. It is possible that these results have somewhat discouraged a more intensive exploration of the potential of Ti-containing AlPO materials as mild oxidation catalysts. However, the chemistry of crystalline aluminophosphate is so different and, in several aspects, richer than that of silica zeolites, that we believe the incorporation of titanium in their framework still deserves further attention.

Several factors might contribute to the reported comparatively low activity of TAPO catalysts. First, AlPO_4 -type materials are much more hydrophilic than their neutral silica counterparts [16]. This would eventually lead to a preferential adsorption of water (and ultimately of hydrogen peroxide too) over that of the hydrophobic organic substrates from oxidation reaction mixtures. As a consequence, the effective concentration of the organic substrate inside the intracrystalline pores would be much reduced, and hence a poor catalytic activity would be observed. A second factor to account for the low activity could be the different chemical environment of the Ti atoms into the AlPO_4 framework and in the silica zeolites. The isomorphous substitution of Si by Ti in the latter renders tetrahedral $\text{Ti}(\text{OSi})_4$ sites [2]. In the case of AlPO_4 structures, tetravalent Ti(IV)

would substitute P(V) [10]. This would give place to Ti-O-Al bonds, and it is well-known that the presence of Al in the framework of Ti-zeolites has a deleterious effect on the catalytic activity [17]. Recently, it has been reported that not only one Ti atom can substitute one P atom, but two Ti atoms can replace simultaneously the Al and P atoms of an Al-O-P pair, in such a way that Ti-O-Ti bonds can be created within the framework [18-21]. This new finding would also contribute to explain the low activity of TAPO materials, because it is well known that the optimum activity of Ti-zeolites requires the titanium atoms to be isolated in the framework, i.e., they must be only present in Ti-O-Si environments, and the formation of Ti-O-Ti bonds should be avoided [22].

According to the current knowledge that has been briefly summarized above, in order to improve the catalytic activity of TAPO materials, other substitution mechanisms of Ti in the AlPO_4 lattice should be explored to avoid both the presence of Ti-O-Ti and Ti-O-Al bonds. The substitution mechanisms of heteroatoms (atoms other than Al and P) into the AlPO_4 frameworks is governed by the oxidation state of the substituent dopant, since its size is generally appropriate to adopt the required tetrahedral coordination in the lattice. It does not exclude the eventual increase of the coordination number of the heteroatom by additional extraframework species, like water molecules. In this regard, titanium atoms in low oxidation state, Ti(III) in particular, would replace Al(III) and not P(V), in order to avoid the excessive negative charge (two units per substitution) that would result from the latter. Moreover, this replacement would lead to a neutral lattice, would produce Ti-O-P environments, and would avoid undesired Ti-O-Ti bonds formation, because this would require the substitution of P(V) by Ti(III). Additionally, the presence of isolated Ti centers bonded to P atoms through oxygen atoms, i.e. Ti(OP)_4 , would

eventually exhibit a catalytic pattern in the oxidation of organic substrates different to that commonly observed for Ti-zeolites.

While Ti(III) in aqueous solution and in absence of any complexing agent is readily oxidized by being exposed to air, water itself is a much less efficient oxidant of this cation, and its oxidation capacity is strongly dependent upon the pH of the media [23], in such a way that, as an example, TiCl_3 solutions in concentrated hydrochloric acid are traded. Moreover, crystals of an open framework titanium phosphate containing an equimolecular ratio of both Ti(III) and Ti(IV), has been made hydrothermally by using titanium metal and 1,3-diaminopropane as template [24]. Interestingly, no Ti-O-Ti bonds are present in this structure, and the Ti(III) centers are octahedrally coordinated to four PO_4 groups and two water molecules in trans position. Other mixed valence Ti(III)/Ti(IV) phosphate-based (actually gallophosphate TiGaPO-1) material [25] has two different octahedral Ti environments, Ti(OP)_6 for Ti(IV) and $\text{Ti(OP)}_4(\text{H}_2\text{O})_2$ in which Ti is basically as Ti(III), and neither has Ti-O-Ti bonds. Both materials maintain Ti(III) for very long time, especially the phosphate-based one as the gallophosphate slows down but does not prevent its oxidation to Ti(IV), which is completed in a few months [25]. In the same sense, mixtures of TiCl_3 and phosphoric acid are very slowly oxidized even by air [26], in such a way that phosphate anions seems to be particularly suitable to stabilize Ti(III) species in aqueous solution.

Based upon these considerations, we have explored the hydrothermal synthesis of crystalline microporous titanium aluminophosphates by using Ti(III) compounds as the source of this element [27]. It has been recently reported that the AFI-type materials obtained by using this synthesis strategy are efficient catalysts for the oxidation of cyclohexene with either hydrogen

peroxide or tert-butylhydroperoxide as oxidants. These catalysts show a very high selectivity to the allylic oxidation of this cyclic olefin [28, 29], a reaction pathway quite different to the oxidation of the double bond to form the corresponding epoxide so characteristic of Ti-zeolites.

This work reports the synthesis procedure of several Ti-containing materials with the AFI topology from gels containing Ti(III), and their physico-chemical characterization, in order to assess the effective incorporation of this metal into the framework and to shed light on the nature of the generated Ti centers, which showed unusual catalytic behavior in the oxidation of cyclohexene [28, 29].

2. EXPERIMENTAL

2.1. Materials preparation

Ti(III)APO-5 samples with different titanium content were prepared with either an aqueous solution of TiCl_3 in hydrochloric acid (~ 10 wt. % of TiCl_3 in 20-30 wt. % HCl aqueous solution, with the exact amount of both components provided by the supplier Aldrich) or TiCl_3 powder (Aldrich) as Ti(III) sources, from gels with the following molar composition: $(1-x) \text{ Al} : y \text{ P} : x \text{ Ti(III)} : z \text{ SDA} : 25 \text{ H}_2\text{O} : n \text{ HCl}$.

N-methyldicyclohexylamine (MCHA, Aldrich) and tetraethylammonium hydroxide (TEAOH, 35 wt. % in water, Aldrich) were used as structure directing agents (SDA); phosphoric acid (85 wt. % in water, Aldrich) and aluminum hydroxide $(\text{Al}(\text{OH})_3 \cdot x\text{H}_2\text{O})$, Sigma) were used as sources of phosphorous and aluminum, respectively. The choice of MCHA and TEAOH amongst the tens of organic structure-directing agents able to produce AlPO_4 -based materials [30] was based on

their high specificity to the AFI structure materials [31, 32] and/or on their quick kinetics of crystallization [31, 33] in order to minimize the Ti(III) oxidation before crystallization. When TiCl_3 in hydrochloric acid aqueous solution was used, z was varied to compensate the changes of pH provoked by the accompanying HCl (n), forcing the gel to have pH values in the range 6.0-7.5 for MCHA systems and in the range 5.0-6.0 for TEAOH ones. When the powder TiCl_3 source was used, no HCl was added ($n = 0$) and therefore the ratio of the SDA/P was always constant ($z = 0.8$ for MCHA systems). The preparation of the synthesis gel and the filling of the autoclaves were done in a glove bag purged with nitrogen. In a representative synthesis procedure, the required amount of the titanium source was added under stirring to a solution of phosphoric acid in deionized water. This results in a purple solution. Then, the aluminum hydroxide and the SDA were subsequently added, and the resulting gel was kept under vigorous stirring for one hour and poured into Teflon-lined stainless steel autoclaves. Once closed, the autoclaves were taken out from the glove bag and statically heated at 175 °C for 4 h or 18 h for the samples synthesized with MCHA, and at 135 °C for 4 h for those prepared with TEAOH as SDA. After that, the autoclaves were cooled down to room temperature, opened outside the glove bag, and the solid recovered by filtration, washed with deionized water and dried overnight at room temperature. It is noteworthy that the content of the autoclave was still of purple color after the heating treatment, and the solid recovered by filtration kept this color for a while during the filtration and washing procedure. However, during the overnight drying at room temperature this color disappeared and the solid became yellowish white.

In one specific experiment, the autoclave was opened inside the glove bag always under N_2 atmosphere, and its content was filtered, washed and dried there, in order to avoid as much as possible the oxidation of the Ti(III) present in the recovered solid.

The nomenclature of the samples prepared with Ti(III) sources has been selected following the next pattern: SDA-Ti content Ti source ('p' for powder and 's' for solution)-crystallization time. As an example, the sample MCHA-4p-4h was prepared with MCHA as SDA, adding an amount of Ti to occupy 4 % of the Al sites in a theoretical $\text{AlPO}_4\text{-5}$ framework (i.e., $\text{Ti}/(\text{Ti} + \text{Al}) \cdot 100$), using TiCl_3 powder as Ti(III) source, and it was crystallized for 4 hours.

A Ti(IV)APO-5 sample was synthesized using titanium isopropoxide (Aldrich) as Ti(IV) source, MCHA as SDA and starting from a gel with the following molar composition: 1.0 Al : 0.96 P : 0.04 Ti(IV) : 0.8 MCHA : 25 H_2O . Unlike the preparation of the Ti(III)APO-5 gel, no special care of the atmosphere was taken along the gel preparation. Aluminum hydroxide was added over the solution of phosphoric acid in deionized water followed, after *ca.* 10 minutes of continuous stirring, by the addition of MCHA. Once the slurry was homogenized, titanium isopropoxide was finally added. The final gel was further stirred for 1 h and subsequently introduced into the Teflon-lined stainless steel autoclave for the static hydrothermal treatment at 175 °C for 7 h. Afterwards the sample was filtered, washed and dried as usually, under ambient atmosphere. This sample was denoted as MCHA-4-Ti(IV).

The as-made samples were calcined at 550 °C for 5 h under a flow of air of $100 \text{ mL} \cdot \text{min}^{-1}$, after heating up to this temperature at a rate of $3 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$ under a N_2 flow (also of $100 \text{ mL} \cdot \text{min}^{-1}$) and keeping at 550 °C for 1 h still under flowing N_2 .

2.2. Characterization techniques

Nature and purity of crystalline phases were studied by powder X-ray diffraction (PXRD) using a PANalytical X'Pert Pro diffractometer (Cu $\text{K}\alpha$ radiation). Unit cell parameters were estimated

using the XRD software CELREF from PXRD patterns of the as-prepared samples physically mixed with Si metal, whose reflection 111 was taken as reference of 2Θ position (28.443°). These patterns were registered with 2Θ steps of 0.01° and radiation time of 50 s per point. The fourteen most intense non-overlapped reflections were selected and adjusted to the space group P6cc (no. 184). Diffuse reflectance UV-visible (DR-UV-vis) spectra were recorded on a Cary 5000 Varian spectrophotometer equipped with an integrating sphere with the synthetic polymer spectralon as reference. The resultant data were expressed according to Kubelka-Munk function. The chemical composition of the solids was determined by inductively coupled plasma (ICP-OES) spectrometry with an ICP Winlab Optima 3300 DV Perkin-Elmer spectrometer. Scanning electron microscopy (SEM) micrographs were registered in a FEI Nova NANOSEM microscope with a vCD detector. Thermogravimetric analysis (TGA / DTG) were recorded in a Perkin Elmer TGA7, from 25°C to 900°C at a heating rate of $20^\circ\text{C}\cdot\text{min}^{-1}$ with an air flow of $40\text{ mL}\cdot\text{min}^{-1}$. Just before the TG measurements, the samples were exposed to a humidity-controlled atmosphere given by a saturated solution of $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$ (33 % of humidity degree), within a desiccator for one day.

All Nuclear Magnetic Resonance (NMR) spectra were acquired in a Bruker AV-400-WB spectrometer operating at 104.26 and 161.97 MHz for registering ^{27}Al and ^{31}P spectra, respectively, under magic-angle spinning (MAS) technique. A 4-mm probe and a spinning rate of 10 kHz were used for all spectra. ^{27}Al MAS NMR spectra were acquired by applying pulse length of $0.4\text{ }\mu\text{s}$ corresponding to a flip angle of $\pi/30$ and using a pulse delay of 2 seconds. The applied pulse length in the ^{31}P MAS NMR spectra was of $3.0\text{ }\mu\text{s}$ corresponding to a flip angle of $\pi/4$ and the pulse delay was of 100 seconds (and 200 seconds for a particular experiment). ^1H to ^{31}P cross-polarization MAS NMR spectra were acquired by applying a $\pi/2$ pulse of $3\text{ }\mu\text{s}$ over the

^1H channel, using a contact time of 3.0 ms and a delay time between two consecutive pulses of 4 s. ^{27}Al and ^{31}P chemical shifts were referenced to the primary references of 1 M $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and H_3PO_4 85 wt.% aqueous solutions, respectively. ^{27}Al MAS NMR spectra were simulated using the Dmfit program, designed by Massiot et al. [34].

3. RESULTS AND DISCUSSION

3.1. X-ray diffraction and chemical analysis

By following the procedure described in the experimental section, several Ti(III)APO-5 samples were prepared from the two titanium sources and with different Ti content, as well as with the two different SDA (Table 1). Powder X-ray diffraction patterns of some as-made solids are shown in Figure 1. These samples were selected as representative ones of the different Ti(III) content, different Ti(III) source, different SDA, and different crystallization time, and their corresponding patterns have been strategically placed in such a way that moving from one to the following one (either up or down) only one of these parameter are changed, excepting moving between MCHA-4s-18h and TEAOH-4s-4h, since both SDA nature and crystallization time are changed. All these XRD patterns (and these of the rest of the samples discussed along this article) show the presence of intense reflections characteristic of AlPO_4 -5 type materials, and no other crystal phases are detected. The differences in relative intensity and in peak broadening must be due to some changes in morphology and crystal size, respectively. Moreover, as it will be discussed below, examination of SEM images of any of the samples does not show the any significant amounts of amorphous material. Table 1 shows that both MCHA and TEAOH are efficient SDA to crystallize the AFI-type materials under the conditions described in Experimental section.

(Figure 1, XRD)

Isomorphic substitutions quite often bring changes in the unit cell parameters of the host framework. Indeed, these structural alterations have been taken as support (and even as evidence) that heteroatom incorporation has really occurred. In the case of $\text{AlPO}_4\text{-5}$ structure, unit cell parameter a (and b) was shown to be particularly sensitive to the heteroatom incorporation, whereas c is practically unaffected [35, 36]. Figure 2 shows the unit cell parameter a of the structure AFI *versus* the Ti content of different as-prepared $\text{AlPO}_4\text{-5}$ and Ti(III)APO-5 samples with different Ti content and after being exposed to air for several days. All samples of Figure 2 were prepared with MCHA as SDA. The magnitude of parameter a linearly correlates with Ti content, at least up to a Ti content of 0.021 (Table 1). Beyond this Ti content, that linearity seems to be lost but the increase of the parameter a with Ti content continues being systematic. Although it is tempting to attribute the tendency observed in Figure 2 to the expansion of the unit cell provoked by the larger ionic ratio of Ti compared with these of the framework cations Al and/or P, so many phenomena associated to the Ti incorporation take place (see below), which can either explain that trend.

(Figure 2, Unit cell parameter a)

Chemical analyses indicate the presence of titanium in the samples (Table 1). However, Ti content does not follow a linear correlation with the amount of titanium in the starting gels. Nevertheless, both Ti contents increase in a parallel way beyond 2 % (referred to the total molar amount of Ti+P+Al in the gel) (Table 1). The amount of Ti incorporated in the samples varies between 0.06 and 1.2 atoms per unit cell, as a function of its concentration in the synthesis gel.

On the other hand, the use of either TiCl_3 powder or its solution in hydrochloric acid as titanium sources do not show a perceptible influence on the final Ti content of the AFI-structured samples. The use of MCHA or TEAOH as SDA neither seems to be determinant in the tendency of Ti incorporation.

Table 1. Molar compositions of Ti(III)APO-5 gels with two different Ti(III) sources, two SDAs and different Ti content, and Ti, Al and P molar content of as-made samples determined by ICP-OES. The data corresponding to an AlPO_4 -5 (MCHA- AlPO_4) and to the sample MCHA-4-Ti(IV) are also included.

	Sample	Gel composition*					Solid composition		
		Ti (x)	Al	P (y)	z	n	Ti	Al	P
TiCl ₃ powder	MCHA- AlPO_4	0	1.00	1.00	0.80	0	0	1.029	0.971
	MCHA-0.5p-4h	0.005	0.995	1.00	0.80	0	0.006	1.012	0.982
	MCHA-1p-4h	0.01	0.99	1.00	0.80	0	0.009	1.011	0.980
	MCHA-2p-4h	0.02	0.98	1.00	0.80	0	0.034	1.025	0.941
	MCHA-4p-4h	0.04	0.96	1.00	0.80	0	0.069	1.026	0.905
	MCHA-4p-18h	0.04	0.96	1.00	0.80	0	0.065	0.928	1.007
	TEAOH-2p-4h	0.02	0.98	1.50	0.80	0	0.033	0.970	0.997
TiCl ₃ solution	MCHA-1s-18h	0.01	0.99	1.00	0.80	0.35	0.014	0.990	0.996
	MCHA-2s-18h	0.02	0.98	1.00	0.80	0.32	0.021	0.962	1.017
	MCHA-4s-18h	0.04	0.96	1.00	0.85	0.52	0.062	0.988	0.950
	MCHA-10s-18h	0.10	0.90	1.00	1.50	0.79	0.128	0.985	0.887
	TEAOH-2s-4h	0.02	0.98	1.50	1.05	0.32	0.025	0.927	1.048

	TEAOH-4s-4h	0.04	0.96	1.50	1.12	0.52	0.042	0.902	1.056
Ti(IV)	MCHA-4s-Ti(IV)	0.04	1.0	0.96	0.8	0	0.047	0.975	0.978

*The general molar gel composition was: $(1-x)$ Al : y P : x Ti(III) : z SDA : 25 H₂O : n HCl.

3.2. Scanning Electronic Microscopy

Figure 3 shows representative SEM micrographs of selected samples on behalf of different morphologies of the crystals and aggregates. All of them are formed by polycrystalline aggregates of different shapes but of similar sizes, in the range from 15 to 30 μ m. The sample MCHA-1s-18h represents the group of samples obtained as spherical-shape aggregates of rod-like crystals. That morphology resembles that of the homologous samples MCHA-0.5p-4h, MCHA-1p-4h and MCHA-2p-4h [29]. The sample MCHA-2s-18h presents a unique morphology in this series of samples, which could be described as wad-shaped aggregates. This morphology shape has been described for some AlPO₄-5-based materials prepared with this SDA [32, 37], although the crystals of the latters were of smaller size. As they were previously described [29], the samples prepared with MCHA as SDA and 4 % of Ti theoretically replacing Al sites, are obtained as hexagonal prism-like agglomerates of fused non-isolable crystals, as shown by MCHA-4s-18h. The sample MCHA-10s-18h is also formed by fused non-isolable crystals aggregated in cylindrical agglomerates. The three samples prepared with TEAOH as SDA, represented in Figure 3 by the sample TEAOH-4s-4h, are constituted by aggregates of spherical shape made by sub-micrometric thin sheets.

(Figure 3. SEM)

3.3. UV-visible spectroscopy

While chemical analysis confirms the effective incorporation of titanium in the crystals, do not give any clue on its oxidation state. The first indication of the actual presence of Ti(III) in the solid recovered from the autoclaves after the hydrothermal treatment is provided by its purple color (Scheme 1), which is quite similar to the color of the starting synthesis gel. This color remains unaltered as far as filtration, washing and drying processes of the solid are carried out inside the glove bag under nitrogen atmosphere. However, the solid becomes yellowish white as it is exposed to air. These observations evidence that at least a large amount of the initial Ti(III) has remained in its low oxidation state along the crystallization process.

(Scheme 1, pictures)

UV-visible spectra of these materials reflect in more detail the environment and oxidation state of the titanium centers in the solids (Figure 4). In the UV region of the as-made purple material, two intense absorption bands centered at 225 nm and 275 nm are clearly observed. As the material is exposed to air, the band at higher wavelength disappears. In order to interpret these results, these spectra have been compared to that corresponding to a mixed-valent Ti(III)/Ti(IV) phosphate containing Ti atoms in a mixture of octahedral-tetrahedral coordination [24]. In this compound, no Ti-O-Ti bonds exist, and the titanium centers are therefore isolated. Moreover, the Ti(III) atoms are found in octahedral coordination linked to four P atoms through oxygen bridges and two water molecules, while Ti(IV) is also octahedrally coordinated to six oxygen atoms linked to P. The UV-visible spectrum of this material shows the presence of two bands, centered at 220 nm and 280 nm, which are characteristic of the charge-transfer process of the oxygen to titanium in Ti-O bonds. Based on this result, the bands observed at lower (225 nm) and higher

(275 nm) wavelength in the spectrum of the as-synthesized sample in this work, could be due to the presence of O-Ti(IV) and O-Ti(III) environments, respectively. In the spectrum of the oxidized yellowish sample, no Ti(III) would be present and hence, no band at 275-280 nm is clearly detected. The presence of Ti(IV) in the sample that has not been exposed to air, should be due to the partial oxidation of Ti(III) initially present in the gel during the crystallization process. However, the oxidation process should affect minor fractions of the initial Ti(III), owing to the intense color of the samples and the relatively high intensity of the bands assigned to this metal in that low oxidation state.

(Figure 4, UV-vis)

In the visible region of the purple as-made material MCHA-4s-4h, two partially overlapping bands are observed at 475 nm and 550 nm, and a broad shoulder is also detected at about 860 nm. The Ti(III)/Ti(IV) reference material shows a single broad band centered at *ca.* 500 nm, which, according to its crystal structure, is due to the d-d transitions of Ti(III) centers coordinated to four (-OP) units and two water molecules. Similarly, the UV-visible spectrum of the valence-mixed TiGaPO-1 material showed also a single broad d-d transition band centered at 495 nm, attributed to the Ti(III) environment $\text{Ti}^{\text{III}}(\text{OP})_4(\text{H}_2\text{O})_2$ [25]. Therefore, the two bands observed in the spectrum of the as-made Ti(III)APO-5 material are also attributed to d-d transitions of Ti (III) centers present in the AFI framework, and the fact that two bands are observed might be due to distortion of the octahedral symmetry of the metal environment. This result also reveals that the Ti(III) present in the AFI framework should be linked to additional molecules, probably water, in order to complete its octahedral coordination. However, the

hydrated Ti(III) in aqueous solution undergoes spontaneous deprotonation to give hydrated Ti-OH species [38], and therefore hydroxo beside water molecules could also coordinate the Ti(III) centers in the framework. In any case, after exposure of the sample to air, the d-d transition bands disappears, as expected due to the oxidation of Ti(III) to Ti(IV), confirming this assignment.

Regarding the assignment of the very wide shoulder centered at *ca.* 860 nm, it is evident the similitude in both wavelength position and substantial broadening with that reported at 870 nm in TAPO-5 samples [18, 19] after being reduced at high temperature under H₂ atmosphere. Interestingly, that band was attributed to Ti(III) incorporated into the AlPO₄ framework in a tetrahedral coordination.

DR-UV-vis spectra of the as-made samples exposed to air, containing different amount of Ti and prepared from both Ti(III) sources, are given in Figure 5. For the samples prepared from solid TiCl₃ and MCHA as SDA, a single intense band centered at wavelength range 213-222 nm domains the spectra, being centered at *ca.* 214 nm for the samples with lower Ti content (samples MCHA-0.5p-4h, -1p-4h and -2p-4h). However, the band becomes slightly broader and more asymmetrical as Ti content increases, being progressively more intense in the region above 250 nm. Moreover, for the Ti-richest sample (MCHA-4p-4h), a slight red shift of the maximum is observed, as it is centered at 222 nm. Similar but no so systematic behavior was found in the samples obtained from TiCl₃ solution as Ti source. In this case, the shoulder is clearly visible even in the spectrum of the sample with the lowest Ti content (not shown). The use of TEAOH as SDA produces a general red shift of the spectra as compared with those of the samples prepared from MCHA, and this effect is more pronounced for the samples synthesized from

TiCl₃ solution (Figure 5). In this last case, the band is very broad and centered at 230 nm. It can be also remarked that no bands at 330-350 nm were observed in any of the spectra, which excludes the presence of TiO₂ anatase phase.

(Figure 5, Different UV-vis spectra)

As it has been discussed above, the intense band centered at 213-222 nm is due to the transfer of charge from oxygen to isolated Ti centers, while the spectral features appearing at higher wavelength in several samples should be due to Ti atoms connected to additional Ti atoms by sharing oxygen atoms, i.e. Ti-O-Ti arrangements. However, the UV-visible spectra of TAPO-5 materials synthesized from Ti(IV) sources containing similar amount of Ti show the maximum of the charge transfer band red shifted to 230-240 nm, and a clearly visible and intense shoulder at 295 nm (spectrum of the top of Figure 5), in good agreement with the literature [14].

Therefore, the samples synthesized from the novel procedure from Ti(III) sources presumably present a more homogeneous distribution of titanium in the framework than those obtained from Ti(IV) sources, and largely avoid the formation of significant amounts of undesirable Ti-O-Ti linkages.

Although the analysis of the UV-visible spectra of the samples allow to conclude that Ti(III) species are indeed present in the framework, these spectra also show some features that require further analysis, and particularly the presence of shoulders around 280 nm, less intense but at similar position than those so characteristics of TAPO materials synthesized from Ti(IV). Recent EPR-based work by Chiesa et al. [18-21] shed new light on the nature of the chemical environment of Ti(IV) atoms in the framework of TAPO-5, which is quite relevant for our purposes.

In TAPO-5 synthesized from Ti(IV) sources, this metal cation would substitute P(V), so no Ti-O-Ti units would be expected in the framework, as it was thought that no Ti(IV) could replace Al(III) in order to avoid positive charge in the framework. Therefore, UV bands in the region of 280 nm are usually attributed to the presence of ill-defined extra-framework Ti species, not necessarily belonging to TiO₂ phases. However, Chiesa and co-workers [18-21] have recently shown experimentally that the simultaneous substitution of Al-P pairs by two Ti(IV) cations is also possible in AFI framework, because the formal charge of two Ti(IV) would equal that of Al(III) + P(V). That substitution mechanism would lead to Ti-O-Ti arrangements that would be responsible for the UV spectral features observed at wavelength around 270-290 nm, which would then appear blue shifted respect to those corresponding to the infinite Ti-O-Ti chains present in anatase. It can be noticed that, besides its incorporation by pairs, these studies do not exclude the isomorphous substitution of a single P(V) atom by one Ti(IV), in this way leading to isolated Ti(IV) centers only linked to Al(III) atoms.

While this mechanism of incorporation of Ti(IV) by pairs would nicely account for the commonly observed UV spectral features at around 280 nm as far as Ti(IV) sources are used, it cannot be simply applied to the samples described in this work synthesized from TiCl₃. The hypothetical simultaneous replacement of Al + P by two Ti(III) would be highly unstable, as it would produce two positive charges closely located in the framework. What could be then the origin of the 280 nm band? We believe that the presence of Ti(IV) in the synthesis gel would be required to form Ti(IV)-O-Ti(III) linkages in the AFI structure. This arrangement would result in just one negative charge in the framework per every two incorporated Ti atoms, in such a way that one Al(III) would be replaced by Ti(III) and a neighbor P(V) atom would be simultaneously replaced by one Ti(IV) atom. The Ti(IV) would result from the partial oxidation of Ti(III),

initially present in the synthesis gel, during the crystallization process, what it is actually thermodynamically favored [23] . Indeed, we have discussed above the presence of the charge transfer from O to Ti(IV) species in the as-made sample not exposed to air.

3.4. Thermal analysis

TG/DTG curves of the as-made samples with different Ti content and after being exposed to air and to a given humidity degree are shown in Figure 6. While the overall weight loss patterns are qualitatively similar, they reveal some noticeable differences from a quantitative point of view (Table 2). Up to five different weight losses can be identified, two of them below 200 °C. The one observed at lowest temperature is centered at 65-80 °C, and can be attributed to the desorption of occluded water, while the one in the range 100-200 °C and centered at ~ 130 °C could be also attributed to water but more strongly held by the sample. The weight losses at $T > 200$ °C are attributed to the decomposition/combustion of the organic species occluded in the AFI channels, i.e. MCHA used as SDA, which takes place in a complex process that renders finally the three high temperature steps observed in the TG/DTG curves. The decomposition/combustion processes of the organic species in the Ti-containing samples differ from the process occurring in the Ti-free $\text{AlPO}_4\text{-5}$. The weight loss of this SDA is anyway given mainly in two steps centered at temperatures in the range of 335-385 °C and 510-565 °C. The first weight loss in $\text{AlPO}_4\text{-5}$ is found at *ca.* 50 °C lower temperature than in Ti(III)-doped samples and it is quantitatively the main one. These differences suggest a stronger retention of the organic species associated to the Ti incorporation into the AlPO_4 framework. The total weight loss corresponding to the organic species is practically constant for all the samples (Table 2). In particular, MCHA content per unit cell estimated from Table 2 is about 0.95 molecules per unit cell. Since an AFI unit cell contains

a unique one-dimensional 12-membered-ring channel, every MCHA molecule would be probably extended along the channel (unit cell of a length of 0.94 nm) [31], in very good agreement with the dimensions of this molecule along its main axis.

Table 2. Weight losses at the three main temperature intervals and total weight loss of as-made Ti(III)APO-5 samples prepared with MCHA as SDA and different Ti contents. Weight losses of Ti(IV)APO-5 and Ti-free AlPO₄-5 samples with the same SDA are also shown.

Assignment	Water weight loss 1 / % (T / °C) ^a	Water weight loss 2 / % (T / °C) ^a	SDA weight loss / %	Total weight loss / %
Sample	T < 100 °C	100 < T < 200 °C	T > 200 °C	Total
MCHA-0.5p-4h	2.33 (70 °C)	8.22 (138 °C)	10.09	20.61
MCHA-1p-4h	2.91 (67 °C)	4.26 (127 °C)	11.07	18.23
MCHA-2p-4h	3.23 (70 °C)	4.14 (135 °C)	10.81	18.17
MCHA-4p-4h	5.07 (77 °C)	3.48 (126 °C)	10.27	18.82
MCHA-4-Ti(IV)	3.96 (71 °C)	No loss ^b	10.51	16.13
MCHA-AlPO ₄	2.25 (72 °C)	2.79 (133, 187 °C) ^c	10.86	15.86

^a In brackets, the maxima of the derivative of the TG curve is indicated for every considered loss.

^b Although some loss was detected (1.65 wt. %) in this T range, it was not detected in the derivative, unlike the TGA of the rest of samples, suggesting that the origin of this weight loss is different from the strongly-retained water.

^c Two different minor weight losses were detected for this sample.

(Table 2)

(Figure 6, TGA)

Contrary to what has been concluded for the organic content, large quantitative differences in the water loss range are observed among the TGA curves of the different samples. The content of water desorbed at high temperature clearly increases as the titanium content decreases. The desorption of water between 100 °C and 200 °C for the sample with lowest amount of Ti, MCHA-0.5p-4h, is so large (8.2 wt.%) that the total weight loss becomes 21 wt.%, exceeding by far the weight loss commonly observed for highly crystalline AFI-type materials. The TG curve of pure $\text{AlPO}_4\text{-5}$ crystals synthesized with the same SDA, shows a negligible weight loss at the same temperature, and a total weight loss of 16 wt.% is found. It is also interesting to notice that the TAPO-5 synthesized from Ti(IV) by using also MCHA shows a small weight loss at that temperature of only 1.65 wt.%. Therefore, the presence of such prominent loss of weight in that temperature range can be taken as a sort of fingerprint of the presence of Ti(III) metal centers in the framework of the as-made materials.

Regarding to the nature of the chemical process that produces such a high weight loss, we could only advance some hypothesis. It could be due (i) to the desorption of water preexisting as discrete molecules in the crystals, (ii) to the desorption of water resulting from hydroxyl groups present in the sample as defects that would recombine at high temperature rendering water as desorption product, or (iii) to a combination of both possibilities. The TG analyses discussed here correspond to the samples exposed to air, where Ti(III) no longer exists, having been oxidized to Ti(IV). However, this oxidation process must necessarily occur by creating defects in the structure, in order to balance the overall framework charges. Hydroxyl groups could eventually result from the oxidation of Ti(III) to Ti(IV) and would remain linked to the titanium center; or the P-O bonds of the P atoms linked to the Ti(III) could also be affected by the oxidation process, maybe leading to some broken P-O bonds, leaving one hydroxyl group

bonded to Ti and one P-OH defect. While much work would be required before fully understand the details of the oxidation mechanism of Ti(III) to Ti(IV) in the framework, the observed effect of this process on the amount of desorbed water, either preexisting or coming from defects, exceeded by far what could be expected if only the Ti centers (and eventually the P atoms bonded to Ti) were the only ones directly affected by the oxidation process. Thus, from the data collected in Table 2, the weight loss centered at about 130 °C for the sample with the lowest Ti content, 0.06 Ti/u.c., would correspond to a total of about 10 H₂O molecules per unit cell, two orders of magnitude higher than the Ti present in the sample. Hence, water or eventually defects, or both, would be present in the crystals beyond the first tetrahedral neighbors of the Ti centers, which shall be P atoms. Most probably, the Al atoms bonded to these P atoms, i.e., those located in the second coordination shell of a given Ti atom, would expand their coordination shell to accommodate water molecules. If this were so, this expansion of the coordination of the Al atoms from 4-fold to higher coordination arrangements should be reflected in the ²⁷Al NMR spectra. Moreover, this would also alter the ³¹P NMR spectral signature. As shown below, both changes are indeed detected.

3.5. NMR spectroscopy

Direct-radiation ³¹P and ¹H to ³¹P cross-polarization (CP) MAS NMR spectra of the as-made, air-exposed samples with different Ti content and prepared with solid TiCl₃ as Ti source, are presented in Figure 7, together with the corresponding spectra of a sample synthesized with Ti(IV) source for comparison purposes. All single-pulse ³¹P MAS NMR spectra (Figure 7, left) are dominated by an intense signal at -30 ppm, which is characteristic of P atoms in tetrahedral coordination present in AFI-type AlPO₄-based materials [39], and which has been previously

reported for TAPO-5 synthesized from Ti(IV) sources [14, 40]. However, the spectra of Ti(III)APO-5 samples additionally show several features at lower field, whose details and relative intensities vary according to the sample nature. A main broad component is detected at ~ -15 ppm, whose intensity increases with the Ti content in the samples. This band is nearly absent in the spectrum of Ti(IV)APO reference sample, but a band of small intensity is detected at -10 ppm. This signal was also found in a Ti-free non-doped AlPO_4 -5 prepared with the same SDA under similar conditions [36]. A third component in that region appears as a shoulder of the main P(4Al) peak at nearly -22 ppm, which can be observed in all the samples regardless the oxidation state of the titanium source. In any case, the increase of the intensity of the broad band at ~ -15 ppm with the titanium content strongly suggests that it is associated to the incorporation of titanium in the crystals, particularly when Ti is incorporated as Ti(III).

(Figure 7, P-31 NMR)

Accordingly, the incorporation of different heteroatom ions in the second coordination sphere of P atoms in AlPO_4 -based microporous materials (i.e., in Al sites of a theoretical AlPO_4 framework) entails the appearance of additional signals to that attributed to P(4Al) [41]. Irrespective of the heteroatom nature (Zn [42, 43], Mg [43-45], Sn(II) [36], etc., and even the paramagnetic Co [46]), these signals are always found at lower field than P(4Al) signal. At high heteroatom content, different almost equidistant signals are detected and attributed to P(4- n Al, n Me) environments [42-44, 46] (where Me represents the heteroatom ion and n is the integers of Me neighbors to tetrahedral P), even being possible to accurately determine the P/Me ratio in the framework that complements the bulk composition given by chemical analysis techniques [43-45]. In contrast, the incorporation of pentavalent heteroatom ions, such as V(V) [45, 47], or

tetravalent ones such as Si [48] or Ti itself [14] does not practically affect the ^{31}P NMR features with respect to a spectrum of a non-doped AlPO_4 . As a consequence of such high sensitivity of ^{31}P NMR to the incorporation of divalent ions and such practical insensitivity to the incorporation of penta- or tetravalent ions, the signals at -15 ppm in the ^{31}P NMR spectra of our samples could be taken as a strong evidence of the incorporation of Ti ions as neighbors of P ones. However, the relative intensity of this band compared to that of the $\text{P}(4\text{Al})$ one is too large in the case of Ti(III)APO-5 samples. Even assuming the ideal case in which each Ti ion is isolated and occupying Al sites in a $\text{Ti}(4\text{P})$ environment, a number of P atoms equivalent to four times the number of incorporated Ti atoms will be affected at most, which is insufficient to explain, for instance, the almost equal intensity of the bands at -15 ppm and -30 ppm estimated from the spectrum of the MCHA-4p-4h sample (Figure 7, left). It must be noted that the spectra from Figure 7-left have been acquired with a pulse delay time as long as 100 seconds and a flip angle of 45° , which are NMR acquisition conditions that secures quantitative spectra unless any signal has extremely low relaxation time. Besides, the latter possibility was discarded by acquiring a single-pulse ^{31}P MAS NMR spectrum (not shown) under exactly the same conditions excepting the pulse delay that was increased up to 200 seconds. The so-registered spectrum was almost identical to that registered with a pulse delay of 100 seconds, particularly in terms of their relative intensity. It confirms that the signal at -15 ppm cannot be simply attributed to $\text{P}(4-n\text{Al}, n\text{Ti})$ environments but a more complex effect seems to be derived from the incorporation of Ti in Al sites in Ti(III)APO-5 materials. The excessive broadening and the no detection of shoulders are also against that assignment. This is not surprising considering that Ti is incorporated as Ti(III) surrounded by four P atoms in the second coordination sphere, but its subsequent oxidation to Ti(IV) by exposing it to the ambient atmosphere would entail a local positive charge

(given by $\text{Ti}^{\text{IV}}(\text{OP}^{\text{V}})_4$ environment). Although the path in which that positive charge is compensated is not clear at this point, it will necessarily affect the P environment (and the ^{31}P NMR spectrum). In this context, the uncommon features of the TGA curves particularly at temperatures in which strongly retained water desorption is detected, suggests that an AlPO_4 framework region of larger dimensions than the immediately neighbor of Ti could be affected. This fact opens so many possibilities of assigning the extra contribution to the complex signal at -15 ppm considering that tens of aluminophosphate-based species of different polymerization degree [49-51] including different $\text{P}(\text{OAl})_x(\text{OH})_y(\text{H}_2\text{O})_z$ ones that resonates in the wide chemical shift region (approximately from 0 to -30 ppm) in which the downfield signals of the spectra from Figure 7-left are extended.

The apparent involvement of water and/or OH^- groups in the downfield signal of ^{31}P MAS NMR spectra of $\text{Ti}(\text{III})\text{APO-5}$ materials makes the ^1H to ^{31}P CP MAS NMR spectra specially relevant. All ^{31}P CP MAS NMR spectra shown in Figure 7-right are formed by basically the same signals as those found in the direct-radiated ^{31}P MAS NMR spectra (Figure 7, left). There is, however, a striking difference in relative intensity of these signals, so that the intensity of the signal with $\delta^{31}\text{P} \sim -15$ ppm is dramatically enhanced with respect to the signal attributed to $\text{P}(\text{4Al})$. This is a direct evidence that the downfield signal is generated by P atoms having very close ^1H nuclei of very low mobility, perfectly compatible with the generation of POH groups in the process of oxidation of $\text{Ti}^{\text{III}}(\text{OP})_4$ environments.

Figure 8A displays the ^{27}Al MAS NMR spectra of the TAPO-5 samples whose ^{31}P MAS NMR spectra are shown in Figure 7. As expected from $\text{AlPO}_4\text{-5}$ based samples, they are dominated by a signal at *ca.* 36-37 ppm, which is typical of tetrahedral Al surrounded by four O-P groups [43].

However, all spectra show two more peaks at higher field. Actually, according to our simulations (Figures 8B and 8C) the two peaks match quite well with a unique ^{27}Al signal of typical shape of a quadrupolar nucleus in a quite anisotropic environment. The isotropic chemical shift δ_{iso} of that signal (do not confuse with the δ directly read from the spectra and take into account that δ_{iso} in general depends on the magnetic field of the NMR equipment) in the cases of MCHA-1p-4h and MCHA-4-Ti(IV) samples is 24 ppm and has a quadrupolar coupling constant (QCC) of 6.5 kHz. Although the similitudes between these two spectra can suggest that Ti(III) and Ti(IV) can have similar effect in $\text{AlPO}_4\text{-5}$, it must be noted that the sample MCHA-4-Ti(IV) is five times richer in Ti than MCHA-1p-4h (Table 1). Therefore, incorporating Ti(III) and Ti(IV) could have similar effect in ^{27}Al MAS NMR, but that effect is very much different in quantitative terms.

When Ti content increases along the Ti(III)APO-5 series (from bottom to top in Figure 8A), the intensity of that signal also increases and, at the same time, its δ_{iso} upfield shifts to 17 ppm and its QCC decreases down to 6.0 kHz. That evolution in quadrupolar parameters is particularly manifest in the spectrum of the sample MCHA-2p-4h, which has an intermediate Ti content and shows the presence of both signals with high QCC. These signals are attributed to framework Al with coordination higher than 4, due to extra coordination to H_2O molecule(s) and/or OH^- group(s). The evolution of the NMR quadrupolar parameters (upfield shift of δ_{iso} and increase of QCC) suggests that the quadrupolar-shaped signal observed in the spectra of the sample MCHA-4-Ti(IV) and MCHA-1p-4h could be due to 5-folded framework Al, whereas the one found in the spectrum of the sample MCHA-4p-4h is probably due to octahedral Al, also taking part of the AlPO_4 framework. The quantification of the ^{27}Al signals considering their quadrupolar character [52], indicated that only 2.8 % of Al is either 5- or 6-folded Al in the Ti(IV)APO-5, but it increases up to 18 % in the Ti(III)APO-5 sample MCHA-4p-4h, both having comparable Ti

content (Table 1). According to these assignments, the increase of the relative intensity of the Al with coordination higher than 4 with the increase of Ti content in the series of Ti(III)APO-5 samples must be related to a greater degree of hydration/hydroxylation of the framework Al. Therefore, both ^{31}P and ^{27}Al NMR spectra indicate that Ti(III) incorporation into the AlPO_4 framework and its subsequent oxidation substantially alter the environment of Al and P atoms located relatively away from Ti sites, mainly through hydration/hydroxylation processes, which are not normally so massive in other AlPO_4 -based materials.

(Figure 8, Al-27 NMR)

4. DISCUSSION

The different techniques used along this article to characterize the samples Ti(III)APO-5 have essentially made clear three fundamental aspects: (i) as aimed, Ti(III) is incorporated into the AlPO_4 -5 framework; (ii) that incorporation, unlike that of other heteroatom ions including Ti(IV), concedes uncommon features to the AlPO_4 framework, not only in its closest environment but in a relative extended region that covers several coordination spheres; and (iii) every singularity arisen from Ti(III) incorporation is somehow associated to a distinctive hydration and/or hydroxylation of the TAPO framework. In this context, this discussion section will be focused on the combined analysis of the atypical characterization results given by the different techniques, in order to shed light on the chemistry behind this behavior.

All techniques detect massive outcomes apparently induced by the proportionally low Ti(III) incorporation, as if it would generate a sort of propagation effect. It is somehow consistent with the assumed involvement of water and/or OH^- groups, due to their hydrophilic character and the possibility of interacting with molecules of their own nature through charge densities of opposite

sign. The above analysis and discussion about the strongly retained water detected by TGA of Ti(III)APO-5 could not clarify its origin, as it could come from either simple desorption of water molecules already existing in the sample or from OH⁻ condensation. Neither ²⁷Al nor ³¹P NMR spectroscopies are conclusive in that sense. However, two facts lead us to think in the possibility of OH⁻ groups must be present. The dramatic increase of the intensity of the downfield ³¹P NMR signal when the spectrum is registered with a CP NMR sequence pulse instead of a single pulse one, evidences the proximity of protons to P sites as well as their very limited mobility. It suggests the presence of large amounts of P-OH groups, as P-OH₂ groups are unlikely and the proximity of P and H₂O without bond could not be responsible of that dramatic increase by application of CP sequences. It does not mean that the signal at ca. -15 ppm is completely due to P-OH groups, which is quantitatively hard to explain, but they are almost certainly present. Some P-OH groups could be formed as a consequence of the oxidation of its neighbor Ti(III) to Ti(IV), which would probably generate framework defects. This reasonable hypothesis, together with the need of compensating positive charges introduced by the oxidation of Ti(III), lead us to tentatively propose the presence of OH⁻ groups linked to Ti as the possible anionic charge compensator. Furthermore, the associated increase in coordination number of Ti could explain the presence of the shoulder at *ca.* 275-280 nm in the DRUV-visible spectra, either in as-prepared (Figure 5) or in calcined Ti(III)APO-5 samples [29], as an alternative to the interpretation based on the presence of Ti-O-Ti bonds [18-21] or extraframework TiO₂-containing species [53] for a similar band found in the DR-UV-visible spectra of the conventional TAPO-5. Indeed, unlike what should be expected from the presence of Ti-O-Ti bonds or extraframework TiO₂-containing species, the presence of this band seems to be an incentive rather than a disadvantage in the catalytic activity of these catalysts [28, 29]. The

chemical viability of the proposed role of OH⁻ groups compensating the charge generated by the Ti(III) oxidation is reinforced by the reported oxidation of Ti^{III}(OP)₄(H₂O)₂ to Ti^{IV}(OP)₄(H₂O)(OH) in TiGaPO-1 [25].

As previously mentioned, the presence of OH⁻ groups linked to the framework Ti or P formed by oxidation of Ti(III) cannot explain the huge intensity of the signal at -15 ppm in single-pulse ³¹P MAS NMR spectra. However, these quite polar P-OH and Ti-OH groups could become a highly-hydrophilic seed that propagates such hydrophilicity through successive hydration spheres. Thus, a single point within the framework can affect relatively large regions of the AlPO₄ network. It must be noted that, unlike the surface P-OH groups commonly found in other AlPO₄-based materials, these P-OH groups are within the framework, only accessible through the micropores delimited by crystalline material. In other words, these P-OH and Ti-OH groups are internal defects and they can (and should) affect water molecules inside of the pores. This tentatively model would roughly explain the high tendency of a great part of Al to reach coordination higher than 4, especially considering that Al in AlPO₄-5 has indeed that natural tendency under forced hygroscopic media [54]. The high anisotropic environment of 5- or 6-folded Al (Figure 8B and 8C, component 2) could be assumed taking into account that those spectra are of as-prepared samples, contrasting to the more isotropic 5- and 6-folded Al environment found in calcined AlPO₄-5 materials. In as-made Ti(III)APO-5 samples, the relatively bulky SDA (MCHA) would force Al to a particular non-relaxed configuration. Regarding the ³¹P NMR signal at -15 ppm, it could be explained by the proximity of P atoms to 5- and/or 6-folded Al ones [54, 55], besides the already-commented very likely presence of P-OH groups.

Nevertheless, a common interpretation of (^{27}Al and ^{31}P) NMR and TG analyses is not straightforward since the higher amount of strongly-retained water detected by TGA was unexpectedly found in the samples prepared with low content of Ti(III). On the contrary, the hydration/hydroxylation degree detected by means of ^{27}Al and indirectly by ^{31}P NMR in these Ti-poor samples is scarcely or even negligible. A possible tentative explanation would be based on the different incorporation mechanism of Ti as a function of Ti content. At very low content, the statistical probability of forming Ti-O-Ti bonds within the structure is scarce, and then high proportion of $\text{Ti}(\text{OP})_4$ environments is expected since Ti ions are in principle incorporated as Ti(III). Its subsequent oxidation to Ti(IV) and the associated generation of local positive charges in the framework, would powerfully attract anions (probably OH^- following the tentative above-given interpretation) with high proneness to be surrounded by successive water coordination spheres. The low concentration of Ti in this sample and the relatively long distance between Ti and Al atoms (expected environment Ti-O-P-O-Al , or even $\text{Ti-OH}\cdots\text{HO-P-O-Al}$ if the oxidation of Ti(III) entails the hydrolysis of Ti-O-P bonds) makes that the proportion of framework Al atoms being hydrated/hydroxylated are the same that in an $\text{AlPO}_4\cdot 5$ [36] or in a Ti(IV)APO-5 sample (Figure 8A). When incorporation of Ti-O-Ti units becomes more probably by increasing Ti loading in the reaction media, Ti-O-Al bonds (or rather Ti-OH-Al because of the charge balance requirements) could be present, and then Al would be more directly affected by any hydration process induced by the presence of Ti. Nevertheless, the different environment of Ti(III), which now could be something like $\text{P-O-Ti}^{\text{III}}\text{-O-Ti}^{\text{IV}}\text{-OH-Al}$, justify a different Ti(III) oxidation mechanism (the presence of an anion is not necessary anymore), and the differences detected in the 25-200 °C region of the TGA profiles as a function of Ti content can reach certain clarification. Even the very different catalytic activity per Ti center of these Ti(III)APO-5

materials-, exponentially growing by decreasing Ti content in the samples [30], could be tentatively explicated by these hypothesis.

In spite of the support given by the literature and the most relevant and uncommon features of Ti(III)APO-5 materials detected by means of different characterization techniques could be at least crudely explained by these models, they must be taken as tentative and preliminary. Further investigations are in progress to clarify these hypotheses. Nevertheless, this hypothesis satisfices some unknowns related to the nature of Ti centers in Ti(III)APO materials and its catalytic behavior [28, 29]. Some of them are: (i) a possible way in which Ti(III) can be oxidized to Ti(IV) within the AlPO_4 framework, implying OH^- as anionic charge compensator; (ii) the probable existence of heterogeneity in Ti centers as a function of Ti content; and (iii), as a consequence of (ii), a reasonable explanation of the substantial increase of catalytic activity of Ti(III)APO-5 per Ti center when Ti content decreases [29].

5. CONCLUSIONS

The synthesis of pure TAPO-5 materials with different Ti(III) sources, different Ti content and two different structure-directing agents has been achieved. The initial purple color of the samples and the consequent d-d transition bands appearing in the visible region of their DR-UV-vis spectra, corroborate the presence of Ti(III) in the samples. By simply drying the sample in air, Ti(III) ions are spontaneously oxidized to Ti(IV), although the resultant light yellow samples anticipates a different environment of Ti than in conventional completely white TAPO-5 samples. ^{31}P MAS NMR confirmed that P is directly affected by Ti incorporation, suggesting the presence of Ti(OP)_4 environment. However, the compulsory charge balance associated to the oxidation of Ti(III) after being incorporated into the AlPO_4 framework, implies the presence of a

monovalent anion (or some bond breaking/reordering) by each Ti(IV) ion coming from the oxidation of a Ti(III) one, giving rise to more complex Ti environments. Indeed, far from finding unique Ti centers, the final nature of Ti environment(s) in these Ti(III)APO-5 materials strongly depends on Ti content. Thus, samples with relative high Ti loading could have certain heterogeneity in Ti environments including Ti-O-Ti units, what indirectly implies a partial oxidation of Ti before being incorporated into the framework. On the other hand, Ti(III)APO-5 samples, in particular those with low Ti content, possess an extraordinary capacity amongst the known AlPOs to strongly retain water, whereas the framework Al atoms of the Ti-richest samples are coordinated to water molecule(s) in a unusually high proportion. All these facts led us to propose a tentative and preliminary model involving OH⁻ as charge compensator of the positive charge generated by the oxidation of the framework Ti(III) and the presence of P-OH groups as crystalline defects within the AFI pores.

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FIGURE CAPTIONS

Figure 1. PXRD patterns of the representative as-prepared TAPO-5 samples prepared with different Ti(III) sources, Ti content, crystallization times and structure directing agent. The spectrum of the sample MCHA-4-Ti(IV) is also included.

Figure 2. Unit cell parameter a of the AFI structure (space group P6cc) *vs.* Ti content of the samples as determined by ICP analysis and expressed like in Table 1.

Figure 3. Scanning electron micrographs of selected Ti(III)APO-5 samples as representing ones of the different morphologies observed.

Figure 4. UV (left) and visible (right) regions of the DR-UV-visible spectra of the as-made MCHA-4p-4h sample after being drying in either N₂ or air. The DR-UV-visible spectrum of the mixed valence Ti(III)-Ti(IV) phosphate material prepared according to [24], is also shown for comparison purposes. The positions of the visible bands in the spectra of the sample MCHA-4p-4h dried in N₂ are indicated. The intensity of the visible region are multiplied by 5 with respect the intensity of the UV region.

Figure 5. DR-UV-visible spectra of the as-made TAPO-5 samples prepared with different Ti(III) sources, Ti content, crystallization times and structure directing agent. The spectrum of the sample MCHA-4-Ti(IV) is also shown, so the samples are those whose PXRD patterns are

shown in Figure 1. The spectra have been normalized to make easier their comparison. Dashed vertical lines marks the wavelength at 225 and 275 nm to facilitate the following of the discussion in the text.

Figure 6. TG (left) and DTG (right) curves of as-made Ti(III)APO-5 samples prepared with MCHA as SDA and TiCl_3 powder as Ti(III) source with different Ti content. TG/DTG curves of an as-made Ti(IV)APO-5 and a Ti-free non-doped AlPO_4 -5 samples synthesized with the same SDA are also shown for comparison purposes.

Figure 7. Direct-radiation ^{31}P (left) and ^1H to ^{31}P cross-polarization (right) MAS NMR spectra of the as-made Ti(III)APO-5 samples prepared with MCHA as SDA TiCl_3 powder as Ti source and with different Ti content. ^{31}P MAS NMR spectra of an as-made Ti(IV)APO-5 sample prepared with the same SDA, is also shown for comparison purposes. The spectra intensity has been normalized with respect to their corresponding maximum intensities.

Figure 8. A) ^{27}Al MAS NMR spectra of the as-made Ti(III)APO-5 samples prepared with MCHA as SDA TiCl_3 powder as Ti source and with different Ti content. The NMR spectrum of an as-made TAPO-5 sample prepared with the same SDA, is also shown for comparison purposes. B) and C) Experimental, simulated and components of the simulation of the ^{27}Al MAS NMR spectra of the sample MCHA-Ti(IV) and MCHA-4p-4h, respectively. All spectra intensity has been normalized with respect to their corresponding maximum intensities.

SCHEME CAPTION

Scheme 1. Pictures of the as-made sample MCHA-4s-4h at different stages of drying, showing the color evolution. Top: still wet, after crystallization. Bottom: left, after drying under inert N₂ atmosphere; right, after drying in air.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Single-pulse ^{31}P MAS NMR spectra

^1H to ^{31}P CP MAS NMR spectra

Figure 7

Figure 8

As-synthesized

Dried in N₂

Dried in air

Scheme 1