



The identity of titanium centres in microporous aluminophosphates compared with Ti-MCM-41 mesoporous catalyst and titanosisilsesquioxane dimer molecular complex: a spectroscopy study

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Dedicated to Professor Renato Ugo on the occasion of his 65th birthday

Abstract

Titanium-aluminophosphate and silico-aluminophosphate with chabazite-like structures (TAPO-34 and TAPSO-34) have been hydrothermally synthesised using morpholine as structure-directing agent. The local environment of Ti(IV) sites in these materials was studied using diffuse-reflectance UV-Vis, photoluminescence and Raman spectroscopies. This study, combined with the study of Ti-grafted MCM-41 mesoporous catalyst and a titanosisilsesquioxane dimer molecular complex with a well-defined co-ordination of the Ti(IV) centers, revealed that a fraction of Ti(IV) ions are present in tetrahedral co-ordination, consistent with some Ti(IV) ions being incorporated into the aluminophosphate frameworks. However, Raman spectroscopy showed that around 20% of the total amount of the titanium used in the gel synthesis is present in a TiO₂-like extra-phase.

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1. Introduction

Titanium ions embedded into the framework of siliceous microporous and mesoporous materials exhibit a range of interesting and useful catalytic properties for various kinds of selective oxidation [1–8].

Ti(IV) tetrahedral sites may, in fact, bond up to two reactant molecules [2]. The discovery of the remarkable catalytic activity of titanium silicalite-1 (TS-1) in oxidation reactions at mild temperature, using H₂O₂ as the oxidant [1], has triggered intensive research in the area of synthesis of titanium-containing catalysts. The insertion of Ti(IV) cations in zeolites and mesoporous silica networks is well documented in the literature: tetrahedral titanium has been

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introduced successfully in silicalite-1 [1], silicalite-2 [1], ZSM-48 [4], zeolite-beta [6], MCM-41 [9–11] and MCM-48 [12].

Titanium ions can be successfully incorporated in the framework of microporous aluminophosphate (AIPO) and silico-aluminophosphate (SAPO) molecular sieves also, by substitution of P(V) ions. Tetrahedral Ti(IV) sites generated in this way have different chemical environments as compared with zeolites and this may lead to materials with different catalytic properties. The synthesis of Ti(IV)-containing AIPO-5 [13–15], SAPO-5 [16,17], AIPO-11 [13,15] and AIPO-36 [14,15,18] structures have been reported along with their catalytic performances.

The local structure around Ti(IV) centers in heterogeneous catalysts has been probed effectively with several complementary approaches, including spectroscopic techniques (FTIR, Raman, diffuse reflectance UV-Vis, photoluminescence, EXAFS and XANES) [2], computational modelling [19,20] and chemical modelling using silsesquioxanes as well-defined homogeneous models [21].

In this contribution we describe the synthesis of titanium-containing aluminophosphate (TAPO-34) and silico-aluminophosphate (TAPSO-34) by using morpholine as the templating agent and report spectroscopic evidence for the Ti(IV) incorporation within the framework. The AIPO-34 and SAPO-34 materials are structural equivalents to the natural zeolite chabasite

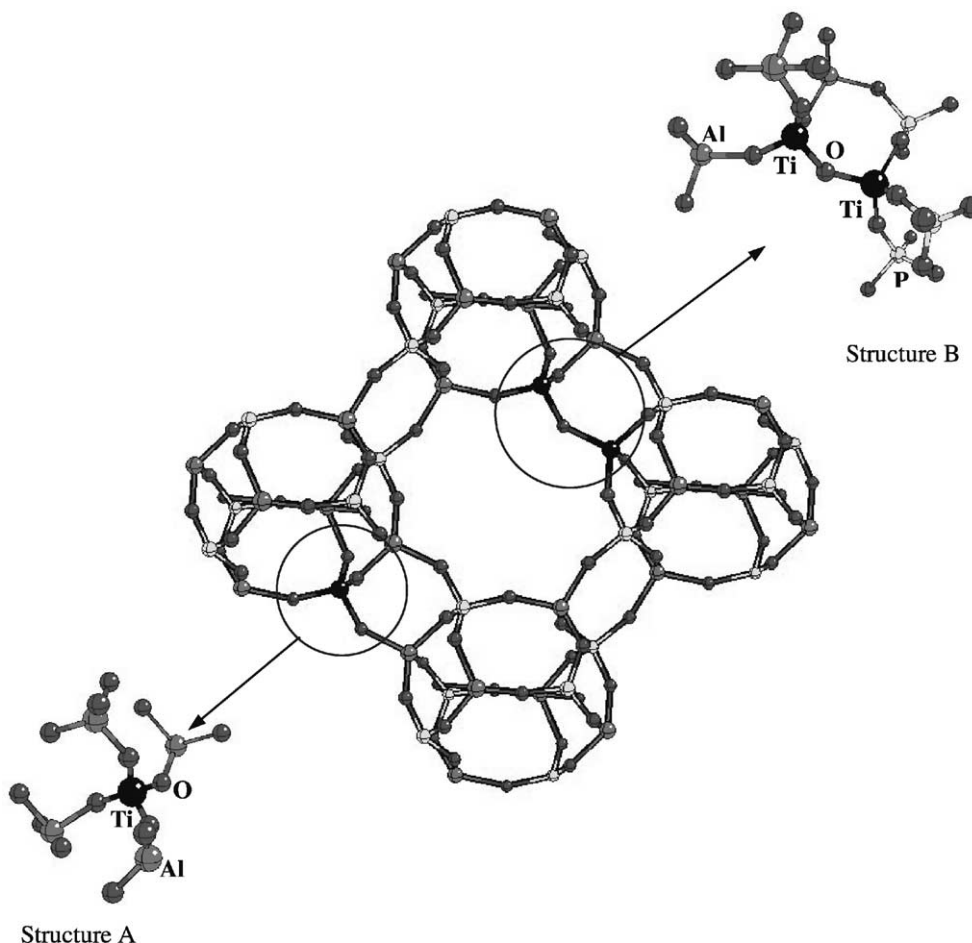


Fig. 1. Representation of the chabasite cage of an AIPO-34 type structure. Structure A: isolated Ti(IV) ion in tetrahedral co-ordination arising from the substitution of P(V) ion. Structure B: dimeric Ti–O–Ti sites arising from the substitution of Al(III) and P(V) couple.

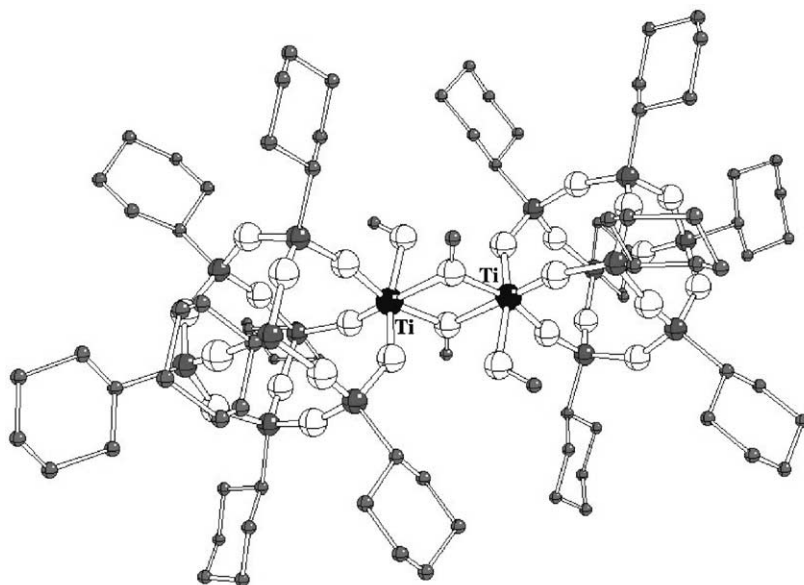


Fig. 2. Representation of a dimeric titanosilsesquioxane; the ligands attached to the corner of the silica boxes are cyclohexyl groups, whereas the ligands bridging the titanium ions are methoxy groups.

(structure code CHA) with ellipsoidal cages which can be accessed through 8-ring windows of 0.38 nm diameter (Fig. 1) [22]. Ti(IV) ions in a chabazite-like structure can substitute P(V) ions, generating Ti(IV) sites in tetrahedral framework positions (Fig. 1, structure A). A counter-cation is needed to balance the framework negative charge. Ti(IV) can also substitute an Al(III) and P(V) couple, forming framework-linked Ti–O–Ti bridges (Fig. 1, structure B), as is reported for TAPO-11 and TAPO-36 systems [15]. In this latter case, the aluminophosphate framework is neutral.

Ti-MCM-41 mesoporous system and titanosilsesquioxane molecular dimer (Fig. 2) [21], with tetrahedral and octahedral Ti(IV) ions respectively, have been used as model compounds for isolated and coupled Ti(IV) ions, respectively, to clarify the electronic spectra (both absorption and emission) of Ti-containing aluminophosphates.

2. Experimental

2.1. Synthesis

TAPO-34 were obtained adapting the procedure reported for AIPO-34 [23], and, in the case of

Table 1
Chemical composition of the gels used for the crystallisation

| Sample | Ti | Si | Al | P | Mor | HF | H ₂ O |
|----------|------|------|------|------|------|------|------------------|
| AIPO-34 | – | – | 1.00 | 1.00 | 1.25 | 0.35 | 50 |
| TAPO-34 | 0.03 | – | 1.00 | 0.97 | 1.25 | 0.35 | 50 |
| SAPO-34 | – | 0.25 | 1.00 | 0.90 | 1.25 | – | 50 |
| TAPSO-34 | 0.03 | 0.20 | 1.00 | 0.77 | 1.25 | – | 50 |

TAPSO-34, a method similar to that described for SAPO-34 [22,24] was used. Ti-isopropoxide (diluted in ethanol) was added to the gel obtained by mixing orthophosphoric acid, Al(OH)₃ and morpholine (Mor). SiO₂ was also added for obtaining the TAPSO-34 and SAPO-34, and HF for TAPO-34 and ALPO-34 [25]. Table 1 summarizes the elemental molar ratios of the gels which were crystallised in a stainless steel, teflon-lined autoclave under autogeneous pressure at 195 °C for 10 days.

Titanosilsesquioxane dimer was synthesised according to [21]. Ti-MCM-41 was synthesised grafting Cp₂TiCl₂ complex on the silica matrix according to [26].

2.2. Characterisation

X-ray powder diffraction pattern of as-synthesised TAPO-34 and TAPSO-34 samples were obtained on a

Philips diffractometer PW1830 using a Co K α radiation.

Diffuse reflectance UV-Vis spectra were recorded on a Perkin Elmer Lambda 19 equipped with an integrating sphere attachment, and photoluminescence spectra by using Spex Fluorog-2 1680 spectrometer. Raman spectra (resolution of 2 cm⁻¹) were obtained with a Bruker FT spectrometer FRA 106/RFS (laser source: 9398 cm⁻¹).

Prior to UV-Vis and photoluminescence measurements, TAPO-34 and TAPSO-34 samples were calcined in 100 Torr O₂ (1 Torr = 133.32 kPa) at 550 °C for 24 h in order to remove the organic template. In the case of Ti-MCM-41 the same calcination procedure was followed to remove the cyclopentadienyl ligands.

3. Results and discussion

X-ray diffraction (XRD) patterns of as-synthesised TAPO-34 and TAPSO-34 samples (Fig. 3) revealed that phase-pure materials with AIPO-34 and SAPO-34 type structures, respectively [22,23], were obtained.

Diffuse reflectance UV-Vis spectroscopy in combination with photoluminescence and Raman spec-

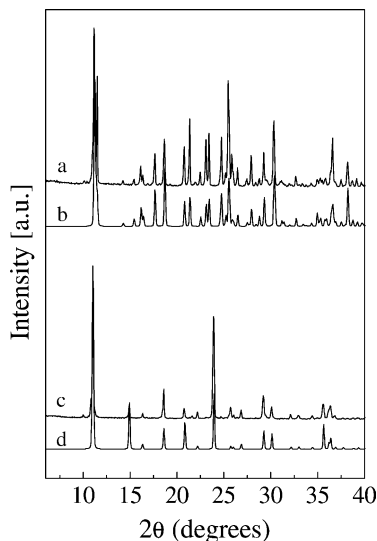


Fig. 3. XRD pattern of as-synthesised TAPO-34 (curve a) compared to the XRD calculated [23] for AIPO-34 (curve b) and of as-synthesised TAPSO-34 (curve c) compared to the XRD calculated [22] for SAPO-34 (curve d).

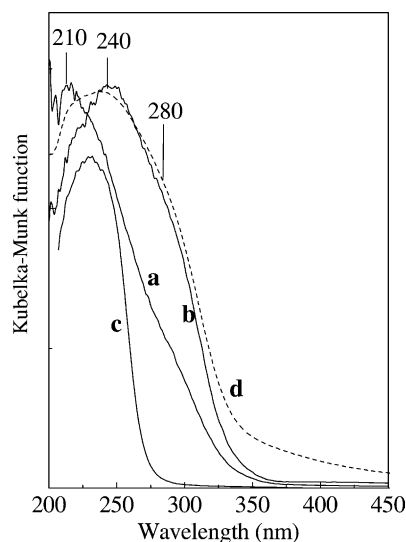


Fig. 4. Diffuse reflectance UV-Vis spectra of TAPO-34 (curve a), TAPSO-34 (curve b), Ti-MCM-41 (curve c) and the titanosilsesquioxane dimer (curve d).

troscopy can be used to define whether Ti(IV) ions are incorporated within the AIPO-34 and SAPO-34 frameworks or alternatively are present in an extra-framework phase. In addition, photoluminescence was also found to be useful in yielding valuable information on the Ti(IV) co-ordination sphere [27–30]. Fig. 4 shows DR UV-Vis spectra of calcined TAPO-34 (curve a) and TAPSO-34 (curve b). The spectra of a Ti-grafted MCM-41 [27] sample (curve c) and of a titanosilsesquioxane dimer compound (curve d), with couples of octahedral Ti(IV) sites linked by oxygen atoms, are also reported for comparison. The Ti-MCM-41 is a well-characterised siliceous catalyst where tetrahedral Ti(IV) species are anchored on the inner surfaces of mesoporous channels [26–29].

TAPO-34 shows a maximum at 210 nm and TAPSO-34 at 240 nm, with a shoulder at $\lambda \leq 230$ nm. Bands at $\lambda \leq 230$ nm correspond to oxygen to tetrahedral Ti(IV) ligand-to-metal charge transfer (LMCT) [27–29,31–36] and their presence demonstrates that Ti(IV) ions are incorporated into the aluminophosphate frameworks. However, both TAPO-34 and TAPSO-34 absorptions are broad and show a strong shoulder at ca. 280 nm, which has been assigned to Ti(IV) ions in oligomeric TiO₂-like extra-framework

phase [29,35]. Indeed, a TiO_2 -like phase was identified by Raman spectroscopy (vide infra).

The origin of the band at 240 nm, which is particularly intense in the case of TAPSO-34 sample, merits to be discussed further, being a common feature of other Ti-aluminophosphate molecular sieves [15]. It is likely, in fact, that besides isolated tetrahedral Ti(IV) ions (Fig. 1, structure A), titanium ions can substitute for a couple of adjacent Al(III) and P(V) ions leading to a neutral aluminophosphate framework where Ti–O–Ti structures are present (Fig. 1, structure B). The electronic absorption of these dimeric species may be reasonably predicted to fall in a range between the isolated Ti(IV) tetrahedral sites and the octahedral Ti(IV) ions in oligomers. This assignment, which will be the object of future work, is supported by the UV spectrum of the dimeric model compound (Fig. 4, curve d), which has a couple of Ti(IV) ions linked by oxygen bridges and shows major absorption at around 240 nm.

Photoluminescence spectra (Fig. 5) confirm the presence of tetrahedral Ti(IV) ions in TAPO-34 and TAPSO-34 materials. Ti-MCM-41 catalyst with Ti(IV) ions in tetrahedral co-ordination (curve a), exhibits an intense and complex photoemission signal with maxima at 425 and 480 nm when excited by radiation of 250 nm [27,29]. Signals at around 425 and 480 nm are also observed for TAPO-34 (curve b) and TAPSO-34 (curve c) systems, and this is further proof, along with DR UV-Vis experiments, that some Ti(IV) ions are incorporated into the aluminophos-

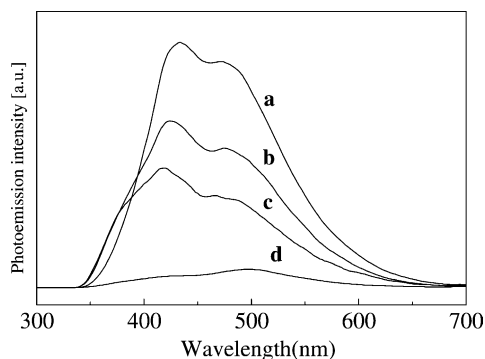


Fig. 5. Photoluminescence spectra collected at room temperature, of the Ti-MCM-41 (curve a) TAPSO-34 (curve b), TAPO-34 (curve c) calcined samples and the dimeric titanosilsesquioxane (curve d). The intensity scale for the Ti-MCM-41 emission was divided by 2.

phate framework. For a more detailed study on the photoluminescence of Ti(IV) oxide species see the data reviewed in [37]. A strong shoulder at ca. 380 nm is also visible in the TAPO-34 and TAPSO-34 spectra and arises from the quartz wall of the cell. The signal of the cell is less relevant in the Ti-MCM-41 as, for sake of comparison, the intensity scale of this spectrum was divided by 2.

Ti–O–Ti bridges in titanosilsesquioxane dimer (curve d) exhibit only an extremely weak photoemission signal, with maximum at 500 nm and a component at 410 nm, and this suggests that dimeric species observed by DR UV-Vis spectroscopy both in TAPO-34 and TAPSO-34 have a very low emission signal, which may be obscured by the more intense signal of the isolated tetrahedral Ti(IV) sites.

Raman spectroscopy was used to estimate the amount of TiO_2 -like extra-framework species (Fig. 6). This technique is, in fact, very sensitive because TiO_2 has a very intense vibrational mode at 143 cm^{-1} (Fig. 6, curve a). TAPO-34 (curve b) and TAPSO-34 (spectra not shown for clarity) show weak bands at around 153 cm^{-1} , which can be assigned to TiO_2 -like extra-phase. The difference of the frequency of this vibration in comparison with that of the massive TiO_2 might account for the nature of the species, which should consist of either very small particles

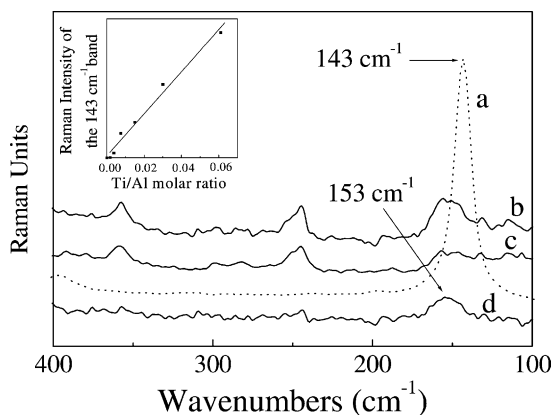


Fig. 6. Raman spectra of TiO_2 (Degussa P25) (curve a), TAPO-34 (curve b) and AlPO-34 (curve c) as-synthesised materials. Curve d represents the difference spectrum obtained by subtracting the spectrum of pure AlPO-34 (curve c) from the spectrum of TAPO-34 (curve b). Inset: integrated intensity of the mode at 143 cm^{-1} of AlPO-34 + TiO_2 mixtures against Ti/Al molar ratio.

or clusters in Ti-aluminophosphate molecular sieves. The convincing proof for this assignment is found in the difference spectrum obtained by subtracting the spectrum of pure AIPO-34 (curve c) from that of TAPO-34 (curve b). This difference spectrum (curve d) shows more clearly the contribution of TiO₂ band at 153 cm⁻¹. Bands at 360 and 245 cm⁻¹ due to morpholine entrapped in the cavities of the as-synthesised samples are also present [25].

The concentration of TiO₂-type extra-phases in the TAPO-34 and TAPSO-34 samples was estimated by means of a calibration curve (Fig. 6, inset), obtained by plotting the integrated intensity of the band at 143 cm⁻¹ of several AIPO-34/TiO₂ physical mixtures against the Ti/Al molar ratios. The amount of TiO₂-like phase found in both materials was determined by measuring the integrated area of the 153 cm⁻¹ band, which, by means of the calibration curve, gave a value of around 20% of the overall Ti(IV) used in the gel synthesis. This result is a further conclusive proof, along with the electronic spectra (both in absorption and emission), that a large fraction of the Ti(IV) ions is in the framework positions of the aluminophosphates.

It is of note that the amount of TiO₂-like phase determined by Raman was similar for both TAPO-34 and TAPSO-34 samples. This result is in favor of the assignment of the strong diffuse reflectance band at 240 nm to electronic transition of framework Ti–O–Ti sites. The TiO₂ extra-phase, in fact, absorbs at 280 nm and this contribution is similar for the two samples (Fig. 4, curves a and b).

4. Conclusions

TAPO-34 and TAPSO-34 molecular sieves have been synthesised by using morpholine as structure-directing template. The diffuse reflectance UV-Vis and photoluminescence study of titanosilsesquioxane dimer molecular compound and Ti-MCM-41 catalyst with a well-defined co-ordination of titanium ions, has been found helpful for clarifying the local environment of Ti(IV) ions in TAPO-34 and TAPSO-34 materials. A significant fraction of Ti(IV) ions is in framework positions both as isolated tetrahedral centres (absorption bands at 210 nm, and emission bands at 425 and 480 nm) and dimeric Ti–O–Ti species (ab-

sorption band at 240 nm). Around 20% of the overall amount of the titanium used in the synthesis gel is present as TiO₂-like extra-phase (absorption band at 280 nm), as shown by Raman spectroscopy.

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