Revealing the influence of the solvent in combination with temperature, concentration and pH on the modification of TiO$_2$ with 3PA

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HIGHLIGHTS

- Functionalization of titanium dioxide with propylphosphonic acid (3PA).
- Solvent, temperature and amount 3PA together affects degree and type of functionalization.
- Ordered layers are formed already at low concentration of 3PA in toluene.
- Titanium propylphosphonates (TiPP) and surface grafting can both be formed in water.
- Formation of TiPP rises with temperature and concentration in water.

GRAPHICAL ABSTRACT
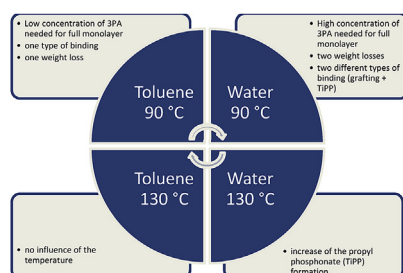
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ABSTRACT

Hybrid materials are being developed to add organic functionalities to inorganic materials. Here, titanium dioxide is modified with organophosphonic acids (PAs). In several applications, the surface properties of the material play a key role in their performance (e.g. separation, sorption, catalysis). Hence, the surface properties of these materials need to be specifically adjusted to meet the requirements of each application (e.g. in membrane separation or chromatography). As the synthesis conditions have an important influence on the obtained surface properties, it is necessary to understand the impact and differences introduced by altering synthesis conditions. Different solvents are being applied for modification, but a comparative study of the impact of this change in environments is missing in literature. Therefore, our aim is to study the impact of concentration, temperature and pH in water and toluene on the properties of TiO$_2$ modified with propylphosphonic acid (3PA). By combining complementary techniques (DRIFT, TGA and ^{31}P/CP MAS NMR), clear differences induced by the solvent can be found. Moreover, in toluene a lower concentration of 3PA is required to obtain closed packed monolayers than in water. Furthermore, both solvent and concentration are influencing the modification degree and binding type formed on the surface. Moreover, only in water, next to the concentration, also the

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temperature and pH have a strong impact on the binding type of 3PA. A clear difference in thermal stability of 70 °C was found between both binding types.

1. Introduction

Organic-inorganic hybrid materials are of specific interest for applications that need the robustness (mechanical and chemical stability) of inorganic materials in combination with the diversity of interaction typical for organic molecules. These hybrid materials can be synthesized in various ways using in-situ synthesis processes at the precursor level or surface post-modifications [1–5]. They are applied in a large variety of applications such as chromatography [6], adsorbents [7], solid-state chemistry columns/supports [8], sensors [9], membranes [10,11], catalysis [12], filtration [13] etc. Hybrid transition metal oxides and metals modified with organic groups receive increasing attention [5,14–20] and TiO_2 is gaining interest because of its intrinsic chemical stability in a wide variety of solvents and pH ranges [21–23]. However, the surface of metal oxides consists of M—OH groups, making it hydrophilic and limiting the diversity of possible interactions. Therefore, to enhance its applicability, organic functional groups are being grafted to its surface. Different precursors can be used for grafting transition metal oxides such as organosilanes [14,24], organophosphonic acids (PAs) [5,25–29], organometallic reagents (e.g. Grignard reagents) [30,31] and others [3,32,33]. The PA forms M—O—P bonds that are more stable and easily formed on metal oxides compared to organosilanes [26,28].

Various studies [5,26,28,34–37] have shown that PAs have an excellent affinity for different transition metal oxides, in particular Al_2O_3, ZrO_2 and TiO_2. On the one hand, for surface grafting, three different binding modes (mono-, bi- and tridentate) are described for modification with PA. On the other, Guerrero et al. [38] described a dissolution-precipitation process, forming a titanium phenylphosphonate layer, when forced conditions were used, i.e. modification of TiO_2 with a solution (water or toluene) of 0.11 M phenylphosphonic acid (PhPA) at 120 °C for one day. These metal phosphonates could also be prepared by heating tetravalent metals, complexated with HF, above 60 °C. The metals then slowly precipitated by the formation of a complex with the PAs [39,40]. Alberti et al. [40] published the crystal structures of such metal organophosphonates. Randon et al. [34] modified TiO_2 with a 0.1 M solution of PA in water at reflux temperature, suggesting the formation of a tridentate binding mode. However, other binding modes could not be excluded, due to the strong absorption band of TiO_2 in the P—O stretch region. Following Gao et al. [35], it was found that modifying ZrO_2 with a low concentration (i.e. 5-fold excess of PA relative to the amount of moles needed for full surface coverage of the metal oxide) of octadecylphosphonic acid (18PA) in a boiling methanol/water mixture resulted in a single broad asymmetric peak in the ^{31}P MAS NMR spectrum, due to a distribution of different binding types and/or binding sites. By assuming a similar trend for the reaction of 18PA with ZrO_2 as with SiO_2, they expected the binding to be monodentate rather than tridentate. They stated that despite the fact that peaks for P=O and P—OH were absent in the infrared spectrum, a definite assignment of those bands is speculative due to the overlap of the P—O stretching bands with the metal oxide bonds and the dependence on the degree of hydrogen bonding or metal binding. They found only a slight shift of the ^{31}P resonance signal in the ^{31}P MAS NMR spectrum for the modification of TiO_2 with 18PA, compared to the

shift of the pure compound, indicating only a weak interaction between PA and TiO_2. For the modification of Al_2O_3, Lassiaz et al. [41] found that the binding mode changed with increasing concentration of octylphosphonic acid (8PA) when the reaction was performed in water at room temperature. However, the binding mode itself was not identified. Next to the modifications in polar solvents, Fadeev et al. [26,27] worked with an apolar solvent (toluene) and investigated the thermal degradation of modified TiO_2 with 18PA by using TGA. Although FTIR was used to describe the order of the alkyl groups, no explanation was given concerning the Ti—O—P region in IR. When modifying Indium Tin Oxide (ITO) with PAs, the solvent has a significant influence. Chen et al. [42] found that grafting of 18PA and PhPA on ITO in a non-polar solvent resulted in the formation of a well-ordered SAM, while in polar solvents only a poorly packed SAM was formed. They attributed this to a diminishing of the intermolecular chain-chain interactions in the polar solvent, affecting the SAM formation. Unfortunately, they did not study the impact of the solvent on the binding type. Furthermore, no influence of reaction temperature and PA concentration was described. Taking the above into account, changes in the binding type and the organic surface loading may be expected upon changing the reaction conditions and environment.

Thus, despite the various studies on PA-modified TiO_2, describing the modification reaction under different reaction conditions (solvent, temperature or concentration) a systematic comparative study on the same material and with the same PA is lacking. This hampers the ability to choose reaction conditions that will lead to the envisaged surface properties (density, number of functional group, presence or absence of phases such as phosphonates etc.) required for a specific application. As the appropriate synthesis conditions may differ for each application, a study is needed comparing different synthesis methods (solvent, temperature and concentration) and rationalizing their impact on the binding type and modification degree.

This article reports the results of such a systematic comparative study to elucidate the influence of solvent, temperature, concentration and pH on the surface characteristics obtained. More specifically, the aim of this work is a detailed investigation of the effect of the reaction conditions on the types of functionalization (surface grafting or phosphonate formation) and density of the organic loading. Moreover, it will show the role of the solvent on differences in impact of changes in concentration and temperature. The modified TiO_2 is characterized by TGA, DRIFT, DRIFT in function of temperature (ex-situ),^{31}P-CP/MAS NMR and SEM EDX. Finally, a correlation is shown between characteristic signals and signal patterns, visualized by a combination of various characterization methods upon changing the surface characteristics of the TiO_2. Only by understanding the impact of the synthesis conditions on the surface properties of 3PA-modified TiO_2, surface properties fitting the application can be designed in a controlled way.

2. Experimental

2.1. Materials

Propylphosphonic acid (3PA) was purchased from Sigma-Aldrich. TiO_2 P25 (80% anatase/20% rutile, BET surface of 50 m^2/g,

average particle size 21 nm) was purchased from Degussa Hulls and used without pre-treatment.

2.2. Synthesis

The non-porous TiO_2 P25 from Degussa Hulls was used as the TiO_2 support. For the modification, 1.0 g of TiO_2 was stirred for 4 h in a heated solution of 20 mL 3PA. The concentration of this solution was varied (0.003 M-0.150 M) as well as the oil bath temperature (90–130 °C). Furthermore, two solvents were used: water and toluene. After modification, the samples were washed with 3×30 mL of the solvent used during the modification and were subsequently dried overnight in an oven at 60 °C.

2.3. Characterization techniques

DRIFT measurements were performed on a Nicolet 6700 Fourier Transform IR spectrometer, equipped with an electromagnetic source in the mid-IR region (4000–400 cm^{-1}). The detector was a liquid N_2 cooled MCT-B detector. A resolution of 4 cm^{-1} was used and for each spectrum 200 scans were measured. The sample holder contained a 2 wt% diluted sample in KBr and was measured under a constant flow of dry air. All samples were measured with two backgrounds: a 100% KBr background and a background of 2 wt % of unmodified TiO_2 in KBr to subtract the TiO_2 background from the spectrum of the modified materials (Figure SI 1). The latter background was used to get a clearer view on the peaks originating from the binding between TiO_2 and PA itself. In these spectra a positive peak was assigned to a newly formed bond upon functionalization with PA, while a negative peak indicated the disappearing of a specific bond.

Thermogravimetric analyses (TGA) were recorded on a Mettler Toledo TGA/SDTA851^e. The measurements were performed in a continuous flow of oxygen and the samples were heated from 30 to 600 °C with a heating rate of 10 °C/min. In the region 270–520 °C the carbon group is burnt, but the phosphorus group remains at the surface [27]. Therefore, the modification degree can be calculated from the weight loss by using the following formula:

$$mod.dg. \left(\frac{\#}{nm^2} \right) = \frac{wt\%(R) \times N_A}{MM(R) \times S_{BET}}$$

In which wt%(R) is the weight loss of the organic group measured in TGA, MM(R) is the molar mass of the carbon group, S_{BET} is the surface area of the unmodified TiO_2 and N_A is Avogadro's constant. The number of organic groups is equal to the amount of PA as each PA only has one functional organic R group. With respect to the formation of the titanium propylphosphonate (TiPP) phase in which the number of phosphate groups/TiO_2 is higher than in the case of surface grafting and TiO_2 has been dissolved, it is useful to calculate the organic loading also in function of mass (PA)/mass (TiO_2). This is calculated with the following formulas in the temperature range T1 to T2:

$$m(PA) = \frac{(m_{T1} - m_{T2})(R) \times MM(PA)}{MM(R)}$$

$$Organophosphonic\ acid\ loading : \left(\frac{mg(PA)}{g(TiO_2)} \right) = \frac{m(PA)}{m_{T1} - m(PA)}$$

$(m_{T1}-m_{T2})(R)$ corresponds with the weight loss of the R-group in TGA, MM(PA) is the molar mass of 3PA and MM(R) the molar mass of the R group. m_{T1} is the mass measured of the sample before the weight loss.

SEM EDX was measured on a Quanta 250 FEG microscope. The powder was attached to a carbon tape and for each sample 3 points were measured. From the average value the modification degree was calculated. The formula is similar to the one of TGA. But, in this case, the amount of %P and MM of P are used.

Phosphorus-31 solid-state CP/MAS (cross-polarization magic angle spinning) NMR spectra were acquired at ambient temperature on an Agilent VNMRS DirectDrive 400 MHz spectrometer (9.4 T wide bore magnet) equipped with a T3HX 3.2 mm VT probe dedicated for small sample volumes and high decoupling powers. Magic angle spinning (MAS) was performed at 10 kHz using ceramic zirconia rotors of 3.2 mm in diameter (22 μL rotors). The phosphorus chemical shift scale was calibrated with orthophosphoric acid (H_3PO_4) at 0 ppm. Other acquisition parameters used were: a spectral width of 50 kHz, a 90° pulse length of 2.5 μs, a spin-lock field for CP of 100 kHz, a contact time for CP of 1.7 ms, an acquisition time of 20 ms, a recycle delay time of 20 s and 200–3000 accumulations. High power proton dipolar decoupling during the acquisition time was set at 100 kHz. The Hartmann-Hahn condition for CP was calibrated accurately on the samples themselves.

All samples received structural names indicating the modification conditions, e.g., 3PA0.025M90W represents the sample modified with 0.025 M of propylphosphonic acid (3PA) at 90 °C in water (W), while 3PA0.100M130T indicates the sample modified with 3PA in a concentration of 0.100 M in toluene (T) at 130 °C.

3. Results and discussion

In the first part, the effect of concentration, temperature and pH is discussed for the modification of TiO_2 with 3PA in water. In the second part, we compare the impact of the solvent (water and toluene) on the functionalization of TiO_2 with 3PA. Although, from a practical point of view, the use of water is cheaper and more environmentally friendly, it also creates important differences compared to toluene that might influence the modification. Water can interact with the surface via hydrogen bonding, possibly creating strong competitive adsorption. Moreover, the PAs are acidic and thus change the pH of the solution. While toluene can only result in weak physical adsorption and there is no effect of the pH. Of course, also an influence of differences in the interaction of the solvent with the organic group can be expected. Furthermore, we specifically chose 3PA as it has much less tendency to create self-assembled layers.

3.1. Modification in water

The concentration of 3PA was varied between 0.025 M and 0.150 M for the modification in water. Two different synthesis temperatures were applied by heating the solution in an oil bath at 90 °C or at 130 °C. After washing and drying, the samples were extensively characterized with TGA, ^{31}P-CP/MAS NMR and (ex-situ) DRIFT.

3.1.1. TGA

Fig. 1A shows the TGA (dotted lines) and DTG curves (full lines) of the modification at 90 °C in water for different 3PA concentrations measured in an oxygen atmosphere. All the curves show a similar progression with a weight loss between 270 and 400 °C, increasing with the concentration of 3PA used. In this region pure TiO_2 P25 does not display a weight loss (Figure SI 2). When the sample is modified in a solution of 0.075 M 3PA, additional weight losses start occurring at 450 °C and in case of 0.150 M also at 490 °C. The total number of organic groups grafted onto the TiO_2 support, i.e., the modification degree or the organic loading, is calculated from the weight losses above 270 °C in the TGA (Table 1). The 3PA
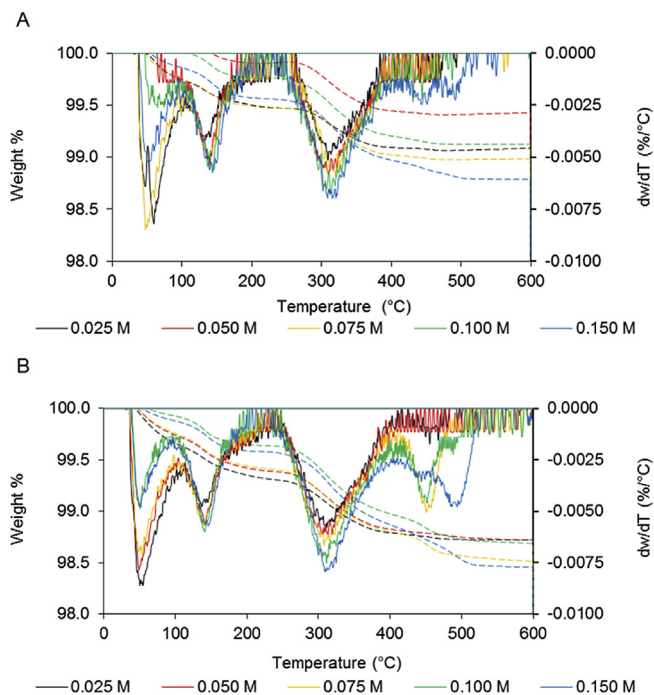
Fig. 1. TGA curves (dotted lines) and DTG curves (full lines) of TiO_2 modified with different concentrations of 3PA at 90 °C (A) and 130 °C (B) in water as measured under an O_2-flow and heating rate of 10 °C/min.

Table 1

3PA loading as measured with TGA for TiO_2 modified with different concentrations of 3PA in water at 90 °C and 130 °C. The loading is calculated in mass 3PA/TiO_2 (mg/g) and in number of 3PA/area (#/nm^2). Also the pH has been measured after the functionalization.

Name	270–400 °C 3PA/ TiO_2 (mg/g)	400–520 °C 3PA/ TiO_2 (mg/g)	270–520 °C 3PA/ area (#/nm^2)	pH
3PA0.025M90W	8	0	1.0	2.5
3PA0.050M90W	10	0	1.3	2.3
3PA0.075M90W	10	2	1.4	2.1
3PA0.100M90W	12	2	1.7	2.0
3PA0.150M90W	13	8	2.1	2.1
3PA0.025M130W	11	0	1.5	2.5
3PA0.050M130W	13	0	1.6	2.2
3PA0.075M130W	14	5	2.4	2.1
3PA0.100M130W	15	6	2.6	1.9
3PA0.150M130W	16	9	3.1	1.8

loading is calculated in *mg 3PA/g TiO$_2$* and in *number of groups of 3PA/nm^2*. The organic surface loading is split into two parts. The first part of the organic surface loading is calculated between 270 and 400 °C. The second part is calculated from the weight loss between 400 and 520 °C, only occurring for the higher concentrations. The surface loading increases in both temperature ranges with enhancing concentration of 3PA. Similar results are observed for a higher modification temperature (130 °C), but all organic loadings are higher at the same concentration and the weight loss observed at 450 °C is relatively more important (Fig. 1B and Table 1). Also, the weight loss at 490 °C becomes visible at lower concentrations (3PA0.100M130W versus 3PA0.150M90W) and even becomes larger than the weight loss at 450 °C in the case of the 3PA0.150M90W. Moreover, the contribution of the weight losses at 450 °C and 490 °C increases for the highest concentrations, showing a clear impact of temperature besides concentration on the binding strengths/interactions upon functionalization of TiO_2.

3.1.2. DRIFT

The P−O region in IR (1300-900 cm^{-1}) is interesting to correlate changes in thermal stability as observed in TGA with differences in binding types. Fig. 2 compares the samples prepared with different concentrations of 3PA. For the lowest concentrations at 90 °C one broad peak (1076 cm^{-1}) is visible, which is composed of a superposition of at least four underlying peaks at 1101, 1076, 1041 and 1017 cm^{-1}. But, for sample 3PA0.150M90W the intensity ratios of the peaks clearly change with more pronounced signals at 1041 and 1017 cm^{-1} and the appearance of a small extra resolved peak at 1155 cm^{-1}. These changes in the DRIFT spectrum coincide with the additional weight loss observed in TGA at 490 °C. For the modification at 130 °C a similar trend is observed (Figure SI 3) but the differences are much clearer and distinct. This follows the trend of the higher relative contribution of the weight loss at 490 °C in TGA for these samples. Note that the sample modified with the highest concentration at 130 °C does not show an increase of the peak at 1155 cm^{-1}, but in that case the peak at 1101 cm^{-1} is becoming more intense. The increase of the peak at 1155 and 1101 cm^{-1} seems to be correlated with the weight loss at 450 °C and 490 °C, respectively. This suggests that the weight losses between 400 and 520 °C and the changes of peak intensities in the P−O region in DRIFT are correlated to each other. Further assignment will be detailed by using ^{31}P-CP/MAS NMR (see 3.1.4).

Furthermore, all samples display the alkyl stretching vibrations between 3000 and 2800 cm^{-1}. By raising the concentration of 3PA during the modification, those peaks logically increase in intensity with increasing loading amounts, while the quantity of free Ti−OH groups diminishes (Figure SI 4). Also, the amount of physically adsorbed water decreases. This means that the sample becomes more hydrophobic with an expanding organic surface loading. The same observations are made for the grafting of 3PA at 130 °C. Peculiarly, for sample 3PA0.150M130W the peaks associated to the C−H stretching vibrations seem to split into two peaks for every type of C−H stretching vibration (Fig. 3A, sample (RT)). For a small percentage of the alkyl groups, the whole C−H vibration region seems to be shifted to lower wavenumbers: from 2964, 2940, 2905 and 2879 cm^{-1} to 2954, 2927, 2900 and 2867 cm^{-1}. These divided peaks are not visible when a solution of 0.075 M or a lower temperature is used. From literature [26,28,36,43−45] it is known that if the wavenumbers are shifted to lower values, the groups are more ordered at the surface, indicating some sort of self-assembly/enhanced interaction even though the chain length is only three carbon atoms long.

3.1.3. Ex-situ DRIFT

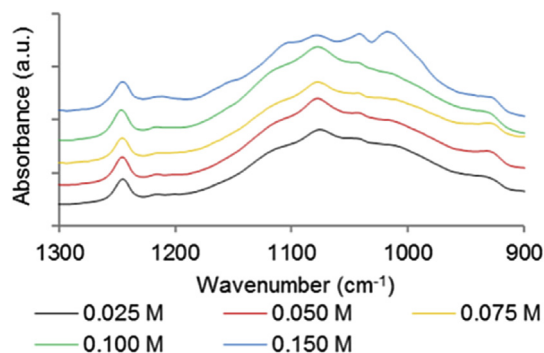To clarify the TGA results, ex-situ DRIFT measurements have

Fig. 2. DRIFT spectra of the P−O region of TiO_2 modified with different concentrations of 3PA at 90 °C in water, measured against a 2 wt% TiO_2 background. Offset has been used to visualize all spectra more clearly.
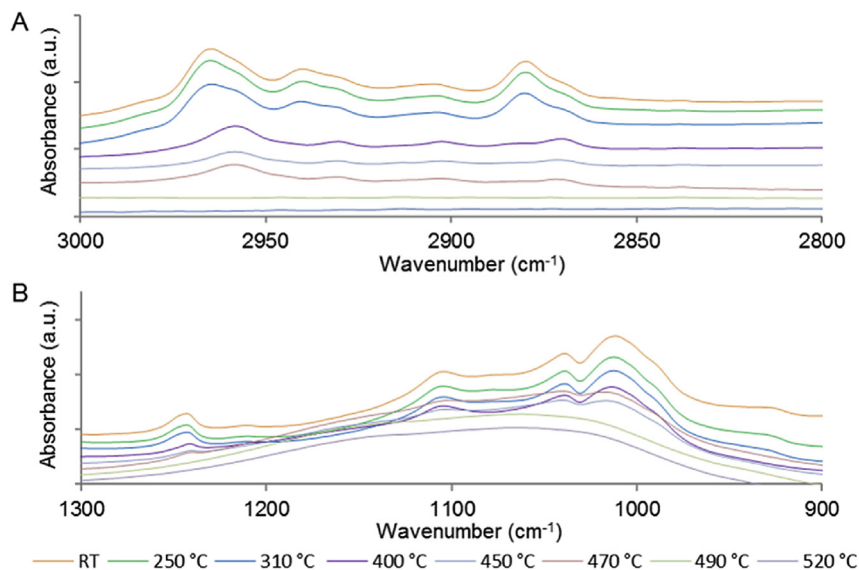
Fig. 3. Ex-situ DRIFT spectra of the alkyl region (A) and the P—O region (B) of sample 3PA0.150M130W and measured against a 2 wt% TiO_2 background. The samples were measured after heat treatment at different temperatures. Offset has been used to visualize all spectra more clearly.

been done. The DRIFT measurements were taken after treatment of the samples at different temperatures. The TGA process is simulated by heating the samples at 10 °C/min in an oven. Samples 3PA0.075M130W and 3PA0.150M130W were measured (Figs. 3 and 4). The samples were heated to the temperature coinciding with the beginning, the maximum and the end of every weight loss in the DTG curve. Sample 3PA0.075M130W was heated until the following temperatures: 250, 310, 400, 450 and 500 °C. For sample 3PA0.150M130W the lowest temperatures were the same (250, 310, 400, 450 °C), but due to the extra weight loss in TGA, this sample was also heated to higher temperatures: 470, 490 and 520 °C.

When sample 3PA0.075M130W is heated below 250 °C, it does not undergo any changes (Fig. 4A and B). By heating the sample further, the peaks of the propyl groups start to become smaller

(Fig. 4A). At 400 °C these peaks remain only slightly visible. As long as these alkyl groups are present, the P—O region remains unaltered (Fig. 4B). When the peaks of the propyl group are almost absent, the spectrum gradually changes in the P—O region up to 500 °C. This can be explained by the release of water due to the condensation of the phosphate group with the TiO_2 surface [46]. The correlation with the TGA results indicates that the largest part of the modified layer thermally oxidizes between 250 and 400 °C. The small number of organic groups that are still present at 400 °C together with the loss of water during phosphate condensation probably causes the extra weight loss in TGA at 450 °C.

This measurement demonstrates that the phosphorus atom remains bound to the surface, confirming previous literature reports [27]. Sample 3PA0.150M130W has two extra weight losses in
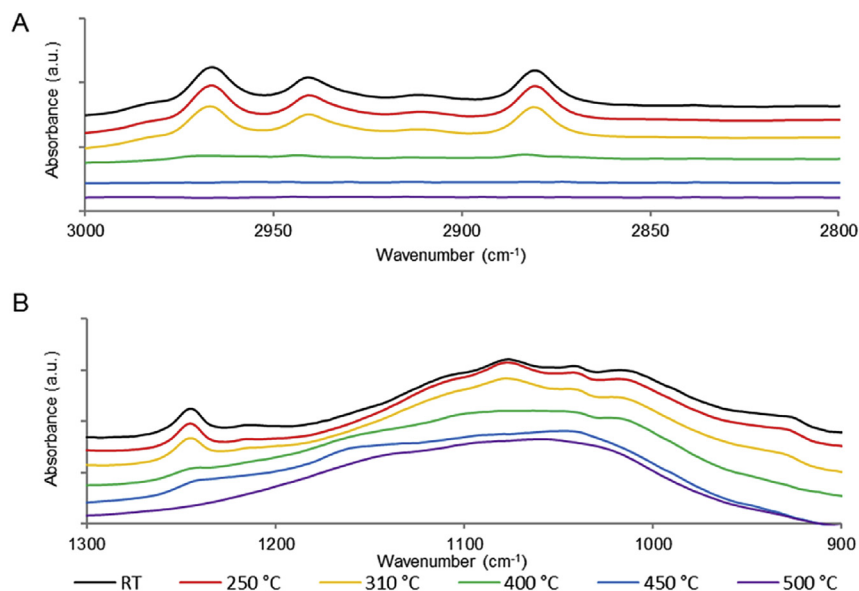

Fig. 4. Ex-situ DRIFT spectra of the alkyl region (A) and the P—O region (B) of the sample 3PA0.075M130W in function of the temperature, simulating the TGA process (measured against a 2 wt% TiO_2 background). Offset has been used to visualize all spectra more clearly.

TGA, one at 450 °C and a second at 490 °C. With ex-situ DRIFT (Fig. 3) the same trend is observed in the P–O region as for sample 3PA0.075M130W (Fig. 4). However, the organic groups clearly remain at the surface even at higher temperatures up to 470 °C. When looking more closely, it becomes clear that the red-shifted peaks at 2954, 2927, 2900 and 2867 cm^{-1} are still present at 400 °C, but are not found at 490 °C, while the peaks at 2964, 2940, 2905 and 2879 cm^{-1} have almost completely vanished at 400 °C and are thus selectively burned off, similar to the sample 3PA0.075M130W. For sample 3PA0.150M130W the oxidation of the phosphonate starts at 450 °C (Fig. 3B). Similar to the behavior of 3PA0.075M130W, the changes in the phosphate region are only initiated when the majority of the organic groups are removed. The removal of the more stable organic part seems to coincide with the weight loss that starts at 470 °C and postpones the weight loss associated with the phosphate formation (broad signal between 1200 and 1100 cm^{-1}) to higher temperatures (490 °C). Thus, in case of 3PA0.150M130W, two binding types of 3PAs with TiO$_2$ are present with different thermal stabilities, of which one type is stable up to 470 °C, which is 70 °C higher than the other type of 3PA modification. The less thermaly stable modification, is similar to those present in the sample 3PA0.075M130W.

3.1.4. ^{31}P-CP/MAS NMR

Souma et al. [47] found that changing the reaction time also had an influence on the thermal stability. Unfortunately, although ^{31}P-CP/MAS NMR was used to assign the different binding modes, no correlation was made with DRIFT. Beside Souma, also Guerrero [48] and Gao [35] studied the functionalization with ^{31}P MAS NMR and were able to assign different types of functionalization to different shifts in ^{31}P MAS NMR. This makes ^{31}P MAS NMR a powerful technique to combine with the TGA and DRIFT results.

The samples prepared at 130 °C in water with concentrations of 0.025, 0.075, 0.100 and 0.150 M have been analyzed with ^{31}P-CP/MAS NMR to correlate differences in the phosphorus environment to the differences observed in DRIFT and TGA (Fig. 5). Pure 3PA has a sharp resonance signal at 37 ppm (Figure SI 5). Upon binding to the surface, an upfield shift is observed for all concentrations resulting in a broad asymmetric peak around 28 ppm. It is clear that this broad signal originates from a non-uniform binding type with minor differences in binding state. This upfield shift indicates that the PA is grafted to the surface but assignment to the different binding types is difficult. Moreover, the signals interfere with each other, which prevents unambiguous quantification. Similar shifts were found in literature for surface modification of dodecylphosphonic acid (12PA) on TiO$_2$ [48].
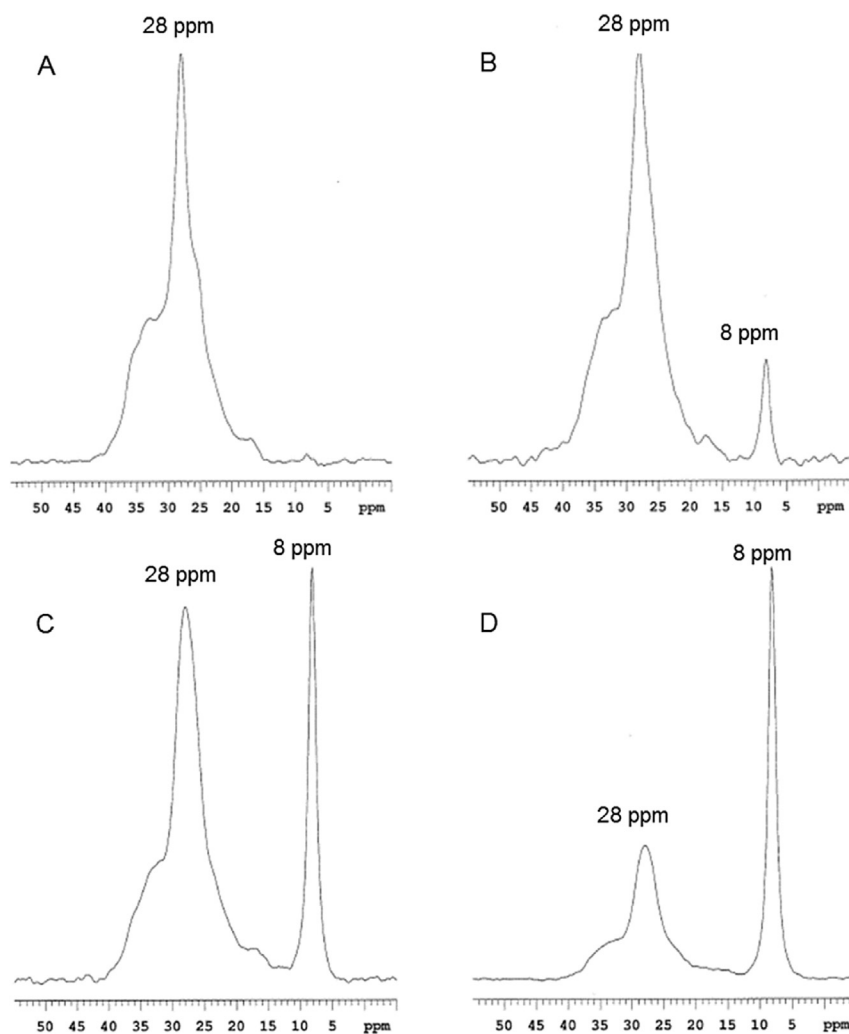

Fig. 5. ^{31}P-CP/MAS NMR spectra of TiO$_2$ modified in water at 130 °C with 3PA in a concentration of A) 0.025 M, B) 0.075 M, C) 0.100 M and D) 0.150 M.

In addition, with increasing concentration, a second chemical shift becomes visible much more upfield, at 8 ppm. The intensity of this second signal rises with increasing concentration of 3PA. The large difference in chemical shift confirms the presence of two binding types and two clearly different coordination environments for the phosphorus atom of 3PA in the material coinciding with the TGA and DRIFT measurements. It has to be noted that each binding type still can consist of different binding modes to the surface, all with a similar thermal stability and P environment. For the modification of TiO_2 with PhPA, it has been reported that the upfield shift in ^{31}P-CP/MAS NMR spectra is due to the formation of titanium phenylphosphonate [38]. Furthermore, Gao et al. [35] assigned a large upfield shift to the formation of octadecylphosphonates with TiO_2, Al_2O_3 and ZrO_2. The formation of these phosphonates is due to a dissolution-precipitation process. When these phosphonates are present, thin plate-like structures of TiPPs can be observed in TEM images (Figure SI 6). These thin plate-like structures are typically larger than TiO_2 particles grafted with 3PA and contain a higher P/Ti ratio as measured via EDX.

By comparing the different characterization techniques, it is observed that the extra weight loss in TGA above 450 °C and changes in DRIFT seem to coincide with a strong contribution of the peak at 8 ppm in ^{31}P-CP/MAS NMR. The shift in wavenumber of the alkyl groups to lower values, the changes in the peaks in P–OTi region and the higher temperature weight loss in TGA can thus be correlated to the formation of TiPP. The increased thermal stability of the TiPP is correlated to its layered structure, which is not porous. This means that the TiPP has a higher thermal stability than the TiO_2 surface grafted with 3PA. Nevertheless, the ^{31}P-CP/MAS NMR is not able to distinguish differences between the weight loss observed at 450 °C and at 490 °C as except for a difference in peak ratio, no other ^{31}P environment can be observed in the 3PA0.150M130W sample compared to the 3PA0.100M130W material.

In contrast to TiPP formation via dissolution-precipitation, when 3PA grafting occurs only a weight loss between 270 and 400 °C is observed in TGA and a broad peak around 28 ppm is present in ^{31}P-CP/MAS NMR. Furthermore, in IR there is no shift of the wavenumber of the alkyl groups and in the P–OTi region, the peak at 1076 cm^{-1} is the dominant one. Thus, raising the concentration of 3PA in combination with a higher reaction temperature (130 °C) promotes the conversion of the grafted PA groups to TiPP. Nevertheless, a contribution of the less thermaly stable binding type (270–400 °C) also remains present (about 64% of the bonded groups; Table 1) under these severe thermal conditions and high concentration and can be assigned to the surface grafting of TiO_2 with 3PA.

3.1.5. Influence of the pH

Thus, at low temperatures and concentrations, the TiO_2 surface is only functionalized via grafting. Only under more severe reaction conditions (high temperatures and enhanced 3PA concentrations) the formation of TiPP will takes place. Gao et al. [35] described this dissolution-precipitation process due to low pH in a water/methanol mixture, high concentration, high temperature and long reaction times (1 week). To study the effect of the pH, an experiment was done by adding HCl to the modification with the lowest concentration (denoted as 3PA0.025M90WpH2.1), to obtain the same pH as the modification with the highest concentration (3PA0.150M90W). In this case, also TiPPs (3 mg/g PA/TiO_2) are found but less than when using 3PA0.150M90W (8 mg/g PA/TiO_2); although in 3PA0.025M90W 0 mg/g PA/TiO_2 is found (Figure SI 7 and Table SI 1). Furthermore, the surface grafting itself has enhanced compared to 3PA0.025M90W and 3PA0.150M90W. Similar results are found for the experiment at 130 °C. Therefore, a low pH not only initiates to some part a dissolution-precipitation process, but it also induces a higher amount of surface grafting, as more surface hydroxyl groups are protonated, favoring surface grafting. Nevertheless, a high concentration seems to be additionally needed to obtain the high amount of TiPP observed in 3PA0.150M130W. On the other hand, NaOH was added to material with the highest concentration being 3PA0.150M90WpH2.5 to obtain the same pH as 3PA0.025M90W resulting in a decrease of TiPPs, although the decrease was larger at 90 °C compared to 130 °C. The amount of surface grafting is however similar to the modification without NaOH. From the results it is clear that a combination of pH with a high temperature and concentration is required to obtain high TiPP phase formation although the pH itself can induce already a partial control.

3.2. Modification with toluene as the solvent

3.2.1. TGA

Besides modification in water, toluene is often described in literature as a solvent for the functionalization of TiO_2 with PAs. To achieve this, low (0.0025 M) [26] as well as high (0.1 M) [34,38] concentrations of PAs were used. For the grafting of 3PA onto TiO_2 in toluene, the concentration has been varied between 0.003 M and 0.100 M. Different concentrations have been used in toluene from those in water because similar surface loadings as compared to the reaction in water are already obtained when using much lower 3PA concentrations. This can be attributed to the absence of competing interactions of the surface with toluene, in contrast to the situation in water.

The DTG curves of the samples modified at 90 °C in toluene are presented in Fig. 6 and the organophosphonic acid loading is listed
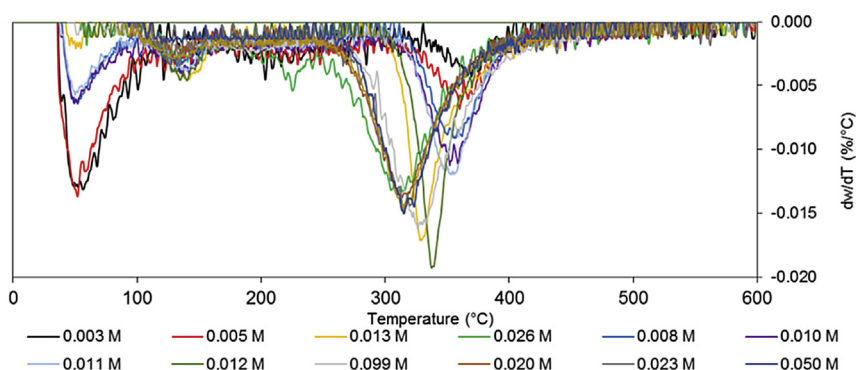

Fig. 6. DTG curves of TiO_2 modified at 90 °C in toluene with different concentrations of 3PA as measured under an O_2-flow and heating rate of 10 °C/min.

Table 2
Modification degree as measured with TGA for TiO_2 modified with different concentrations of 3PA in toluene at 90 °C. The loading is calculated in mass $3PA/TiO_2$ (mg/g) and in number of 3PA/area (#/nm²). The last column indicates the wavenumber of the asymmetric CH_2 stretch in DRIFT. (/is not measured).

Name	T (°C)	$3PA/TiO_2$ (mg/g)	3PA/area (#/nm²) TGA	3PA/area (#/nm²) SEM EDX	ν(cm^{-1}) CH_2
3PA0.003M90T	90	6	0.7	0.9 ± 0.5	2942.42
3PA0.005M90T	90	9	1.1	0.8 ± 0.8	2941.26
3PA0.008M90T	90	11	1.4	2.0 ± 0.5	2940.25
3PA0.010M90T	90	14	1.8	/	2940.09
3PA0.011M90T	90	14	1.8	2.4 ± 0.5	2939.97
3PA0.012M90T	90	16	2.0	2.7 ± 0.6	2939.73
3PA0.013M90T	90	17	2.2	2.7 ± 0.8	2939.51
3PA0.020M90T	90	22	2.8	4.0 ± 0.5	2939.28
3PA0.023M90T	90	22	2.9	4.0 ± 0.5	2939.25
3PA0.026M90T	90	24	3.0	4.7 ± 0.5	2939.13
3PA0.050M90T	90	22	2.9	4.0 ± 1.1	2939.32
3PA0.099M90T	90	26	3.2	4.3 ± 0.6	2939.08

in Table 2. In addition, the modification degree is also calculated from the amount of P measured with SEM EDX (Table 2). A difference of 0.1% P (detection accuracy) corresponds with a difference in modification degree of 0.4 groups/nm². Therefore, this technique is only used to validate the method of calculating the organic loading with TGA. The sample with the lowest concentration (3PA0.003M90T) has a single weight loss with a maximum at 370 °C. The weight loss increases with increasing concentration of 3PA. At a concentration of 0.02–0.03 M, the maximum organic loading (modification degree of 3.0 PA groups/nm² as measured with TGA) is achieved (Table 2 and Figure SI 8); for the modification at 130 °C, a similar observation is made (Figure SI 9 and Table SI 2). No TiPP phases are observed under none of the conditions. Therefore, to exclude kinetics, the reaction time has been varied between 15 min and 24 h (Table SI 3 and Figure SI 10). Even after 24 h there is no formation of the TiPP. Moreover, the modification is already completed after 15 min.

Peculiarly, in case of toluene at both temperatures (90 and 130 °C), the maximum of the weight loss in TGA shifts to lower temperatures, opposite to what was observed with increasing 3PA concentrations in water. This shift occurs gradually until a concentration of 0.02–0.03 M 3PA is reached. For the lowest 3PA concentration in water, the maximum weight loss was already observed at 310 °C (Fig. 1); in toluene, the weight loss starts at 370 °C and decreases to 310 °C with increasing 3PA concentration (Fig. 6). The shift to lower temperatures of the weight loss between 250 and 400 °C seems to be originating from the burn-off of surface grafting of 3PA on TiO_2. It has been stated [26] that the modification of TiO_2 with PA in toluene was random, but became more ordered with an increase in the number of surface groups in the organic layer. Hence, this interaction between groups on the surface might be at the origin. Chen et al. [42] described that domains of SAMs were formed for the modification of PA on ITO in water. This would suggest that in the presence of water local ordering in the modification would take place even at low modification degrees explaining a uniform thermal oxidation at 310 °C at lower loadings of TiO_2 in case of water as a solvent. The totally different thermal behavior for modification in water and toluene could thus reflect the difference in surface properties and binding types as the result of the solvent effect.

3.2.2. DRIFT

The peak intensities of the CH_2 and CH_3 stretching vibrations logically increase with the loading of organic groups (Figure SI 11), so more 3PA molecules are attached to TiO_2 leading to a more hydrophobic sample. When looking more closely at the wavenumbers

of the CH_2 groups (Table 2), it can be concluded that the wavenumbers slightly decrease with loading increase, revealing that the organic groups are indeed becoming more ordered [26,28,36,43–45]. Plotting these values in the same graph as the modification degree (Figure SI 8), reveals that the curves of surface loading and wavenumber of CH_2 stretching vibration are strongly correlated.

When looking at the P–O spectral region of sample 3PA0.003M90T, a peak at 1245 cm^{-1} is observed (Fig. 7). This peak shifts to higher wavenumbers with an increasing concentration. This shift is not observed when working in water. Furthermore, for the lowest concentrations, a broad band is seen composed of a superposition of at least four signals, at 1110, 1045, 1077 and 1014 cm^{-1}. These peaks become more intense with increasing 3PA concentration. Additionally, the intensity ratio between these peaks is changing; the peak intensity at 1077 cm^{-1} is the highest for concentrations between 0.005 M and 0.012 M 3PA. A further increase in concentration will result in supplementary changes in the intensity ratio of the peaks to a pattern similar to the one observed at high temperature and 3PA concentrations in water. In case of toluene, the temperature has no influence on the DRIFT spectra (Figure SI 12). Moreover, in case of toluene, the observed changes in the IR spectra do not coincide with a weight loss at higher temperatures in TGA nor with a clear red shift in the CH_2 and CH_3 signals (Figure SI 11), as found for water (Fig. 3). The reason behind these findings is still unclear. Therefore, it can be concluded that in the case of toluene as a solvent, only the concentration of 3PA has an influence on the modification degree and the binding type, while the increase in temperature does not induce any changes in
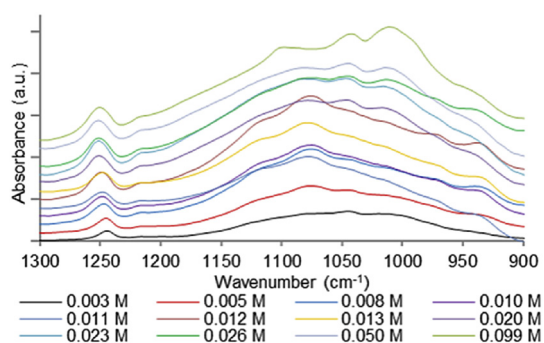

Fig. 7. DRIFT spectra (measured with TiO_2 background) of the P–O region of TiO_2 modified with different concentrations of 3PA at 90 °C in toluene. Offset has been used to visualize all spectra more clearly.

the binding type or surface loading. This is an indication for a difference in binding mechanism, which could be due to several reasons, such as competitive adsorption of water, proton release of the acid, solubility of the 3PA, dielectric constant etc. in the case of the different solvents. Moreover, it is clear that the obtained modified surfaces have a totally different thermal stability, irrespective of similarities in the IR patterns. In ongoing research the differences in surface properties will be investigated further in more detail.

3.2.3. $^{31}P/CP$ MAS NMR

To study the discrepancy between observations in modification in toluene with respect to IR (with similar peak patterns as in water) and TGA (with strongly divergent behavior), ^{31}P/CP MAS NMR has been done to clarify the binding types. The samples prepared at 90 °C are characterized via ^{31}P/CP MAS NMR to evaluate the changes in phosphorus environment induced by elevating the 3PA concentration (Fig. 8). For the lowest 3PA concentration only a broad signal is observed around 28 ppm. The broadening can be explained by the presence of a distribution of slightly different chemical environments for the grafted PAs. With increasing 3PA

concentration, the resonance signal at 28 ppm becomes sharper, indicating a progression towards a more uniform way of binding, in good agreement with the enhanced ordering observed from TGA and DRIFT data and different from what can be observed in case of water (Fig. 5) where the 28 ppm signal stays broad. For the sample with the highest loading, the 28 ppm peak changes further and a small peak appears at 8 ppm. This in agreement with DRIFT, showing (minor) changes in the P–OTi spectral region, which were also correlated with the 8 ppm chemical shift in the case of water. Nevertheless, this does not coincide with an additional weight loss in TGA.

These observations demonstrate that high concentrations of 3PA in water as solvent are needed to form TiPP. Of course, in case of toluene, small amounts of water will be released in the condensation reaction between 3PA and the TiO_2 surface hydroxyl groups, and, as the reactions were not performed under anhydrous conditions, trace amounts of water were always present. Therefore, these traces of water could be responsible for the small signal at 8 ppm. These observations indicate that the presence of water, low pH and high concentration of PA is essential in the formation of TiPP.

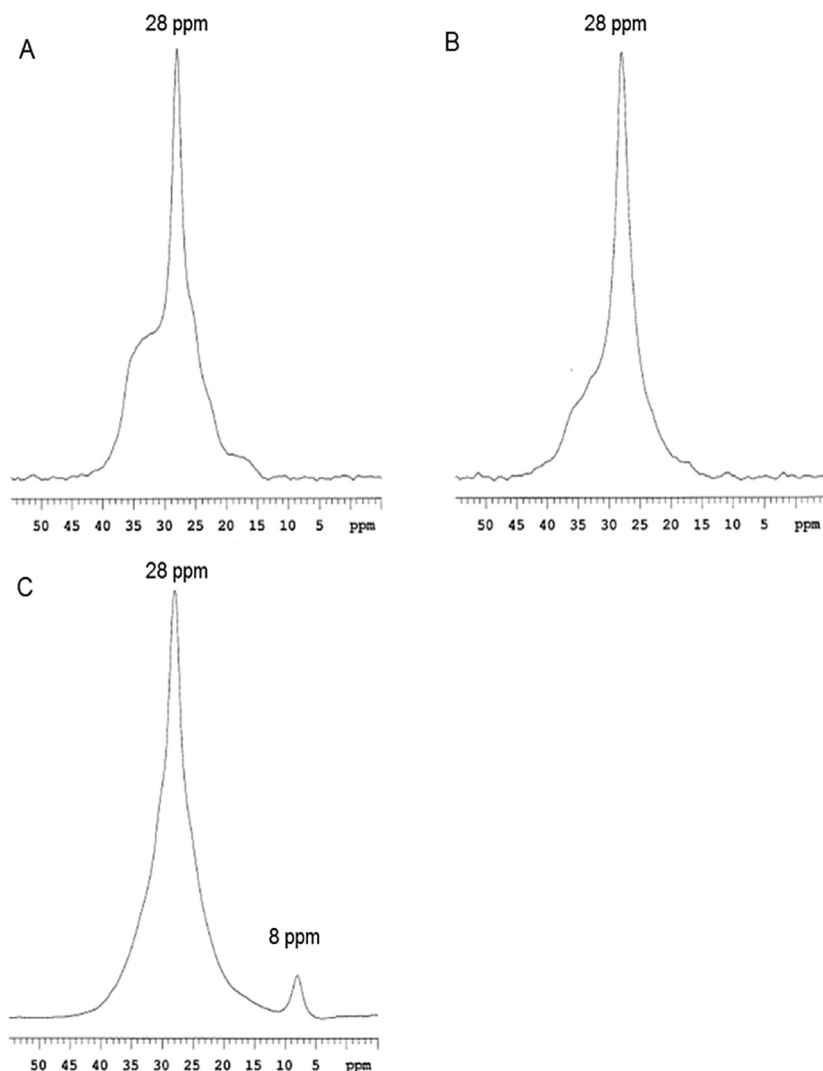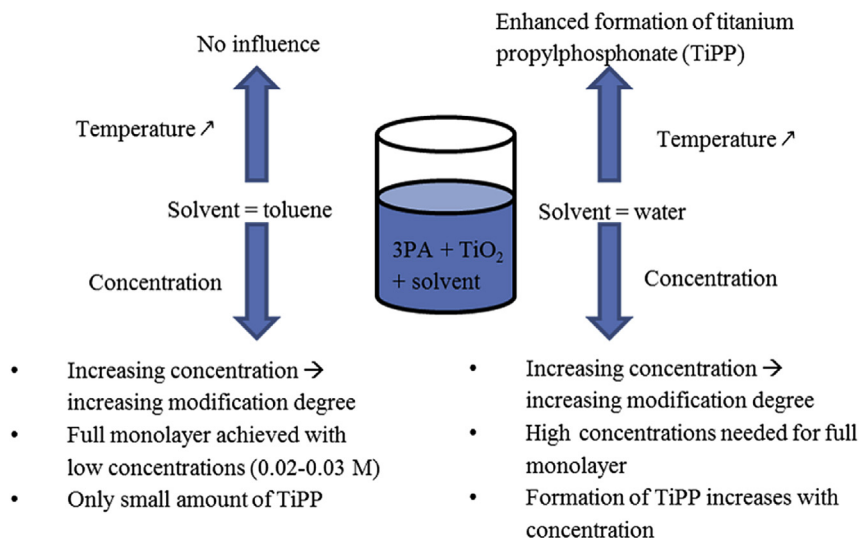Moreover, comparing toluene as solvent with water, it is clear

Fig. 8. ^{31}P-CP/MAS NMR spectra of TiO_2 modified with 3PA at 90 °C in toluene at a concentration of A) 0.005 M, B) 0.012 M and C) 0.100 M. *(1.5 columns).*

Scheme 1. A summary of the influence of solvent, temperature and concentration on the modification of TiO$_2$ with 3PA.

from ^{31}P/CP MAS NMR, TGA and even IR in the C−H vibration region, that the local binding types are different in both solvents. Moreover, in case of toluene, maximum surface coverage can be reach with much lower concentrations of PA. A summary of the most important influences of solvent, temperature and concentration is presented in Scheme 1.

4. Conclusions

In this study it is demonstrated that solvent, temperature and 3PA concentration have a substantial impact on the degree and type of functionalization. Furthermore, a correlation was made between the characteristic signals in different analytical methods showing coinciding changes as well as important discrepancies that might induce misinterpretations if only one of the techniques would be applied for analysis.

Regarding the reaction in water, an increase of concentration in combination with temperature induces the formation of TiPPs with a higher thermal stability. However, surface grafting always remains. The pH of the solution is a driving force to dissolve the TiO$_2$ and precipitate it as TiPPs. Nevertheless, by working at similar pH with low concentrations of 3PA, less TiPPs are formed and more surface grafting is achieved. Therefore, both pH and concentrations are important in the TiPP formation. In comparison, in toluene organic ordered layers with a high surface loading are already formed at much lower 3PA concentrations than in water. Moreover, raising the reaction temperature during modification does not influence the surface properties of the grafted layer, while it has a considerable influence when water is used as a solvent both in grafting and in TiPP formation. In contrast to the modification in water, increasing the 3PA concentration in toluene results in a decrease in thermal stability coinciding with an indication of an increase in uniformity of the binding. Furthermore, in the case of toluene, a peak with a chemical shift at 8 ppm in ^{31}P/CP MAS NMR is only present in small amounts, which proves the need of water and high concentrations of PA for the formation of TiPP. Both solvents (water and toluene) clearly result in a different binding mechanisms and significant differences in surface properties. By revealing these influences of 3PA concentration in different solvents, concentrations and temperature, it becomes clear that materials with different surface properties can be made in a controlled way by choosing the most appropriate solvent, concentration, pH and temperature to adjusted it to a specific application.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.matchemphys.2016.09.059

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