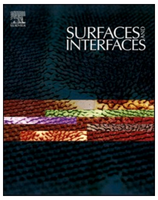
Surfaces and Interfaces 44 (2024) 103697

Contents lists available at ScienceDirect

Surfaces and Interfaces

journal homepage: www.sciencedirect.com/journal/surfaces-and-interfaces



Understanding surface (un)reactive sites of titania supports towards propyl-phosphonic acid surface modification

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ARTICLE INFO

Keywords:
TiO_2 supports
Methanol chemisorption
Propylphosphonic acid modification
Hydroxyl groups

ABSTRACT

Organophosphonic acids (PAs) surface modification on metal oxides is important for applications, nevertheless, a detailed study evaluating the influence of metal oxides surface properties on PAs modification is lacking. This work presents a method to qualitatively probe surface (un)reactive sites of titania towards propyl-phosphonic acid (3PA) grafting by methanol. It identifies the more or less reactive sites, i.e., hydroxyl groups and Lewis acid sites, allowing to understand relative differences in maximum modification degrees of 3PA among different titania supports. Therefore, three different types of titania were used, while all other 3PA modification conditions were kept constant. A clear difference in the maximum modification degree on the three titania supports was observed. *In-situ* diffuse reflectance Fourier transform infrared spectroscopy revealed that not all surface OH groups had reacted with 3PA at the highest modification degree, which were similar to most of the OH groups remaining after methanol chemisorption. Also the adsorption capacities of the strongly bonded chemisorbed methanol elucidated differences in the three titania, which was related to the maximum modification degree of 3PA. Methanol chemisorption can thus aid in the understanding of the kinds of reactive surface sites that play a role in the divergence of 3PA coverage on different types of titania supports.

1. Introduction

Metal oxide supports are of interest in many different fields (e.g., energy conversion and storage [1,2], heterogenous catalysis [3,4], pollutant adsorption and separation [5,6] due to their robustness, semiconducting nature, surface reactivity and other unique properties. Especially titania (TiO_2) has been extensively investigated due to its high thermal and chemical stability [7]. It is also the support studied in this work. Although widely applied, its hydrophilic surface often causes limitations in its performance in applications such as organic solvent nanofiltration [8], wastewater treatment [9], biomedical drug delivery [10] and *etc*. Fortunately, the surface properties can be adapted through the grafting of organic groups that widen interaction versatility. Many different precursors have been successfully applied to modify the surface with organic groups, including organophosphonic acids (PAs) and derivatives [11], organosilanes [12], carboxylic acids [13], Grignard reagents [14,15] and others [13,16]. For organophosphonic acids and carboxylic acids modification, covalent bonds are formed via either the condensation of P–OH/COOH groups with the surface hydroxyl groups on the metal oxides and/or through coordination of P=O/COO^- with Lewis acid sites (e.g., Ti^{4+}on TiO_2) of the metal oxides [13,17]. Organosilanes functionalization is achieved by the condensation reactions of reactive groups with surface OH groups of the support [12], while the mechanism of Grignard modification is more complicated and not fully clear yet [14]. Among the different modification methods and precursors, PAs modification attracts attention due to the higher hydrolytic stability of the formed M–O–P bonds than that of M–O–Si or M–O–R bonds produced by the functionalization of organosilanes or carboxylic acids, respectively [13,18–20]. Moreover, the PAs surface modification reaction is facile and requires less restricted experimental conditions than other methods. For example, Grignard reagents modification needs degas pretreatment and anhydrous environment [15], while organosilanes requires dry conditions with precisely controlled water content during the process [12,21].

After the seminal report by Ries and Cook [22], PAs modification has been developing for many years. Among others, a large part of the experimental research focuses on the effects of synthesis conditions, such as the influence of different chain lengths and terminal groups of PAs on the surface properties [23,24], as well as the effect of different temperatures and solvents used on the modification degree and

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https://doi.org/10.1016/j.surfin.2023.103697
Received 3 June 2023; Received in revised form 9 October 2023; Accepted 30 November 2023

distribution of the grafted groups [17,25,26]. Roevens et al. also investigated the interaction of solute-solvent-support surface by varying the types of solvents (water, toluene and their mixture) and PAs (propylphosphonic acid and phenylphosphonic acid). They found that the mutual interactions of the solvent and solute with the surface and with each other play an important role during the surface modification [17,25]. In several studies that explored PAs modifications, researchers found that supports have crucial effects on the modification [27–31]. For example, TiO_2 was more reactive to PAs than silica (SiO_2) and the bond of P–O–Ti showed higher hydrolytic stability than of P–O–Si [29]. Besides, Hofer et al. extensively studied the influences of the isoelectric point of oxide supports, including SiO_2 and various metal oxides (TiO_2, alumina, zirconia, *etc.*), on the dodecyl-phosphate and 12-hydroxyl dodecyl-phosphate modification (alkyl phosphate monolayers were formed), but no correlation was found [27]. Some other research reported that the strong acid sites on the alumina improved the interaction of the phosphoryl groups with the surface [30] and a higher number of surface hydroxyl groups of alumina (the ratio between the atomic concentration of the hydroxide to the oxide part of the oxygen signal increased from 0.27 to either 0.52 or 0.88) could accelerate the reaction kinetics of PAs [31]. Although many studies related to the effects of support properties on the modification have been done, a thorough knowledge on the correlation of the PAs modification (e.g., the maximum modification degree) and the surface properties of the support (e.g., reactive sites) is still lacking, thereby the types of reactive surface sites (OH groups and Lewis acid sites) that are important in the differences in coverage of PAs for different types of supports have not been fully understood.

Methanol has been reported to probe the catalytic active sites of TiO_2 and other metal oxides, including OH groups [32] and Lewis acid sites [33–35], due to the small steric hinderance and high reactivity of this solvent molecule. Burcham et al. investigated the chemisorption of MeOH on different metal oxides (including TiO_2) at high temperature (110 °C) and found that methanol would chemisorb on a Lewis acid site to generate the associative intact Lewis-bound species (L-MeOH) and/or dissociative methoxy species ($–OCH_3$), which was closely correlated to the supports used [33,36]. By applying *in-situ* infrared titration, they determined the number of catalytic active surface sites on metal oxides [33,36]. Moreover, Shen et al. proposed that molecularly adsorbed MeOH on TiO_2 could be converted to methoxy groups via condensing with Ti–OH [37]. Based on this, we started this work through the hypothesis that MeOH is potentially able to identify the metal oxides' surface reactive sites, i.e., the Lewis acid sites and OH groups, responsible for PAs modification (i.e., they will be consumed during the modification reaction).

In this study, we thoroughly analyze the impact of titania surface properties on the propyl-phosphonic acid (3PA) modification (e.g., the type of reactive sites and modification degree), elucidating the specific role of different types of surface OH groups present in TiO_2. MeOH chemisorption was introduced to probe the (un)reactive surface sites of different TiO_2 supports towards 3PA surface grafting. The modification conditions including the type of PAs (3PA), concentrations of the 3PA, solvents (water and toluene), reaction temperature (90 °C), and time (4 h) were kept the same, while three TiO_2 with different surface properties were selected as supports. Therefore, any changes identified after modification could only be induced by the differences in surface properties of the selected titania supports. *In-situ* diffuse reflectance Fourier transform (*in-situ* DRIFT), thermogravimetric analyses (TGA) or thermogravimetric analysis coupled with mass spectrometry (TG/DTG-MS) were applied to determine the differences and changes in surface properties of titania. After MeOH chemisorption, *in-situ* DRIFT was again used to identify the types of surface interaction site (i.e., OH groups and Lewis acids sites). The adsorption capacity of chemisorbed methanol was applied to estimate the number of these surface interaction sites.

2. Experimental section

2.1. Materials

Propylphosphonic acid was purchased from Cayman (≥ 98 %). TiO_2 Sachtopore-NP (Zirchrom) and P25 (Sigma-Aldrich) are commercial titania materials, which were respectively denoted as Z-TiO_2 and P-TiO_2. The third type of titania material was a mesoporous sol-gel based titania (F-TiO_2), which was prepared in the laboratory via a sol-gel process according to Van Gestel et al. [38]. These TiO_2 materials were used as the three different titania supports. Toluene (> 99 %, extra pure) was purchased from Fischer Chemical and acetone (> 99.5 %) was from Acros. All chemicals were used as received unless otherwise stated. Methanol (99.9 %), purchased from Acros, was stored with molecular sieve and placed in glovebox (flowed by dry air) to remove moisture. The water used in the synthesis was deionized water produced in the lab.

2.2. Surface modification

The surface modification procedure used in this study was based on our previous work [17,25]. An illustration of the modification process can be found in Scheme 1. Specifically, the synthesis was done separately in 2 different solvents, water and toluene. One gram of TiO_2 was added and stirred in a heated solution of 3PA with different concentrations (0.025 M, 0.075 M, 0.100 M, 0.150 M and 0.300 M for water; 0.008 M, 0.013 M, 0.026 M, 0.100 M and 0.300 M for toluene) at 90 °C for 4 h under reflux conditions. The lower concentrations of 3PA used in toluene than in water were based on our previous work, showing that they result in similar modification degrees due to a difference in solvent interaction with the surface [17,25]. After modification, the samples were consecutively rinsed with 30 mL of the solvent used in the synthesis for 3 times. For samples modified in toluene, an additional washing in acetone and water (respectively 3 × 30 mL as well) was done after washing with toluene itself. Subsequently, the modified materials were dried in an oven at 60 °C for 24 h. The synthesis has been repeated at least three times to estimate the error of modification degree. The blank experiments were performed in an identical way, but without the addition of 3PA.

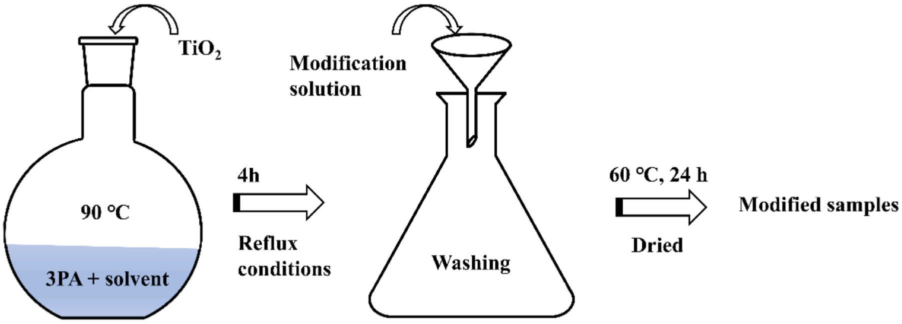
In order to represent the samples in a short and systematic way, the samples were denoted as follows: First, the three titania supports are respectively denoted as F-TiO_2, P-TiO_2, Z-TiO_2. After modification with 3PA, their structural names include the synthesis information. For example, 3PAF-0.100T refers to F-TiO_2 modified in toluene (T) with 0.100 M of 3PA. If the modification was done in water, the letter behind the concentration is W.

2.3. Characterizations

Thermal analysis measurements, including thermogravimetric analyses (TGA) and differential thermal gravimetric analysis (DTG) were recorded on a Mettler Toledo TGA-DSC 3+. The measurements to determine surface modification degree were carried out under a constant flow of 80 mL/min of O_2 and were done by heating from 30 °C to 600 °C with a heating rate of 10 °C/min. The modification degree with 3PA was calculated from the mass loss of the burned carbon groups in the region of 250–420 °C by the formula (1), taking into account that the phosphorus group remains on the surface [39].

$$\mathrm{mod.dg.}\left(\frac{\mathrm{groups}}{\mathrm{nm}^2}\right) = \frac{\mathrm{wt\%(R)} \times \mathrm{N_A}}{MM(\mathrm{R}) \times S_{BET}} \times 10^{-18}\left(\frac{m^2}{nm^2}\right) \quad (1)$$

In which wt%(R) and MM(R) are respectively the mass loss percentage of the organic group from the TGA measurement and the carbon group's molar mass (propyl groups, 43 g/mol), S_{BET} (unit is m^2/g) is the specific surface area of the unmodified TiO_2 as determined by nitrogen sorption and N_A is the Avogadro's constant (6.02×10^{23} mol^{-1}). The



Scheme 1. Schematic illustration of the modification process.

experimental error of the obtained modification degree is around 0.1 groups/nm^2 based on five repeated measurements of different batches of samples, which confirms the error measured in our previous work [17,25].

Thermogravimetric analysis coupled with mass spectrometry (TG/DTG-MS) was performed to identify the differences in surface species on three titania supports, using a Mettler Toledo TGA-DSC 3+ coupled with a Hiden HPR20 Mass spectrometer. The samples were flushed with an Ar flow of 50 mL/min at 30 °C for 30 min prior to measurement. Afterwards, the samples were heated to 1000 °C with a heating rate of 10 °C/min under the Ar flow (50 mL/min). The data was recorded and analyzed by the EGA software package.

The *in-situ* diffuse reflectance infrared Fourier transform (DRIFT) measurements were carried out on a Nicolet 6700 Fourier Transform IR spectrometer, equipped with an electromagnetic source in the mid infrared region (4000–400 cm^{-1}) and a DTGS detector. The resolution was 4 cm^{-1} and for each spectrum 100 scans were accumulated. Here, a Praying Mantis High Temperature Reaction Chamber (Harrick, USA) was applied for the *in-situ* DRIFT measurements at different temperatures. All the measurements were measured on undiluted samples under the flow of Ar. KBr was used as a background, which was collected at 500 °C to remove any water and CO_2. At each temperature, 30 min of thermal stabilization time was taken before cooling the sample back to room temperature (30 °C), afterwards the spectra were collected at RT to exclude thermal effects [40].

Nitrogen sorption measurements were carried out at −196 °C on a Quantachrome Quadrasorb SI automated gas sorption system. Before the measurements, the samples were degassed for 16 h under high-vacuum conditions at 110 °C to remove surface water while avoiding the decomposition of grafted propyl groups. The pore size distribution was determined by BJH on the desorption branch.

The morphology of titania supports was characterized by a scanning electron microscopy, field emission gun – environmental scanning electron microscope (FEG-ESEM), equipped with an energy dispersive X-Ray (EDX) detector (FEI Quanta 250, USA). The used measurement parameters were as follows: 20 kV of accelerating voltage, 10 mm of measurement distance, 30° take-off angle and 10^{-4} Pa chamber pressure. Prior to the observation, the samples were sputter-coated with gold.

The crystal phases were analyzed by a micro-Raman Horiba Xplora Plus Microscope (40–1000 cm^{-1} Raman shift) with an excitation laser of 532 nm, using 10 % filter at room temperature.

X-ray powder diffraction (XRD) spectra were obtained by a D8 advance Eco diffractometer (Bruker) equipped with Cu-Kα radiation ($\lambda = 1.5406$ Å). The measurement parameters included a scanning range of 5–80 ° 2θ and a scanning rate of 0.04 °/4 s. The software used for Rietveld analysis was x'pert highscore plus from Panalytical.

Two-cycle adsorption measurements at 110 °C with methanol as a probe molecule were conducted on a home-made volumetric adsorption system (see the illustration in Scheme S1 in Supporting Information) operating at high vacuum (using a combination of rotation and turbo molecular pump). Based on literature [33,36], the operation temperature of 110 °C was employed to facilitate the interaction of methanol as strongly bound methoxylated surface species. At lower sorption temperatures, the methanol adsorption results in the formation of both strongly bound methoxylated surface species and weakly bound physisorbed methanol. However, temperatures above 110 °C prompt the methoxylated surface species to undergo reactions resulting in the formation of formaldehyde and other products [33,36]. To measure the pressure differences, a pressure detector, MaxiGauge, which was purchased from Pfeiffer vacuum company was applied. The methanol sorption capacity was used to determine the adsorption capacity of the strongly bonded chemisorbed methanol on TiO_2, quantifying the number of surface interactive sites. Prior to the two-cycle adsorption, methanol was purified on the vacuum adsorption system by at least three freeze-pump-thaw cycles using liquid nitrogen. Then, the sample was degassed at 110 °C under high-vacuum condition (1×10^{-4} mbar) for 16 h. The sample weight was noted after drying to use in the calculations of the adsorption capacity. Subsequently, the measurements were carried out on the dried sample. Two-cycle methanol adsorption was performed at 110 °C: a certain amount of methanol vapor was gradually dosed to the sample holder containing 0.2–0.3 g of dried sample. After each addition of methanol, the pressure and temperature was recorded when the pressure reached equilibrium. The methanol adsorption was finished when the saturated vapor pressure was reached. Then, to completely remove the physisorbed methanol, a degassing process was performed also at 110 °C by evacuation for 16 h. Next, a second methanol adsorption cycle was done, which was the same as the first cycle. The first adsorption cycle consisted of both the chemisorbed and physisorbed methanol, and the second cycle only included the weakly physisorbed methanol as the chemisorbed methanol would not be removed during the degassing. Therefore, the difference between the first and the second methanol adsorption would give rise to the number of strongly chemisorbed methanol and thus representing the number of Lewis acid sites and strongly interacting OH groups that were not regenerated during degassing. Afterwards, the closed sample holder was transferred inside of the glovebox to avoid contact of the sample with moist from the air and then went for the *in-situ* DRIFT characterization to identify the reactivity of the OH groups and Lewis acid sites. Here, the methanol adsorbed samples are respectively denoted as P-MeOH, F-MeOH and Z-MeOH.

3. Results and discussion

3.1. Physico-chemical properties of the applied titania supports

The physico-chemical properties of the three titania supports were analyzed by *in-situ* DRIFT, TGA-MS, nitrogen sorption, Raman, XRD and EDX. Table S1 shows the overview of pore size, surface area, crystal phases, crystal size and presence of impurities of the used titania supports. The nitrogen sorption isotherms and pore size distributions can be found in Fig. S1 (Supporting information). The surface area of the F-TiO_2

is a factor of two higher than P-TiO_2 and Z-TiO_2, and the pore size is smaller than Z-TiO_2, while P-TiO_2 is not porous. With respect to the crystal phase composition, Z-TiO_2 is pure anatase, while F-TiO_2 and P-TiO_2 additionally have brookite and rutile phases, respectively. Moreover, F-TiO_2 and P-TiO_2 also show the presence of an amorphous fraction, and the content of amorphous titania in F-TiO_2 is expected to be much higher than in P-TiO_2, based on electron energy loss spectroscopy (EELS) measurements on the same materials (but different batches) reported in our previous work [14]. The amorphous content of Z-TiO_2 was not determined. All these differences indicate that the three titania supports have divergent (surface) properties.

The *in-situ* DRIFT spectra of the three supports at different temperatures from RT to 600 °C are presented in Fig. S2 (Supporting Information), indicating the presence of different surface species, *i.e.*, adsorbed surface water molecules and hydroxyl groups. The bands at around 1620 cm^{-1} and 3630 cm^{-1} are assigned to adsorbed surface water molecules and surface hydroxyl groups hydrogen-bonded to coordinated water, respectively [41]. The broad band between 3600 and 2500 cm^{-1} is attributed to the overlapping signals of adsorbed water and the stretching modes of the surface hydroxyls in hydrogen bond interaction with either water molecules and/or surface hydroxyl groups on the TiO_2 surface [42]. All three titania support materials show the disappearance of surface water (1620 cm^{-1}) at 250–300 °C. In the same temperature interval (RT–300 °C), the intensity of the broad band between 3600 and 2500 cm^{-1} on all supports decreases gradually with temperature, suggesting that the detectable surface water is being removed and a part of the hydrogen bonding interactions between surface hydrogen groups possibly is being lost as well. The three titania were further measured by TG/DTG-MS (Fig. S3, Supporting Information) to compare the content of surface water based on the weight loss between RT and 300 °C. The results showed that the surface water content is a factor of two higher for F-TiO_2 than Z-TiO_2 and P-TiO_2, which could be due to its two times higher surface area. Apart from the differences in content of surface water, the interaction with water also differs for all samples (Supporting Information, Result A).

Additionally, there are also several other peaks visible originating from different OH groups on the surface. Here, the three types of titania differ not only in the type of OH groups present and their wavelengths but also in their relative intensity at room temperature and 300 °C (without the presence of adsorbed surface water molecules) as well as in their thermal stability up to 600 °C (Fig. 1).

Previous research reported that the ν(OH) bands could be formed by the dissociation adsorption of H_2O on pairs of coordinatively unsaturated Ti^{4+} (Lewis acidic) and O^{2-} (Lewis basic) surface sites [43,44]. The wavenumbers higher than 3700 cm^{-1} were assigned to isolated hydroxyl groups, while the lower ones were attributed to bridged OH [45]. The spectra (Fig. 1) at room temperature showed that the hydroxyls at 3671 cm^{-1} attributed to the bridged OH on anatase were present on the three supports [46], which is logical as all of them have anatase phase. In addition, they also have other OH groups on their surface where differences could be observed. P-TiO_2 shows the OH groups at 3655 cm^{-1} assigned to a band of OH on rutile [46], as well as unresolved isolated hydroxyl groups at 3720 cm^{-1}. F-TiO_2 shows signals of resolved isolated hydroxyls at 3735 cm^{-1} with unresolved ones at 3720 cm^{-1}, while Z-TiO_2 exhibits resolved isolated OH groups at 3735 cm^{-1}, as well as other two unresolved hydroxyl groups at 3708 cm^{-1} and between 3735 cm^{-1} and 3708 cm^{-1}.

With the desorption of surface water at 300 °C, differences in presented OH groups confirm the discrepancies in surface OH groups. Although some same OH groups were visible on the three titania supports, different intensities were observed (e.g., 3735 cm^{-1}, 3671 cm^{-1}, Fig. 1; more details about OH groups at 300 °C in Supporting Information, Result B). When looking more closely to thermal stability, the presented OH groups on the three titania showed different condensation behaviors (thermal stability). In contrast to P-TiO_2, F-TiO_2 and Z-TiO_2 have hydroxyl groups with high thermal stability that are still present at 600 °C. The signals at 3671 cm^{-1} and 3735 cm^{-1} decreased in intensity at 600 °C on the three types of TiO_2 due to their condensation. While almost invisible on P-TiO_2, they were still clearly present on F-TiO_2 and remained pronounced on Z-TiO_2. This suggests a difference in the amount and distribution of the hydroxyl groups on the surface, leading to the divergent condensation behavior (detailed discussion about the possible changes in crystal phase composition after heating at 600 °C can be found in Result C and Fig. S5, Supporting information). Also all other signals on F-TiO_2 and Z-TiO_2 decreased with temperature, i.e., 3720 cm^{-1} on F-TiO_2 as well as 3715 cm^{-1} and 3708 cm^{-1} on Z-TiO_2, but remained present at 600 °C. While almost no OH signals could be observed on P-TiO_2 at 600 °C. These observed differences at 600 °C on the three supports suggest a higher thermal stability of (isolated) OH groups on F-TiO_2 and Z-TiO_2, again pointing out the differences in surface OH groups on the three titania supports. In addition, there might still be subtle differences among the OH groups that were not well resolved and thus not discussed here.

An overview of the different OH groups which are not affected by

Table 1

Comparison of υ(O−H) values of OH groups not affected by surface water on the three TiO_2 supports.

	F-TiO_2	P-TiO_2	Z-TiO_2
Isolated OH	3735 (A)* 3720 (A)*	3735 (A) 3720 (A)	3735*,# 3715 (A)* 3708 (A)*
Bridged OH	3671 (A)*	3691 (R) 3655 (R) 3671(A) 3666 (A) 3640 (A)	3671 (A)*

The letter inside of the bracket is short for anatase (A) and rutile (R).

* OH groups are visible at 600 °C.

\# Supporting Information, Result D.

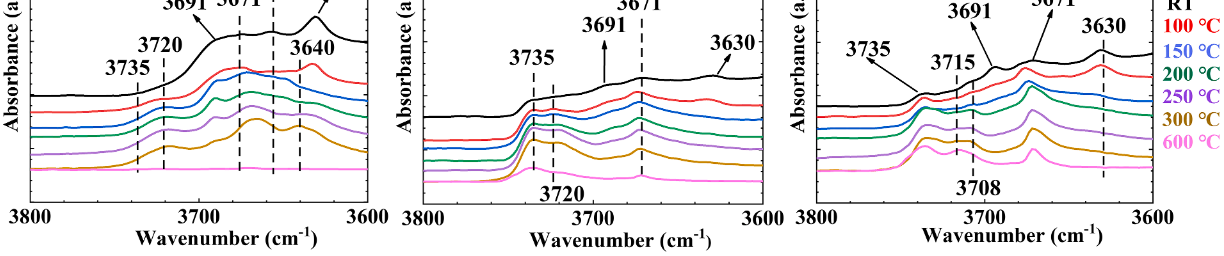


Fig. 1. *In-situ* DRIFT spectra at 3800–3600 cm^{-1} of undiluted P-TiO_2, F-TiO_2 and Z-TiO_2, collected at RT after being heated to different temperatures between RT and 600 °C under an argon flow of 80 mL/min. A background of KBr at 500 °C under Ar atmosphere at the same flow rate was used for all measurements.

surface water (visible at 300 °C) and their thermal (in) stability up to 600 °C are summarized in Table 1 for the three supports. In general, the OH groups on P-TiO_2 are the easiest to condense and almost no OH groups can be found at 600 °C, while some types of hydroxyls on Z-TiO_2 and F-TiO_2 are difficult to condense at temperatures up to 600 °C. The reason that these OH groups have not condensed is unclear, but must relate to differences in e.g., amount/distribution/topology, because similar OH groups on P-TiO_2 did condense while the condensation did not happen on F-TiO_2 and Z-TiO_2.

In all, apart from the different contents of surface water, the three TiO_2 supports also possess different interactions with surface water, have divergent types, distribution, and thermal stability in hydroxyl groups as well as different impurities (the discussion of impurities can be found in Supporting Information, Result E). The goal of this work is to evaluate whether these differences in surface properties also impact the modification with organophosphonic acids.

3.2. *Propyl-phosphonic acid surface modification*

The three titania supports were modified under the same synthesis conditions, including a reaction temperature of 90 °C, two solvents (water or toluene) and five different concentrations in each solvent, allowing to observe the possible differences in modification degrees for the different titania supports. The TG/DTG results of samples modified at low (0.025 M in water, 0.008 M in toluene) and high (0.150 M in water, 0.100 M in toluene) concentrations, in water and toluene, were displayed in Fig. 2.2, assuming that the most pronounced changes could be observed. Fig. 2a and b show the TG/DTG results of F-TiO_2, P-TiO_2 and Z-TiO_2 modified in water with 0.025 M and 0.150 M of 3PA, respectively. The results in toluene with 0.008 M and 0.100 M of 3PA are presented in Fig. 2c and d.

In contrast to the pristine titania supports (Fig. S3), a pronounced weight loss between 250 and 420 °C was present on 3PA modified supports, which could be assigned to the grafted organic groups. All curves exhibit a similar higher weight loss between 250 and 420 °C at higher concentrations of 3PA, independent of the solvent. For both F-TiO_2 and P-TiO_2, an extra weight loss between 420 and 500 °C was present, while it is absent for Z-TiO_2. These weight losses at different temperature ranges are more prominently reflected by different maxima in the DTG curves. Moreover, on modified P-TiO_2, the presence of this extra weight loss at 420–500 °C depends on the modification conditions, i.e., could only be found when modified in water at higher concentrations. While for F-TiO_2 it appears in both water and toluene, even at the lowest concentrations, and becomes more pronounced with increasing concentrations. Roevens et al. reported a similar phenomenon when P25 (same with our P-TiO_2 but from different suppliers) was modified in water with higher concentrations. They correlated it to the formation a of titanium propylphosphonate (TiPP) phase, resulting from the dissolution-precipitation reaction of titania when the local acidity was too high [25]. Therefore, its appearance was unexpected on F-TiO_2 in toluene, which might be due to the enhanced surface water adsorption of F-TiO_2, providing a sufficient water layer to cause the dissolution-precipitation mechanism to occur (supports were not dried prior to modification). Moreover, more amorphous phase content in F-TiO_2 also enhances the ability for dissolution compared to more crystalline materials [47], which could account for the formation of TiPP even at low concentrations of 3PA. To rule out the contribution of the TiPP phase, the modification degree of 3PA was thus calculated only in the temperature interval between 250 and 420 °C. The modification degrees of 3PA on the three titania supports are summarized in Table 2.

Table 2 lists the modification degrees of the three titania supports after modification in water or toluene with four different concentrations

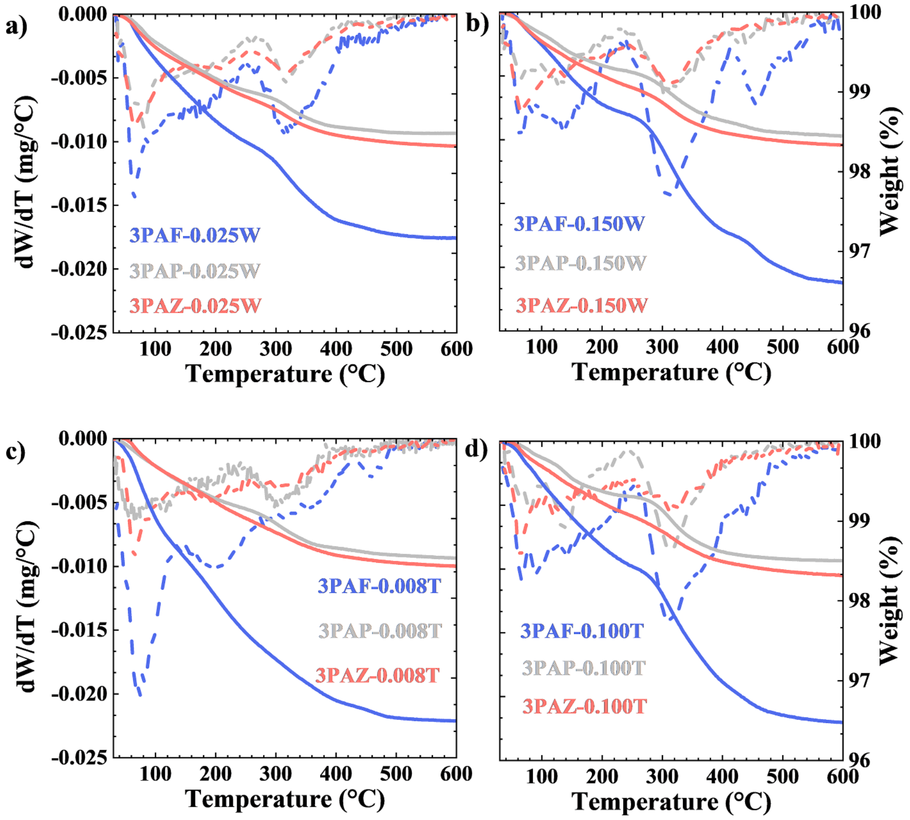


Fig. 2. TG/DTG curves of the three 3PA modified titania samples (a and b were modification in water with 0.150 M and 0.025 M of 3PA, respectively; c and d were in toluene with 0.008 M and 0.100 M of 3PA, respectively), as measured under an 80 mL/min of oxygen flow, ramping from 30 °C to 600 °C at 10 °C/min. The solid and dashed lines are for TG and DTG results, respectively.

Table 2
Overview of modification degrees for the three supports with four concentrations of 3PA at 90 °C in water or toluene. The experimental error is around 0.1 group/nm^2, based on five repeated TGA/DTG measurements of different batches of samples and our previous work [17,25].

Synthesis in water				Synthesis in toluene			
Conc. (M)	Mod. deg. (#/nm^2)			Conc. (M)	Mod. deg. (#/nm^2)		
	F-TiO_2	P-TiO_2	Z-TiO_2		F-TiO_2	P-TiO_2	Z-TiO_2
0.025	1.3	1.3	1.2	0.008	1.1	1.4	1.3
0.075	1.5	1.4	1.3	0.013	1.5	1.8	1.5
0.100	1.6	1.6	1.4	0.026	1.7	1.9	1.5
0.150	2.1	1.9	1.5	0.100	2.2	2.0	1.6

of 3PA in each solvent. It can be concluded that the organic loading increases with enhancing 3PA concentration, independent of the supports/solvents. However, P-TiO_2 and F-TiO_2 present more pronounced differences in the modification degree in function of concentration than Z-TiO_2. At high concentration of 3PA, the modification degree on P-TiO_2 and F-TiO_2 is higher than Z-TiO_2 regardless of the solvents. Table 2 also presents that the modification degree on P-TiO_2 was higher in case of toluene than water, which was already reported in literature to be caused by the lack of competitive interactions between toluene and the titania support in contrast to the use of water [17]. This phenomenon is much more visible on P-TiO_2 than other two types of titania where the differences are less/not significant, close to or equal to the error of the measurement.

In order to confirm that the maximum modification degrees were reached on the three titania supports used in this study, higher concentrations of 0.300 M were applied for both water and toluene. The specific TG/DTG curves can be found in Fig. S6 (Supporting Information). The results confirm that the modification degree on the three titania supports remained unchanged within the experimental error of 0.1 #/nm^2. Therefore, the highest modification degrees in Table 2 can be considered the maximum modification degrees under the synthesis conditions applied in this study. Hence, a clear difference in the maximum obtainable modification degrees was observed on the three titania supports.

Although the three titania supports showed differences in crystal phase and crystal size (Table S1), no straightforward correlation between the crystal phase and size and the maximum modification degree was found. Moreover, according to the information from the supplier, Z-TiO_2 contains 2.8 % of sulfur, however, it was not detected by EDX (surface techniques, Fig. S4, Supporting information). Table S1 also indicates the presence of other impurities on the three titania supports. Nevertheless, although we cannot exclude their contribution (e.g. 3PA preferentially bonds to TiO_2 rather than SiO_2 [29]), the impurities are present in less than 1 %, which limits their impact on the total modification degree. Therefore, as 3PA bonds to the surface via condensation between Ti–OH and P–OH and/or the coordination of P=O to Lewis acid sites on TiO_2 [13], it is of interest to investigate whether the observed differences in maximum modification degree are related to differences in surface hydroxyl groups and Lewis acid sites on three titania supports.

3.3. In-situ drift of 3PA modified tio$_2$ supports

To evaluate the potential correlation between the surface hydroxyl groups and the 3PA modification, the *in-situ* DRIFT results of modified titania supports were compared to those of the pristine titania materials in function of temperature. Here, samples with maximum modification degrees in water or toluene were studied. The spectra of the samples were recorded after heating to 300 °C under an argon flow to assure the complete removal of the surface water, making the peaks related to hydroxyl groups clearer. Moreover, the organic groups are not decomposed at 300 °C, which was confirmed by the onset of decomposition of organic groups above 400 °C in the DTG-MS measurements featured in Fig. S7. Thus, the observed changes in surface hydroxyl groups resulted from the modification.

The spectra of modified titania show the characteristic alkyl stretching vibrations at 3000–2800 cm^{-1}, a band at 1245 cm^{-1} that might relate to phosphoryl vibration, OH groups at 3750–3600 cm^{-1} and C–H deformation at 1500–1300 cm^{-1} (Fig. S8, Supporting Information) [5,17,25,48]. The consumption of OH groups is clearly visible on all modified samples, due to the condensation reaction between Ti–OH and P–OH. However, differences can be observed depending on the solvent and support, as seen in the enlarged spectra in Fig. 3.

For the modification on P-TiO_2 (Fig. 3a), applied solvents seem to have little influence on the types of hydroxyl groups consumed, while the consumption of isolated OH groups on F-TiO_2 and Z-TiO_2 (Fig. 3b, c) seems to be closely related to the solvent used in the modification. After modification in water or toluene on P-TiO_2 (Fig. 3a), almost all OH groups became unresolved and much less intense, indicating they are active to bond 3PA. Similar to P-TiO_2, bridged OH groups at 3671 cm^{-1} on F-TiO_2 and Z-TiO_2 are also consumed through condensation with 3PA, irrespective of the solvent. While changes in other OH groups at 3640 cm^{-1} are difficult to observe as the signal existed but was unresolved before the modification. Moreover, the intensity changes of the isolated OH groups after modification are clearly different, depending on the solvent, pointing to a difference in interaction or in reactivity towards 3PA triggered by the solvent present. The isolated OH groups (3735 cm^{-1} and 3720 cm^{-1} on F-TiO_2, and 3735 cm^{-1}, 3718 cm^{-1}, 3710 cm^{-1} on Z-TiO_2) were much less resolved in water than in toluene, which implies that these OH groups were more reactive towards 3PA in water. This might be due to some type of activation towards 3PA in the presence of water or differences in interaction with the supports that hinders the consumption of these particular OH groups in toluene (e.g., OH…π-electrons interaction [49]).

To further investigate the difference in consumption behaviors and/or condensation of OH groups on the modified titania, blank experiments were performed (Fig. S9). Indeed, all OH groups on P-TiO_2 have a similar condensation/thermal behavior, irrespective of the use of water or toluene (Fig. S9a-c). However, the condensation of isolated hydroxyl groups on F-TiO_2 and Z-TiO_2 showed a close correlation with the solvent used. The isolated OH groups on F-TiO_2 and Z-TiO_2 were more prone to condense after rinsing with toluene (Fig. S9e, f and Fig. S9h, i) than with water (Fig. S9d, 9 g). This confirms that differences in solvent-support interactions in case of F-TiO_2/Z-TiO_2. Whereas the effect of the solvent is reversed in case of thermal condensation versus 3PA reactivity. Specifically, the toluene-rinsed samples lose more OH groups as temperature increases, while these OH remain less reacted with 3PA when toluene is used as the solvent compared to water. The results confirm the impact of the solvent on the thermal condensation behavior of the hydroxyl groups, pointing to an influence of solvent-surface interaction on hydroxyl reactivity.

In addition, the types of remaining hydroxyls after 3PA functionalization seem to be the same as those that were left on pristine F-TiO_2 and Z-TiO_2 after heating at 600 °C except OH at 3640 cm^{-1} (Fig. 3). Interestingly, no OH groups were left at 600 °C on P-TiO_2, coinciding with the lack of solvent dependence. This might imply that the underlying reason for the thermal condensation behavior of OH groups (e.g., topology, amount, type, or distribution) also relates to their reactivity towards 3PA.

Furthermore, the effect of modification degree on the consumption of OH groups is observed in Fig. S10 by comparing the titania modified with the highest and lowest modification degree. With increasing modification degree, the signals of OH groups on the three modified titania prepared in water or toluene became less resolved, indicating that all these OH groups are active in the bonding of 3PA and play an important role in the modification, although not in the same way.

Moreover, the above results indicate that the consumption of OH groups on the three titania supports depends on the support and solvent

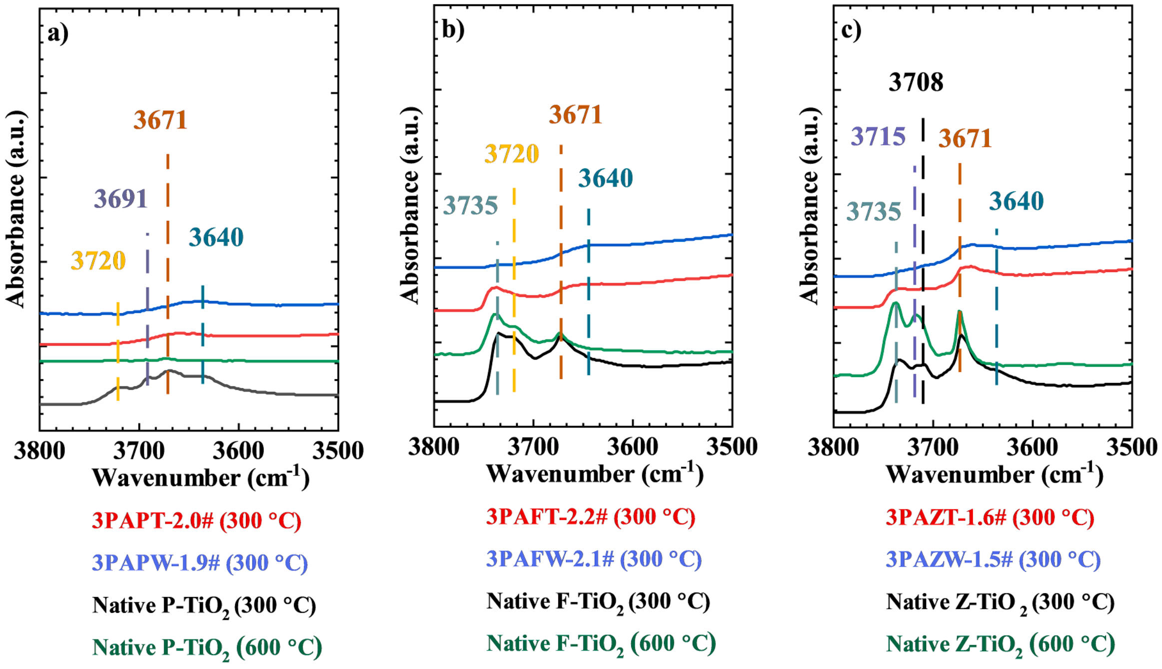


Fig. 3. *In-situ* DRIFT spectra at 3800–3500 cm^{-1} of P-TiO$_2$, F-TiO$_2$ and Z-TiO$_2$ modified in water or toluene and of native supports, as measured with undiluted samples at RT after being heating to 300 °C or 600 °C under an 80 mL/min of Ar flow.

used. Furthermore, thermal condensed OH groups on supports (without solvent treatment) seems to coincide with the OH groups that are more or less prone to react with 3PA.

3.4. MeOH chemisorption technique

The aforementioned discussion has showed that although all the OH groups on the three titania supports are reactive to 3PA, they still show differences in maximum modification degree of 3PA. To gain further insights into these surface reactive sites (OH groups and Lewis acid sites) responsible for 3PA modification on the three different supports, the hypothesis to apply methanol chemisorption as a method to estimate differences in PAs modification on the three titania surfaces was evaluated here, by determining the type (with *in-situ* DRIFT) and the amount (chemisorption capacity) of condensable OH groups and strong Lewis acid binding sites.

Fig. 4 shows that the different types of adsorbed methanol on the three titania supports are composed of the intact Lewis-bound surface methanol species (L-MeOH, 2955–2950 cm^{-1} and 2850–2846 cm^{-1}) and methoxy species (–OCH$_3$, 2925 cm^{-1}, 2890–2895 cm^{-1} (a combination band) and 2825–2821 cm^{-1}) [36]. The bands at 2955–2950 cm^{-1} and 2850–2846 cm^{-1} were attributed to symmetric stretching (ν_s) and the first overtone of the symmetric bend (2δ_s) of CH$_3$ in L-MeOH, respectively [36]. The bands at 2925 cm^{-1} and 2825–2821 cm^{-1} were assigned to the same modes occurring in –OCH$_3$ [36]. These bands suggest that MeOH can probe Lewis acid sites and/or hydroxyls surface interaction sites on the three TiO$_2$ supports. Although all of them show these two types of chemisorbed MeOH, the relative intensity and specific wavenumber of these two kinds of characteristic bands as well as their thermal stability are different, confirming the different surface properties (e.g. acid type and strength).

In specific, at RT, the relative intensity of the characteristic peaks of L-MeOH on F-MeOH and P-MeOH were both lower than those of –OCH$_3$, while the relative intensity of the L-MeOH peaks were higher (2950 cm^{-1}) or lower (2846 cm^{-1}) than –OCH$_3$ on Z-MeOH. The thermal stability of –OCH$_3$ was similar for the three titania, that is, the peaks of –OCH$_3$ were barely visible at 350 °C. However, L-MeOH shows different thermal behaviors on the three titania supports. The peaks of L-MeOH were present at 350 °C on F-TiO$_2$ and Z-TiO$_2$ although in lower intensity, while they were invisible at 250 °C on P-TiO$_2$. Moreover, differences in L-MeOH were also observed between F-TiO$_2$ and Z-TiO$_2$. With the majority being removed between 300 °C and 350 °C while traces remained until 400 °C on F-TiO$_2$ (Fig. 4b). On Z-TiO$_2$, traces also remained visible up to 350 °C but there was already a stronger decrease between 150 °C and 200 °C (Fig. 4c). In all, these differences in thermal behavior of L-MeOH indicate the presence of varying strengths and/or types of Lewis acid sites on the three titania supports. Furthermore, an interesting observation is the shift in the signals of L-MeOH and –OCH$_3$ with increasing temperature. More specific analysis can be found in Result F, Fig. S11 (Supporting Information).

A part of the chemisorption of MeOH correlates to surface hydroxyl groups, these changes are also shown in the three titania supports (Fig. 4). In the spectra of P-MeOH, the hydroxyl groups were present at 3671 cm^{-1} and 3630 cm^{-1} at RT, then they all disappeared at 250 °C with the desorption of L-MeOH. It could be that the L-MeOH was converted to –OCH$_3$ on these OH groups with heating but this is less likely as no increase in signals of –OCH$_3$ was observed. Whatever the reasons, this phenomenon implies that all OH groups on P-TiO$_2$ seem reactive to MeOH, which coincides with the reactivity towards 3PA modification.

When looking more closely to the hydroxyl region in F-MeOH and Z-MeOH (Fig. 4b, c), the OH signals present at RT before methanol chemisorption were still visible, although they were less resolved and lower in intensity due to their reaction with MeOH. In contrast to P-TiO$_2$, they do not disappear with rising of temperature. The presence of these hydroxyl groups could indicate that some of these OH groups are not reactive with methanol under the conditions applied in this study, which might be due to steric hindrance or their low reactivity towards MeOH. Interestingly, most of these remaining OH groups on F-MeOH and Z-MeOH are the same as those remaining after 3PA modification (Fig. S12), indicating that they have similar reactivity towards 3PA and MeOH. Other interesting observations with respect to the OH groups' self-condensation were discussed in Result G (Supporting Information).

With the desorption of –OCH$_3$, all types of the hydroxyl groups on three TiO$_2$ supports get restored to the original surface hydroxyl groups, which demonstrates that the presence of –OCH$_3$ originates from the MeOH dissociative adsorption on OH groups (although partial

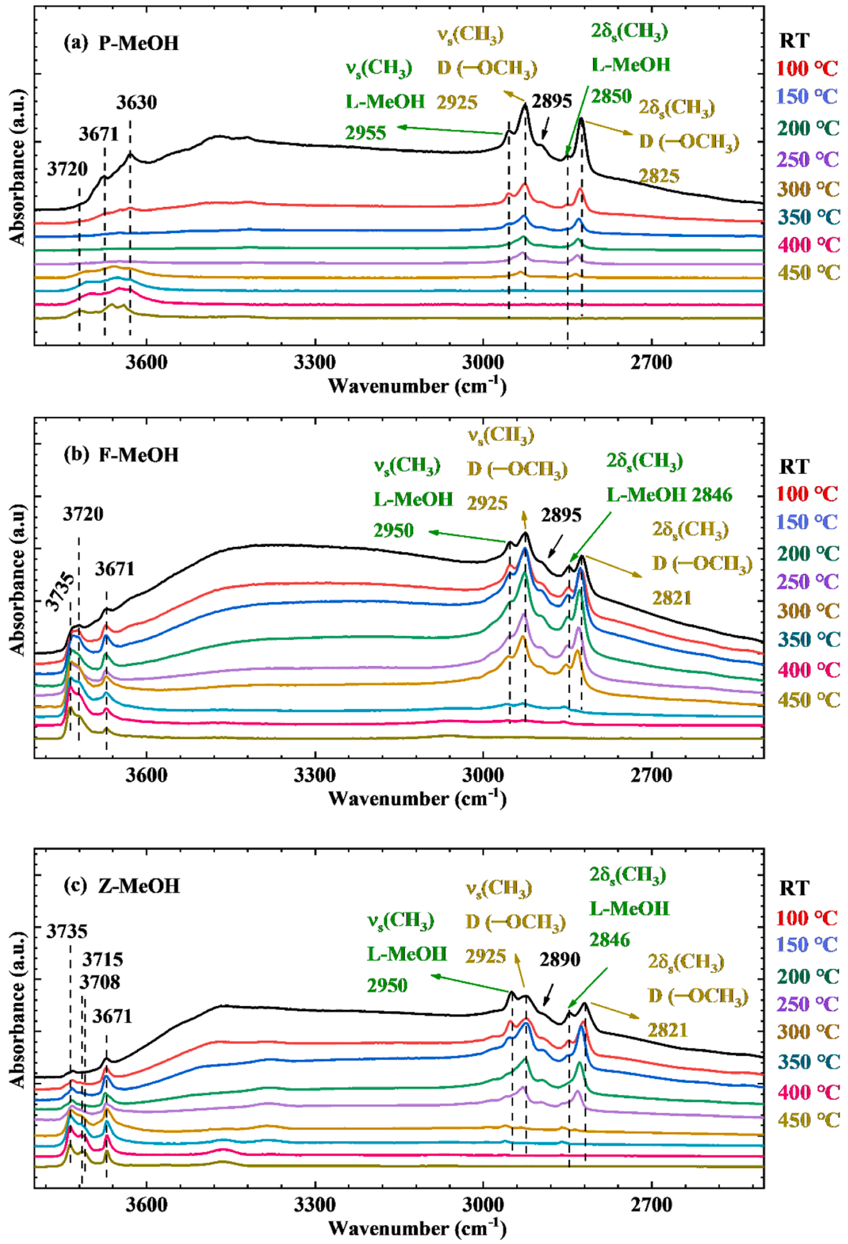


Fig. 4. *In-situ* DRIFT spectra at 3800–2500 cm^{-1}of MeOH chemisorbed P-TiO$_2$, F-TiO$_2$ and Z-TiO$_2$, as measured with undiluted samples against KBr as a background at different temperatures under an Ar flow.

dissociative adsorption on Lewis acid sites with oxygen anions around cannot be excluded either). This also confirms that most OH groups on three TiO$_2$ supports are active to and react with MeOH, which is consistent with that most of the hydroxyl groups on these TiO$_2$ are active towards 3PA modification (Fig. S10).

The above results imply that it seems possible to correlate MeOH chemisorption results with 3PA modification's, at least in identifying the type of surface (un)reactive sites towards surface grafting. Furthermore, methanol chemisorption could provide quantitative data (see below).

Based on the similarity in surface (un)reactive sites of titania towards methanol chemisorption and 3PA modification, a quantitative correlation of the adsorption capacity of the strongly bonded chemisorbed methanol and the maximum modification degree of 3PA was evaluated. The number of strongly chemisorbed methanol, calculated based on 2-cycle adsorption (Fig. S13), on P-TiO$_2$, F-TiO$_2$ and Z-TiO$_2$ were 1.6 #/nm^2, 1.9 #/nm^2, and 1.2 #/nm^2 respectively, which is the highest on F-TiO$_2$ and the lowest on Z-TiO$_2$, i.e., the same as their maximum 3PA modification degree order (in both water and toluene). To validate if this correlation is linear, the maximum modification degree of 3PA (in both water and toluene) on three different TiO$_2$ supports was plotted in function of the supports' adsorption capacity of the strongly bonded chemisorbed methanol (Fig. 5). A clear correlation was found. Hence, adsorption capacity of the strongly bonded chemisorbed methanol can be used to understand the maximum 3PA modification degree on different titania supports with divergent surface properties. More MeOH chemisorption sites correlates to more reactive sites for 3PA, i.e., higher maximum modification degrees of 3PA. Important to note, the standard error used in Fig. 5 is different from the error range calculated in Table 2. It indicates the likely accuracy of a number (its calculation can be found in Result H, Supporting Information).

Furthermore, although 3PA has a bulkier organic group than methanol, the maximum modification degree of 3PA is somewhat higher than the number of chemisorbed methanol (0.3–0.4 #/nm^2 higher in toluene, 0.2–0.3 #/nm^2 higher in water), possibly due to the effect of the self-

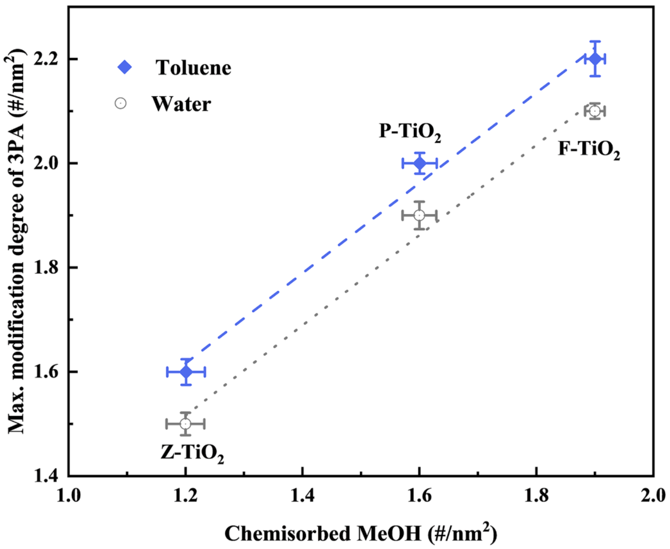


Fig. 5. The correlation between the amount of chemisorbed MeOH and the maximum modification degree of 3PA for the three different supports. Blue dots are for the modification in toluene, grey ones are in water. The error bars were obtained from standard errors based on three repeated experiments.

assembly of 3PA [17]. It is important to note that the method might also overestimate modification degrees when steric effects might be present in case of microporous supports that limit diffusion of larger molecules versus the relatively small methanol or in case of bulky organic groups on the PA that create steric hindrance. Nevertheless, although differences might occur due to self-assembly on the surface or steric effects in case of e.g. bulky PAs, a similar relative trend between the capacity of chemisorbed methanol and the maximum modification degree of 3PA among different titania supports can still be observed. This suggests that it can provide an understanding of the differences in the maximum modification degree of 3PA on different types of titania, rather than providing an absolute number of the maximum modification degree of 3PA on different types of titania, given the similar surface (un)reactive sites for methanol chemisorption and 3PA modification.

In short, *in-situ* DRIFT analysis of the MeOH-chemisorbed titania can help to understand which surface sites can be involved in the 3PA bonding and how they differ in the different types of titania used. The capacity of strongly chemisorbed methanol could provide insights into the potential reasons for deviation of the maximum modification degree of a particular phosphonic acid on different titania supports, due to differences in the amount of surface reactive sites. However, it only provides trends while direct correlation of the absolute numbers between methanol chemisorption and 3PA modification is not feasible and might even point to steric or self-assembly effects present in the PA which are different for methanol.

4. Conclusion

This work investigates the relationship between the TiO_2 support surface properties and PAs modification in detail, through grafting 3PA molecules onto three different TiO_2 supports. Although the same modification conditions were applied, divergent modification degrees were obtained for the three types of titania. Moreover, methanol was applied to probe the surface (un)reactive sites (hydroxyl groups and Lewis acid sites) of titania towards 3PA modification. *In-situ* DRIFT revealed that the three TiO_2 surfaces have different types, relative amounts and distribution of hydroxyl groups, showing a different tendency towards condensation, 3PA modification and solvent interaction. The types of remaining OH groups after 3PA modification and after MeOH chemisorption were similar. A correlation was found between the sorption capacity of strongly chemisorbed methanol and the maximum 3PA modification degree.

Therefore, chemisorbed methanol on the three different titania supports applied in this study can provide insights in the reactive surface OH groups prone to condensation reactions and the strong interacting Lewis acid sites. As similar surface sites are involved in 3PA modification, the methanol chemisorption sheds light on the role of these surface groups in the divergence in surface modification degree for the different titania materials and provides understanding in the tendency of 3PA to interact with different types of titania, while using the same modification conditions.

CRediT authorship contribution statement

Kaimin Zhang: Conceptualization, Methodology, Validation, Investigation, Writing – original draft. **Jinxin Wang:** Conceptualization, Methodology, Writing – review & editing. **Vera Meynen:** Supervision, Conceptualization, Methodology, Resources, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

K. Z. acknowledges the financial supports from the EASiCHEM project funded by the Flemish Strategic Basic Research Program of the Catalisti cluster and Flanders Innovation & Entrepreneurship (HBC.2018.0484). J. W. acknowledges the State Scholarship funded by the China Scholarship Council (201806060123). V. M. acknowledges the Research Foundation – Flanders (FWO) for grant number K801621N and BOF project 44042 of UAntwerp. V.M. acknowledges the BOF Equipment funding of UAntwerp (ID: 41358). We thank Wouter Van Hoey for the Rietveld data processing.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.surfin.2023.103697.

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