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## Isomorphous Substitution of Framework Atoms by Titanium in VPI-5 Aluminophosphate Molecular Sieve

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Extra-large pore aluminophosphate molecular sieve TiVPI-5 was synthesised hydrothermally in the presence of di-*n*-butylamine and transformed by the calcination process at 500 °C to a large pore TAPO-8. Incorporation of titanium(IV) into VPI-5 framework was studied by elemental and thermogravimetric analyses, combined with X-ray Absorption Near Edge Structure (XANES) spectroscopy and UV-VIS absorption spectroscopy. We found that titanium(IV) incorporated in TiVPI-5 isomorphously substitutes framework aluminium on octahedral sites and that it is not present in the structure in the form of TiO<sub>2</sub> anatase. *In situ* IR measurements of pyridine adsorption/desorption were used to check the presence of catalytically active centres in the product resulting from titanium incorporation into the VPI-5 framework. Weak Lewis and Brønsted acid sites were found in small amounts in the calcined product TAPO-8.

**Key words:** aluminophosphate, molecular sieve, TiVPI-5, titanium, isomorphous substitution, acid sites.

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## INTRODUCTION

Aluminophosphate molecular sieves ( $\text{AlPO}_4\text{-}n$ ,  $n$  denotes the specific structure type) are crystalline microporous materials comprising corner sharing  $\text{AlO}_4$  and  $\text{PO}_4$  tetrahedra.<sup>1</sup> They possess a regular pore system with diameters in the range of 3–14 Å and they act as sieves on the molecular level. On the basis of their pore diameters, they are defined as small pore (< 4 Å), medium pore (4–6 Å), large pore (6–8 Å) and extra-large pore (>8 Å). The isomorphous substitution of  $\text{AlPO}_4\text{-}n$  framework atoms with transition metals generates negative charge sites in the framework with Brønsted, Lewis and redox catalytically active centres.<sup>2</sup> It has been shown that transition metal ion containing aluminophosphates are interesting catalysts for a variety of heterogeneously catalysed reactions such as oxidations ( $\text{MeAPO-5}$ ,  $\text{MeAPO-11}$  etc., Me = Co, Mn, Fe, Ti, Cr). Recently, large pore molecular sieves have become interesting from the catalytic point of view,<sup>3</sup> because they are suitable for recognising, discriminating and organising molecules with kinetic diameters greater than 6 Å.

VPI-5 aluminophosphate is an extra-large pore molecular sieve with 18-member ring channels built from alternating 4- and 6-member rings and 12 Å free diameter.<sup>4</sup> Catalytic applications of VPI-5 are limited by its thermal stability, which depends on the synthesis and post-synthesis treatment conditions. The structure transforms at low temperatures to another large-pore aluminophosphate molecular sieve,  $\text{AlPO}_4\text{-8}$ , with 14-member ring channels and 8 Å free diameter.

The structure of VPI-5 was determined by X-ray powder diffraction<sup>5</sup> and later confirmed by single crystal X-ray diffraction<sup>6</sup> on the as-synthesised VPI-5. There are three inequivalent aluminium sites in the framework. On two of them, aluminium is co-ordinated tetrahedrally and links 4- and 6-member rings in the framework. The aluminium at the third site links two 4-member rings and is co-ordinated octahedrally with four oxygen atoms from the framework and two molecules of water. Water molecules are found to be ordered inside the 18-member ring channel so as to create a triple helix *via* hydrogen bonding. After structure transformation from VPI-5 to  $\text{AlPO}_4\text{-8}$ , the third aluminium framework site remains co-ordinated octahedrally, but the triple helix of water molecules in the channels disappears. Structure characteristics described above were also confirmed by several NMR experiments.<sup>4</sup> Incorporation of heteroatoms into the VPI-5 structure was determined for  $\text{Si}^{7-11}$  on extra-framework positions and for  $\text{Co}^{9,12}$  and  $\text{Fe}^{13}$  on framework positions.

Recently, it was shown that, in contrast to Ti-silicalites, the catalytic oxidation activity of  $\text{AlPO}_4\text{-}n$  containing titanium ( $\text{TAPO-}n$ ,  $n = 5, 11, 36$ ) is associated only with the framework Ti atoms and not with any hypothetical Ti

species in the reaction solution.<sup>14</sup> Isomorphous substitution of framework atoms of the extra-large pore aluminophosphate molecular sieve VPI-5 with titanium is thus a promising way to prepare materials for oxidation of larger molecules by H<sub>2</sub>O<sub>2</sub> or by larger organic peroxides. In this paper, we describe the preparation procedure for TiVPI-5 molecular sieve, its characterisation and some direct evidence for the incorporation of titanium into the VPI-5 framework.

## EXPERIMENTAL

### *Synthesis*

TiVPI-5 was synthesised hydrothermally in the presence of di-*n*-butylamine (C<sub>8</sub>H<sub>19</sub>N, Sigma) as a template in stainless steel teflon-lined autoclaves under static conditions. Aluminium and phosphorus sources were pseudoboehmite (PURAL SBI, Condea, 75.3% Al<sub>2</sub>O<sub>3</sub>) and phosphoric acid (H<sub>3</sub>PO<sub>4</sub>, Merck, 85%), respectively. Titanium(IV)-isopropoxide (Ti(OC<sub>3</sub>H<sub>7</sub>)<sub>4</sub>, Alfa) was used as metal source.

The synthesis procedure was chosen according to the literature data on VPI-5,<sup>15</sup> systematically studied and optimised. The final molar composition of the reaction mixture for the pure TiVPI-5 product was:



The TiVPI-5 reaction mixture having the above molar composition was prepared by adding orthophosphoric acid and titanium(IV) isopropoxide successively dropwise into the stirred suspension of pseudoboehmite in water. The resulting mixture was stirred for 2 hours with a magnetic stirrer. After 3 hours of ageing, di-*n*-butylamine was added dropwise. The reaction mixture was then thoroughly blended for 20 minutes using a disperser.

The resulting gel was transferred to a 50 mL stainless steel teflon-lined autoclave and heated under static conditions in an oven. TiVPI-5 crystallised at 150 °C in 1 day. After crystallisation, TiVPI-5 crystals were dried at room temperature in vacuum for 6 hours. The template-free sample was prepared by heating the corresponding as-synthesised product to 500 °C (heating rate of 2 °C min<sup>-1</sup>) and keeping it at that temperature in oxygen for 6 hours.

### *Characterisation*

X-ray powder diffraction (XRPD) measurements of the product at room temperature were performed on a Siemens D-5000 diffractometer using Cu-K $\alpha$  radiation. The diffraction pattern was measured in the  $2\theta$  range from 5 to 35° in steps of 0.04°, with 1 s per step.

X-ray powder patterns of the product were monitored also at higher temperatures, up to 900 °C, on the same diffractometer equipped with a HTK-16 high-temperature chamber. XRD patterns were collected in the  $2\theta$  range of 5 to 38°, with

0.026° steps and a counting time of 4 s per step. Between scans, the sample was heated in air at a rate of 10 °C min<sup>-1</sup>.

The size and morphology of the crystals in the product were studied with a scanning electron microscope Jeol JXA-840A.

Elemental analysis was carried out with an EDAX (Energy Dispersion Analysis by X-ray) analytical system TRACOR EDX, attached to the scanning electron microscope Jeol JXA-840A.

The C, H, N elemental analysis was performed using a Perkin-Elmer 2400 elemental analyser.

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on a TA 2000 Thermal Analyser (TA Instruments, Inc.) in an inert atmosphere. Measurements were carried out in a flow of He (50 mL min<sup>-1</sup>) at the heating rate of 10 °C min<sup>-1</sup>.

UV-VIS spectrum of the solid sample was recorded on a UV-VIS spectrophotometer Spectrometer Lambda 19 (Perkin-Elmer). The product was suspended in nujol on filter paper and measured in a normal solution cell container.<sup>16</sup>

The X-ray absorption spectra were measured at the E4 beamline of HASYLAB synchrotron radiation facility at DESY (Hamburg, Germany). The E4 beamline provides a focused beam from an Au-coated mirror and a Si(111) double-crystal monochromator with 1 eV resolution at the Ti K-edge. Harmonics were effectively eliminated by a plane Ni coated mirror. Powdered samples of the as-synthesized and calcined TiVPI-5 and reference samples (TiO<sub>2</sub>) were prepared on multiple layers of adhesive tape with the total absorption thickness of  $\mu\text{d} \sim 2$  above the Ti K-edge. Due to the low concentration of titanium in the TiVPI-5 and samples, the Ti K-edge jump was only about 0.1. Reference spectra were taken on empty tapes. The exact energy calibration was established by simultaneous absorption measurements on the Ti metal foil.

The acidity of the potential catalyst TAPO-8 was assessed, qualitatively and quantitatively, by pyridine using a Nicolet 710 spectrometer. TAPO-8 was activated *in situ* at 450 °C under vacuum (10<sup>-5</sup> Torr). The detailed experimental procedure has already been described in the literature.<sup>18,19</sup>

## RESULTS AND DISCUSSION

### *XRPD, Elemental and Thermogravimetric Characterisation*

XRPD patterns of the as-synthesised TiVPI-5 sample measured during the thermal treatment in the air show transformation of the TiVPI-5 structure to TAPO-8 already at 100 °C (Figure 1). The process is non-reversible and TAPO-8 is thermally stable at least up to 900 °C (Figure 1). XRPD patterns of the template-free product after calcination at 500 °C (see Experimental part) revealed the calcined product as TAPO-8.

Scanning electron micrographs (SEM) of TiVPI-5 and TAPO-8 reveal mesh-like aggregates (dimensions range from 50 to 100  $\mu\text{m}^3$ ) composed of

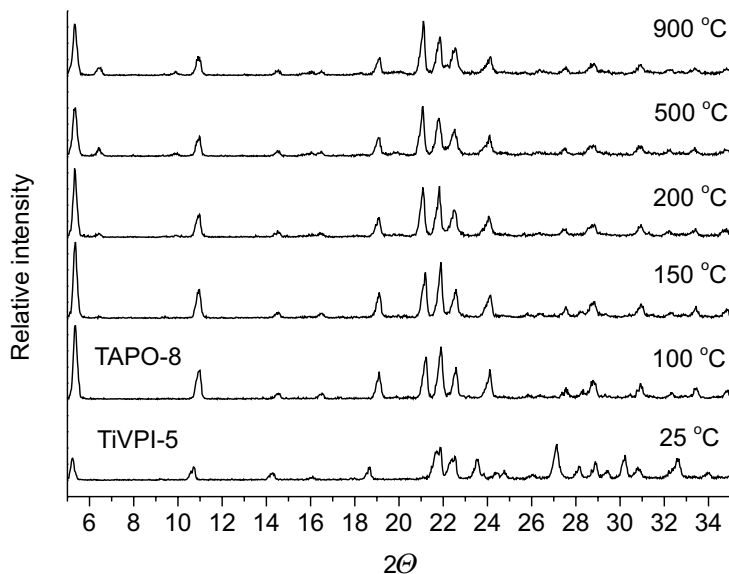


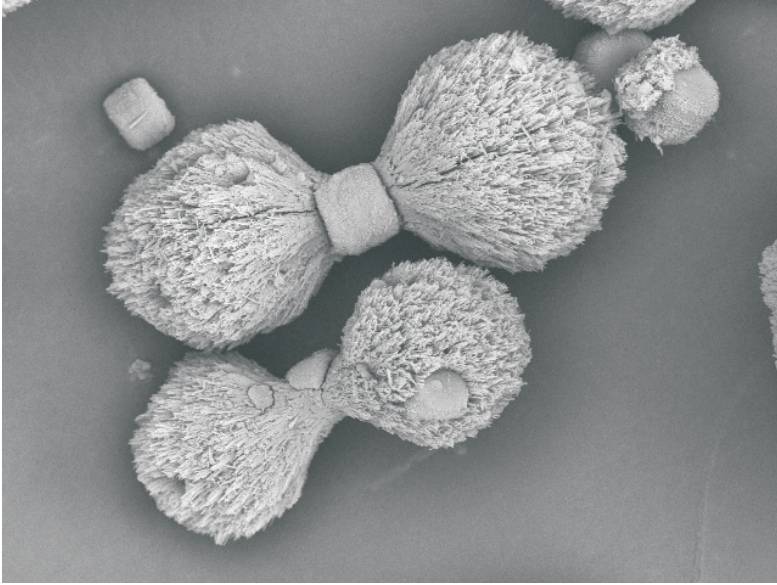
Figure 1. XRPD patterns of TiVPI-5 measured during the thermal treatment of the sample in the air.

needles which are typical of this structure type (Figure 2).<sup>4</sup> The micrographs of the sample also confirm phase purity.

Results of thermogravimetric analysis of as-synthesised TiVPI-5 (Figure 3) in the inert atmosphere show that the desorption of water takes place up to 150 °C and that the decomposition of di-*n*-butylamine occurs between 150 and 500 °C. The character of weight loss, *i.e.*, whether it is due to the desorption of water or, the removal of the template, was determined using C, H, N analysis of the as-synthesised sample.

On the basis of thermogravimetric and elemental analyses of TiVPI-5 crystals, the general formula  $(\text{Me}_x\text{Al}_y\text{P}_z)_2\text{O}_2$  was calculated (Table I). The value of  $x + y \approx z \approx 0.5$  in the general formula suggests that aluminium in TiVPI-5 framework was isomorphously substituted by titanium.<sup>20</sup> It should be emphasised that the elemental analysis of the framework composition was not done on the bulk sample. It was performed with the analytical system attached to the scanning microscope. The observed framework composition can thus be considered reliable and it does not include a potential contribution from elements in the amorphous phase. However, the isomorphous substitution of framework aluminium only has not yet been observed for titanium. So far it has been a widely accepted fact that titanium replaces phosphorous or phosphorous and aluminium framework sites in aluminophosphates. It is known from the structure determination of VPI-5 that

a)



b)

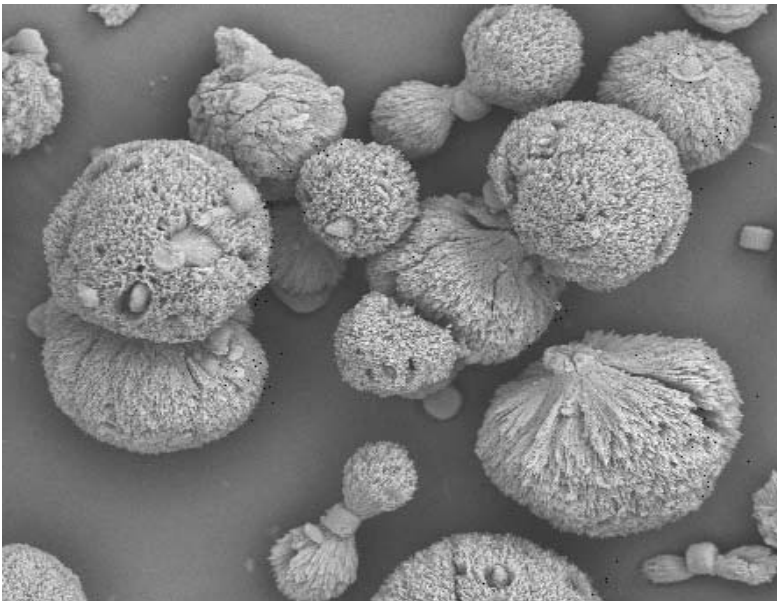


Figure 2. Scanning electron micrographs of a) as-synthesised TiVPI-5, and b) calcined TAPO-8.

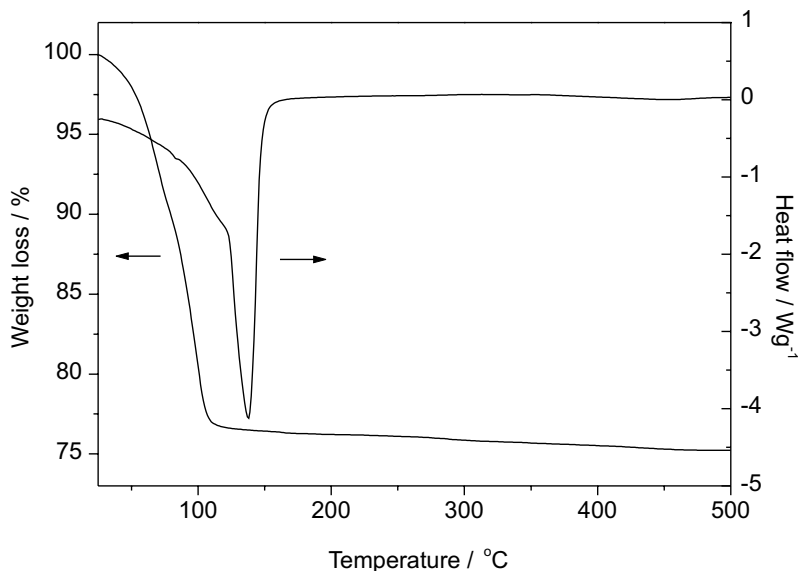


Figure 3. Thermogravimetric curves of TiVPI-5.

there are three inequivalent aluminium sites in the VPI-5 framework: two tetrahedral and one octahedral, additionally co-ordinated with two molecules of water from the channel. If titanium replaces the tetrahedral aluminium framework site, the framework of TiVPI-5 is positively charged. If titanium replaces the octahedral aluminium framework site, the framework of TiVPI-5 is negatively charged as soon as octahedral titanium is co-ordinated with two OH groups instead of two water molecules. From the literature data<sup>4</sup> on VPI-5, it is known that the template has no structure directing impact, but it has an impact as pH moderator and it is not found in the pores of as-synthesised VPI-5. In our case, the template was found in a small amount (Table I). The reason is probably the compensation of the framework charge generated in the product as a consequence of titanium incorporation into the VPI-5 framework.

TABLE I

Chemical composition of the product (uncertainty of data is  $\pm 0.005$ )

Sample	TO <sub>2</sub> formula (Me <sub>x</sub> Al <sub>y</sub> P <sub>z</sub> )O <sub>2</sub>			DIB/TO <sub>2</sub>	H <sub>2</sub> O/TO <sub>2</sub>
	<i>x</i>	<i>y</i>	<i>z</i>		
TiVPI-5	0.009	0.486	0.505	0.0116	0.9029

DIB = di-*n*-butylamine



*UV-VIS Absorption Spectra – Co-ordination Geometry of Titanium*

The observed UV-VIS absorption spectrum of TAPO-8 shows the absorption band at *ca.* 240 nm and a hardly visible shoulder at *ca.* 220 nm (Figure 4). The latter might indicate the presence of the tetrahedrally co-ordinated framework titanium due to the charge transfer processes between empty d-orbitals of titanium(IV) cations and oxygen atoms.<sup>21</sup> However, identification of the framework titanium in TAPO-8 was impossible because of the matching of charge transfer absorption bands of framework titanium with those of framework aluminium<sup>22</sup> in aluminophosphate molecular sieves. The absence of a broad absorption band around 330 nm in the UV-VIS spectrum of TAPO-8 is a firm proof that titanium is not present in the form of TiO<sub>2</sub> anatase. TiO<sub>2</sub> anatase is otherwise a common impurity in titanium containing aluminophosphates.<sup>23</sup>

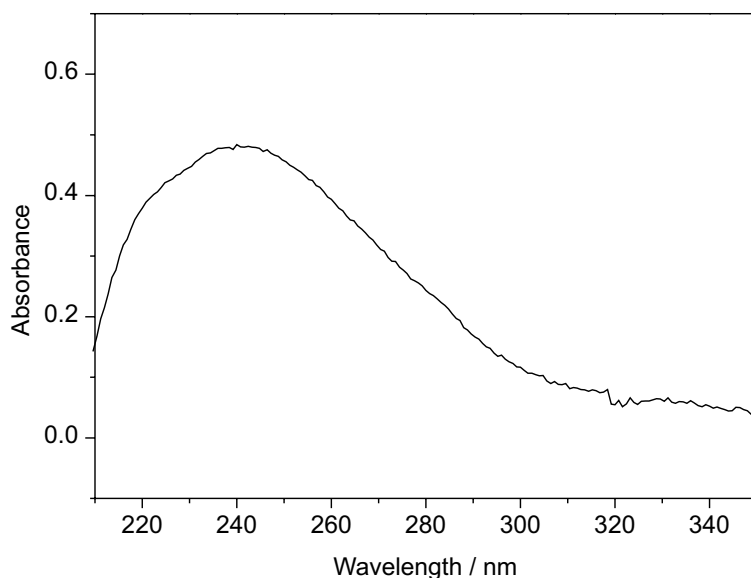


Figure 4. UV-VIS absorption spectra of TAPO-8.

*XANES Studies – Co-ordination Geometry and Valence State of Titanium*

Normalised Ti XANES spectra of the as-synthesised TiVPI-5 and calcined TAPO-8 samples are shown in Figure 5 together with the spectra of reference TiO<sub>2</sub> anatase and rutile samples. The spectra were obtained from the absorption measurements by a standard procedure.<sup>17</sup> Zero energy is taken at the first inflection point in the titanium metal spectrum at 4964.5 eV.

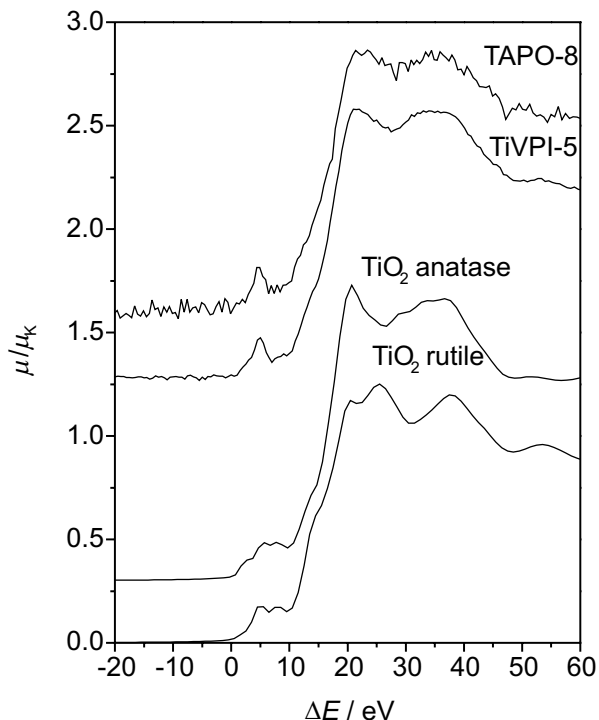


Figure 5. Normalized Ti K-edge profiles, displaced vertically, for the as-synthesised TiVPI-5, calcined TAPO-8, reference TiO<sub>2</sub> rutile and reference TiO<sub>2</sub> anatase. Energy scale is relative to the Ti K-edge in metal (4964.5 eV).

The shape of the Ti K-edge and especially the pre-edge resonances can be used as fingerprints of the local symmetry of the titanium atom site in the sample.<sup>17,24</sup> XANES spectra of TiO<sub>2</sub> anatase and rutile show three low intensity pre-edge peaks, characteristic of octahedrally coordinated titanium atoms.<sup>25,26</sup> On the other hand, tetrahedrally coordinated titanium materials, lacking an inversion centre, can easily be identified by a single intense pre-edge peak, shifted by about  $-2$  eV compared to rutile pre-edge resonances.<sup>25,26</sup>

The Ti XANES spectra of the TiVPI-5 samples are very similar to the reference TiO<sub>2</sub> spectra (Figure 5). Both exhibit weak pre-edge resonances characteristic of the octahedral titanium symmetry. However, the shape of the pre-edge resonant structures is different from those observed in the XANES spectrum of rutile or anatase. We can therefore conclude that titanium atoms in the TiVPI-5 product are octahedrally co-ordinated, but not in the form of TiO<sub>2</sub> anatase or rutile.

Ti XANES spectra can also be used to determine the average valence state of titanium in the sample. The energy position of the K-edge and pre-edge absorption features linearly increases with the valence state of the atom.<sup>17,24</sup> The energy shift is most prominent for the absorption edge, where shifts of about 2–3 eV per oxidation states are found.<sup>17</sup> The energy position of the Ti K-edge of TiVPI-5 samples is identical (within experimental error  $\pm 0.2$  eV) with those measured on the  $\text{TiO}_2$  samples, indicating that the valence state of titanium is (IV).

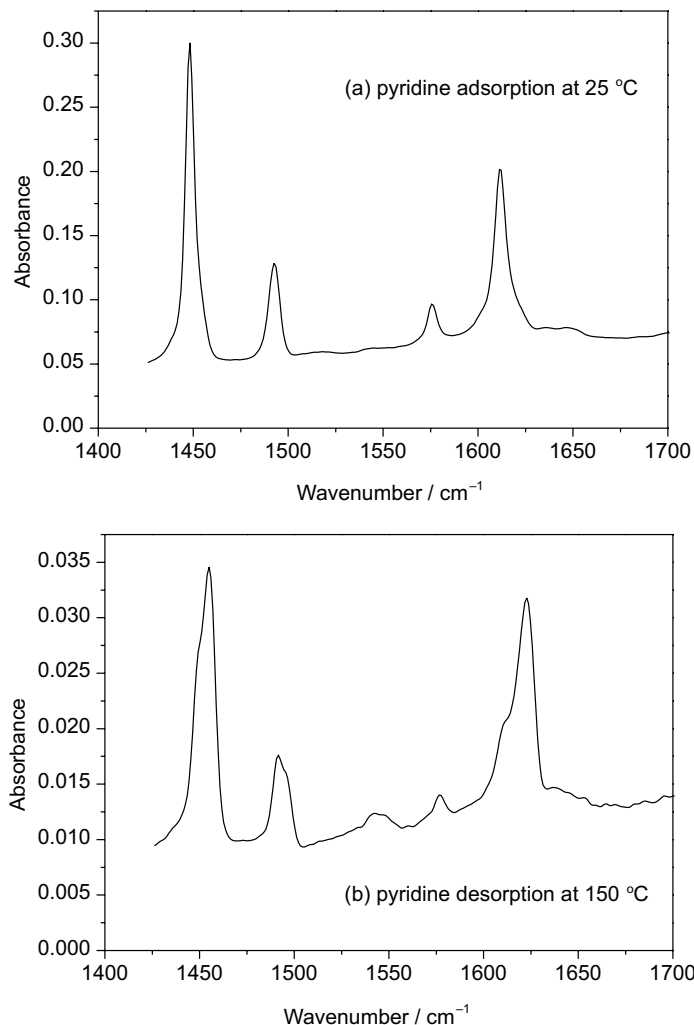


Figure 6. IR spectar of a) pyridine adsorption at room temperature, and b) pyridine desorption at 150 °C on TAPO-8.

### In situ IR Studies of Acid Sites in TAPO-8

Acid sites of TAPO-8 were characterised by pyridine adsorption/desorption experiments. After pyridine adsorption at room temperature, pyridine was present ( $1448\text{ cm}^{-1}$ ) on Lewis sites together with Brønsted sites in a small quantity ( $1612$  and  $1545\text{ cm}^{-1}$ ) and physisorbed pyridine (Figure 6). The band at  $1494\text{ cm}^{-1}$  is a combined band of Lewis and Brønsted sites.

After desorption of physisorbed and weakly bound pyridine at  $150\text{ }^{\circ}\text{C}$  under vacuum, a small amount of Lewis sites remained and some Brønsted sites were present as traces, which could be associated with  $\text{TiO}_4(\text{OH})_2$ . The amount of sites estimated using extinction coefficients measured on Y zeolite<sup>19</sup> was:  $n_{\text{Lewis}} (1448\text{ cm}^{-1}) = 40\text{ }\mu\text{mol g}^{-1}$  and  $n_{\text{Brønsted}} (1545\text{ cm}^{-1}) = 3\text{ }\mu\text{mol g}^{-1}$ . This corresponds to 1/3 of titanium sites in the structure, but the extinction coefficient might be slightly different on TAPOs than on Y zeolites, and the amount of sites detected is therefore reasonable.

## CONCLUSIONS

Titanium(IV) was incorporated into extra-large pore aluminophosphate VPI-5 by hydrothermal crystallisation in the presence of di-*n*-butylamine. Calcined product TAPO-8 was prepared by the calcination process at  $500\text{ }^{\circ}\text{C}$  in the air atmosphere. Phase transformation of TiVPI-5 to TAPO-8 occurs at  $100\text{ }^{\circ}\text{C}$ . The relatively low temperature of the phase transition is a peculiarity of this structure type. TAPO-8 is thermally stable at least up to  $900\text{ }^{\circ}\text{C}$ .

The obtained  $\text{TO}_2$  formula of the as-synthesised TiVPI-5 indicates that titanium isomorphously substitutes the framework aluminium. This mechanism was observed for the first time. Previous reports of titanium incorporation comprise only the mechanisms of the isomorphous substitution with titanium of the phosphorus framework sites or combined isomorphous substitution with titanium of phosphorus and aluminium framework sites.

Additional information on the incorporation of titanium are obtained by UV-VIS and XANES spectroscopic methods. UV-VIS spectra demonstrate that the incorporated titanium is not present in the form of  $\text{TiO}_2$  anatase in the pores of the material. On the other hand, the XANES analysis confirms octahedral co-ordination of titanium(IV) in the samples and also shows that titanium is not in the form of  $\text{TiO}_2$  anatase or rutile. These results lead to the conclusion that titanium(IV) isomorphously substitutes only one of the three aluminium framework sites – the octahedral one. Lewis and Brønsted acid sites found in the product support the idea that some octahedral units  $\text{AlO}_4(\text{H}_2\text{O})_2$  in VPI-5 were substituted with octahedral  $\text{TiO}_4(\text{OH})_2$  units in TiVPI-5.

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**SAŽETAK****Izomorfna supstitucija atoma okosnice molekuskog sita  
VPI-5 aluminofosfata atomima titanija**

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Frederic Thibault-Starzyk i Venčeslav Kaučič*

Sintetizirano je molekulsko sito TiVPI-5 s izuzetno velikim porama, i to hidrotermalno u prisutnosti di-*n*-butilamina, a zatim je transformirano u TAPO-8 procesom kalcifikacije na 500 °C. Inkorporiranje titanija(IV) u kostur sustava VPI-5 ispitano je elementnom i termogravimetrijskom analizom, kombiniranom sa XANES i UV-VIS apsorpcijskom spektroskopijom. Apsorpcija/desorpcija piridina mjerena je *in situ* IR tehnikom da bi se utvrdila prisutnost katalitički aktivnih centara produkta kao posljedice ugradnje atoma titanija u okosnicu VPI-5. Nađena su slaba Lewis-ova i Brønsted-ova kisela mjesta u kalcificiranom produktu TAPO-8.