

## Single-step synthesis and structural study of phosphate modified titania through seeding method

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A single-step organic-free process has been evolved to prepare phosphate-modified titania, a nanomaterial, from titanium oxysulphate solution. The adsorption of phosphate ions from aqueous solution onto titania has been studied by XRD, XPS, and DRIFT which show strong adsorption of phosphate, as Ti-O-P on the surface of titania. An increase in crystallinity and decrease in surface area are observed with calcination temperature. XPS results reveal a pentavalent oxidation state for P and the substitution of P for oxygen. The phosphate-modified titania displays good thermal stability, an essential property required for the application as catalyst and active support.

**Keywords:** Catalyst, Mesoporous phosphated titania, Phosphated titania, Titania, Titanium oxysulphate, Seeding method

High surface area mesoporous titania ( $\text{TiO}_2$ ) is an interesting material in view of their utility in catalysis, energy conversion, and membrane and optical applications<sup>1</sup>. Mesoporous titania has been synthesized by controlling the reactivity of Ti(IV) with the addition of stabilizing agents, like phosphate<sup>2-4</sup>. The preparation of mesoporous amorphous titania was first reported in 1995 by using alkyl phosphate surfactant as template through a modified sol-gel process<sup>2</sup>. It was reported that the thermal stability and acidity of mesoporous materials could be improved through post-treatment with phosphoric acid<sup>5,6</sup>. The uncondensed surface hydroxyl groups may react with the phosphate ions, leading to complete cross-linking<sup>7</sup> which provides good thermal stability. Moreover,  $\text{H}_3\text{PO}_4$  can be polymerized to polyphosphoric acid with network structure at high temperatures. This network structure, which is tightly attached to the surface of mesoporous materials, can effectively resist the shrinkage of pore channels during thermal or hydrothermal treatment<sup>8</sup>. It has been shown that incorporation of phosphate ion in titania framework enhances stabilisation of surface area, crystal phase, and improvement in surface acidity<sup>9</sup>. It has been observed that the phosphated titanium dioxide has excellent catalyst properties when used in organic chemical reactions<sup>10</sup>. Yu *et al.*<sup>11</sup> studied one-step synthesis of phosphate-modified titania using triblock copolymer as the template and titanium isopropoxide as the titania source.

Titania supports treated with phosphate or silica possess good thermal stability with sufficient porosity, which makes them suitable for use in auto-exhaust VWT catalysts. The key objective of the present work is to develop titania support with good thermal stability by modifying with phosphate. We have also aimed at eliminating organic solvents and organic titania sources which will have a significant impact on the environment, by employing inorganic precursor as a source of titania. When organic titania precursors are used, the complete removal of carbon from the samples requires calcination above 600 °C which is likely to lower the surface area of titania. Herein, we discuss a single-step preparation of phosphate-modified titania by seeding method and provide XRD, XPS, and DRIFT spectral evidences for the polydentate type phosphate adsorption on titania surface.

### Materials and Methods

Titanium oxysulphate (Aldrich), ortho-phosphoric acid (Qualigens), P-25 titania (Degussa),  $\text{TiO}_2$  (Fluka) and sodium hydroxide (Qualigens) were used without further purification. Doubly distilled water was used as a solvent.

### Preparation of seed

Titanium oxysulphate (4 g) was dissolved in 40 mL of water in a 100 mL SS container and the solution was heated to 70 °C with continuous stirring. To this

was slowly added 10 wt.% of sodium hydroxide until the pH was 3. The temperature of the solution was maintained at 75 °C for 1 h. The obtained solution was used as a precipitation seed, which is essential to obtain a higher surface area and smaller particles of titania.

#### Synthesis of phosphate modified titania

To 42 g of titanium oxysulphate solution containing 12 % TiO<sub>2</sub> and 24 % H<sub>2</sub>SO<sub>4</sub>, sodium hydroxide solution (10 wt.%) was added with uniform stirring until the pH was 1.7. Then, 5 mL of seed was added to initiate the precipitation process. The hydrolysis was performed in a constant boiling apparatus at 98 ± 2 °C for 3 h. At the end of this period, 17 g of 5 wt.% H<sub>3</sub>PO<sub>4</sub> was added dropwise to precipitate titanium ions completely. The phosphate-modified titania was obtained after thoroughly washing the precipitate with water to remove sodium sulphate and sodium phosphate. The precipitate obtained was dried at 100 °C for 12 h and thereafter calcined for 2 h at 500 °C, 700 °C and 900 °C in air to study the effect on crystallization and surface area. A temperature less than 98 °C required additional time for completion of precipitation and the addition of sodium hydroxide to titanium oxysulphate was found to be essential for enhancing the rate of precipitation. The phosphate content of the samples was maintained at 10 % and the samples are designated 10P-TiO<sub>2</sub>-X, where X represents the temperature of drying and calcination.

The XRD pattern for the various temperature-treated phosphate-modified titania samples were obtained using a Rigaku Miniflex II, using Cu-K<sub>α</sub> irradiation. The Rigaku XRF spectrometer-Primini was used for the elemental analysis of the samples. The XPS was recorded on Omicron spectrometer in the range of 0 – 1100 eV. Photoelectron lines of the main constituent elements, O1s, Ti2p, P2s, and P2p, were recorded at 50 eV pass energy by 0.1 eV steps and a minimum 1 second dwell time. All binding energies were referenced to the C1s peak at 284.8 eV. The DRIFT spectra for the samples were recorded using Bruker Tensor-27 instrument.

#### Results and Discussion

The composition of 10P-TiO<sub>2</sub> samples calcined at various temperatures analysed on XRF spectrometer was 9.8 wt.% of P<sub>2</sub>O<sub>5</sub> and 90.1 % of TiO<sub>2</sub>. Although the material was synthesized using titanium oxysulphate, the absence of sulphate shows the

effective removal as sodium sulphate by the washing process. The BET-surface area, particle size, and crystallinity of the 10P-TiO<sub>2</sub> samples calcined at various temperatures are given in Table 1. The 10P-TiO<sub>2</sub>-100 material showed a surface area of 340 m<sup>2</sup>/g. This value decreased with treatment temperature and attained a value of 70 m<sup>2</sup>/g for 10P-TiO<sub>2</sub>-900. The particle size ranged between 4 and 20 nm for the 10P-TiO<sub>2</sub> samples which demonstrates that they are nanomaterials. The XRD patterns of the anatase (Fluka) and 10P-TiO<sub>2</sub> samples calcined at various temperatures are shown in Fig. 1. The heat treatment of the samples was anticipated to strengthen the bond between the Ti(IV) and PO<sub>4</sub><sup>3-</sup> ions. The XRD patterns showed the presence of only anatase phase in the 10P-TiO<sub>2</sub> samples irrespective of the calcination temperature. The 10P-TiO<sub>2</sub> samples calcined at temperatures between 500 and 900 °C in air for 2 h showed increasing crystallinity with

Table 1— BET surface area, particle size (S<sub>BET</sub> method) and crystallinity of the 10P-TiO<sub>2</sub> samples calcined at various temperatures

Sample	BET surface area (m <sup>2</sup> /g)	Calc. particle size (nm) S <sub>BET</sub> -method	Calc. crystallinity (%)
10P-TiO <sub>2</sub> -100-12 h	340	4	14
10P-TiO <sub>2</sub> -500-2 h	75	8	16
10P-TiO <sub>2</sub> -700-2 h	130	11	24
10P-TiO <sub>2</sub> -900-2 h	70	20	25
10P-TiO <sub>2</sub> -900-4 h	20	71	73

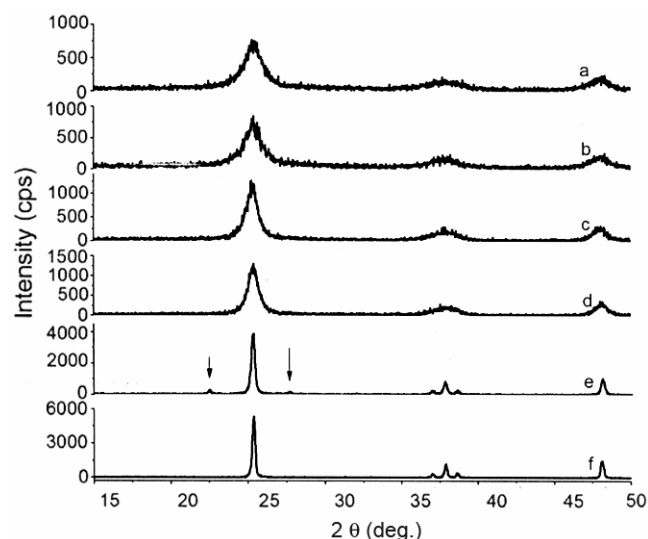


Fig. 1—XRD patterns of anatase and 10P-TiO<sub>2</sub> samples calcined at various temperatures. [(a) 10P-TiO<sub>2</sub>-100-12h; (b) 10P-TiO<sub>2</sub>-500-2h; (c) 10P-TiO<sub>2</sub>-700-2h; (d) 10P-TiO<sub>2</sub>-900-2h; (e) 10P-TiO<sub>2</sub>-900-4h; (f) anatase].

temperature, as discerned from the narrowing of the peaks. The crystallinity for 10P-TiO<sub>2</sub> was calculated based on the intensity of XRD peak obtained at a 2θ of 25.3. The 10P-TiO<sub>2</sub>-100 was found to have an anatase content *ca.* 14 %. The crystallinity increased from *ca.* 14 % through 25 % when the calcination temperature was increased from 100 °C to 900 °C. Interestingly, the crystallinity increased further to 73 % when the sample was calcined at 900 °C for 4 h. The enhanced crystallinity manifests itself in the surface area which decreased with crystallinity. The 10P-TiO<sub>2</sub>-900 calcined for 2 h was anticipated to produce a 100 % crystalline anatase. Nevertheless, the obtained crystallinity was merely 25 %, which could be due to the strong adsorption of phosphate on the surface of titania and its hindering effect on crystal growth. Such an adsorption results in formation of Ti-O-P linkages which does not aid the transformation to crystalline form. The particle size calculated using the surface area data showed an increasing trend with temperature. Generally, the heat treatment leads to particle growth. However, the increase in particle size in the case of 10P-TiO<sub>2</sub> samples is not significant due to their thermal stability, and it is this property which is essential for its application as a catalyst and catalyst carrier. The treatment at 900 °C for 4 h showed a steep enhancement in crystallinity to 73 % with two additional reflections at a 2θ of 22.5 and 27.8. These two peaks are not due to rutile as the latter forms a major peak at a 2θ of 27.5. Hence, the peaks formed at 2θ of 22.5 and 27.8 may be attributed to the formation titanium pyrophosphate<sup>12</sup>.

The X-ray photoelectron spectra were measured to examine the oxidation state and the quantity of PO<sub>4</sub><sup>3-</sup> on the surface of titania. The high resolution XPS of P2p, Ti2p and O1s core electrons taken on the surface of anatase and 10P-TiO<sub>2</sub>-700 are presented in Fig. 2a-c. The P/Ti ratio at the surface was determined to be 0.09 for 10P-TiO<sub>2</sub>-700. The 10P-TiO<sub>2</sub>-700 exhibited a binding energy for P2p at 134.5 eV, indicating that phosphorus in the sample exists in pentavalent-oxidation state and most probably as P-O bonded species<sup>13</sup>. It is improbable that Ti-P bonds are present in the calcined 10P-TiO<sub>2</sub> samples since the characteristic binding energy of 128.6 eV for Ti in Ti-P was not observed<sup>14</sup>. The peak at 134.5 eV has a binding energy similar to that of NaH<sub>2</sub>PO<sub>4</sub> (133.9 eV)<sup>15</sup>, which suggest that only PO<sub>4</sub><sup>3-</sup> is present in 10P-TiO<sub>2</sub>. However, as the phosphate ions were adsorbed from an acid solution, it is less probable for

the free PO<sub>4</sub><sup>3-</sup> ions to be present in the sample. Alternatively, the titanium phosphate formed by the adsorption of PO<sub>4</sub><sup>3-</sup> ions from phosphoric acid is present in the material either as (TiO)<sub>2</sub>(PO)<sub>2</sub> or Ti(HPO<sub>4</sub>)<sub>2</sub>·xH<sub>2</sub>O<sup>16, 17</sup>. Ti2p<sub>3/2</sub> in 10P-TiO<sub>2</sub>-700 can be fitted as one peak at 458.4 eV, indicating that Ti ions are in an octahedral environment, coordinated with oxygen<sup>15</sup>. In bulk phase TiO<sub>2</sub>, where Ti ions are in an octahedral environment, only one peak at a binding energy of 458.1 eV is observed. The oxidation state of the Ti element in 10P-TiO<sub>2</sub>-700 (Ti2p<sub>3/2</sub>, binding energy 458.4 eV; Ti2p<sub>1/2</sub>, binding energy 464.2 eV) does not match with that of anatase TiO<sub>2</sub> (Ti2p<sub>3/2</sub>, binding energy 458.1 eV; Ti2p<sub>1/2</sub>, binding energy 463.8 eV) suggesting the substitution of P for oxygen. The O1s region of the anatase is composed of a single peak at 529.3 eV, corresponding to the Ti-O in TiO<sub>2</sub>. On the other hand, the O1s binding energy of the 10P-TiO<sub>2</sub>-700 is observed at 529.7 eV which is attributed to the presence of Ti-O-P linkage. From the XPS results, the atomic incorporation of P atoms or their substitution for O atoms in the anatase TiO<sub>2</sub> lattice can be confirmed.

The DRIFT spectra of 10P-TiO<sub>2</sub>-500, 10P-TiO<sub>2</sub>-700, and 10P-TiO<sub>2</sub>-900 measured in the range of 700–2000 cm<sup>-1</sup> are compared with that of the anatase in Fig. 3. The unmodified crystalline anatase exhibits a narrow band at 920 cm<sup>-1</sup>. However, the 10P-TiO<sub>2</sub> samples showed significant changes in the DRIFT spectra. The 10P-TiO<sub>2</sub>-500 sample showed a broad absorption peak in the range of 1300–800 cm<sup>-1</sup>

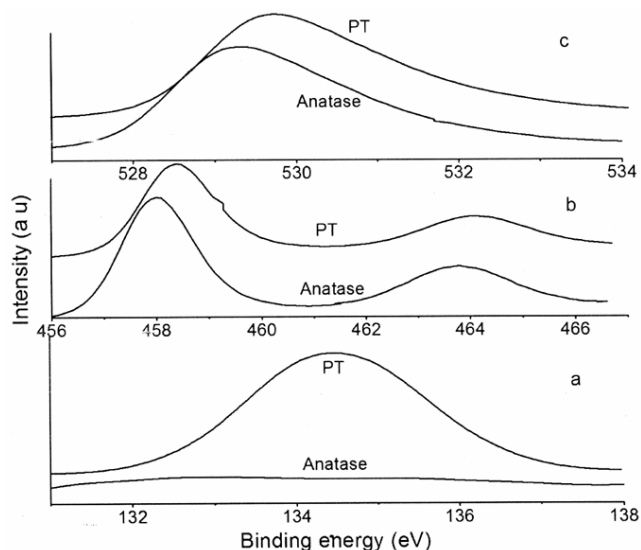


Fig. 2—XPS spectra of the (a) P2p, (b) Ti2p and (c) O1s taken on anatase and 10P-TiO<sub>2</sub> samples.

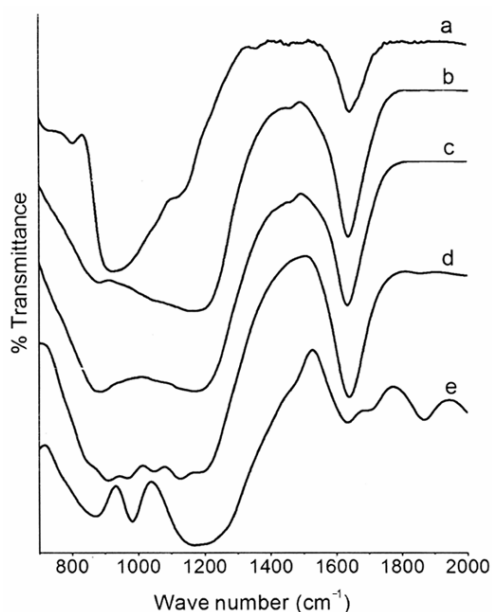


Fig. 3—DRIFT spectra of anatase and 10P-TiO<sub>2</sub> samples calcined at various temperatures. [(a) anatase; (b) 10P-TiO<sub>2</sub>-500-2h; (c) 10P-TiO<sub>2</sub>-700-2h; (d) 10P-TiO<sub>2</sub>-900-2h; (e) 10P-TiO<sub>2</sub>-900-4h].

resulting from the lowering of symmetry ( $C_{3V}$  or  $C_{2V}$ ) of phosphate groups due to the adsorption on the surface of titania<sup>10</sup>. The calcination at 700 °C showed two broad peaks at about 885 and 1180  $\text{cm}^{-1}$ . The peak at 885  $\text{cm}^{-1}$  is shifted to 860  $\text{cm}^{-1}$  and a broader peak was observed in the range of 1050–1230  $\text{cm}^{-1}$  in the case of 10P-TiO<sub>2</sub>-900 calcined for 2 h. In addition a small peak appeared at about 960  $\text{cm}^{-1}$ . When the calcination duration was increased to 4 h at 900 °C, the intensity of all the peaks (at 860, 960, and 1180  $\text{cm}^{-1}$ ) increased. The peak at 1630  $\text{cm}^{-1}$  is ascribed to hydroxyl groups. The intensity of this peak is higher for 10P-TiO<sub>2</sub> samples relative to the crystalline anatase sample and is attributed to the presence of significant concentration of hydroxyl groups in the 10P-TiO<sub>2</sub> samples. Interestingly, the 10P-TiO<sub>2</sub>-900 sample calcined for 4 h displays additional peaks at about 1680 and 1850  $\text{cm}^{-1}$  which could be due to the formation of various titanium phosphates other than the one adsorbed on the surface of titania. This observation is further supported by XRD results in which peaks are obtained for titanium pyrophosphate in addition to anatase titania peaks. The calcination at 900 °C for 4 h showed splitting and shifting of absorption bands to higher frequencies suggesting that (i) a stronger adsorption of phosphates on the surface of titania, (ii) its enhanced thermal stability and (iii) the bidentate or tridentate structure of adsorbed phosphate on the surface of titania.

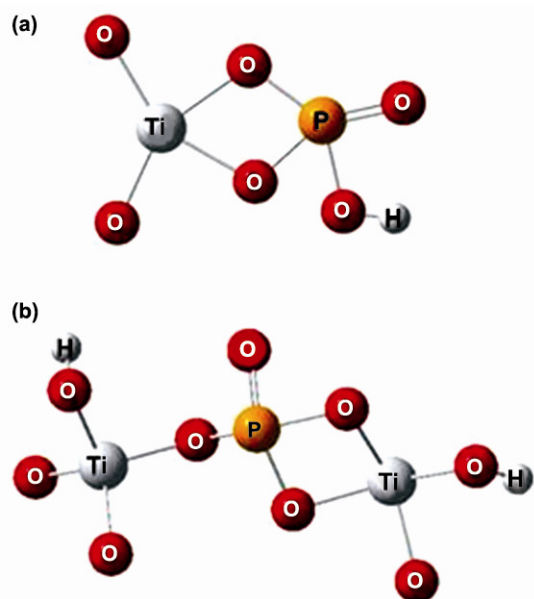


Fig. 4—Proposed structures of the phosphate adsorption on hydrated titania. [(a) Polydentate structure-I; (b) Polydentate structure-II].

The species adsorbed on titania surface from *ortho*-phosphoric acid solution at a pH of 0.8 could be a bridging bidentate surface complex  $(\text{TiO})_2\text{PO}_2$  with  $C_{2V}$  symmetry. The phosphate species interact through the P–O groups with the titanium ions exposed on titania surface to form Ti–O–P bond. The published reports<sup>18</sup> suggest the adsorption of phosphates as bidentate and monodentate species on the surface of titania. However, the conversion of amorphous titania to crystalline anatase only to the extent of 73 % even under vigorous calcination at 900 °C for 4 h shows the complexity in the removal of adsorbed phosphates and the possible polydentate phosphate adsorption on the surface of titania (Fig. 4). This postulate is evidenced by XRD, XPS and DRIFT spectral studies.

### Conclusions

In summary, a single-step organic-free process has been developed to prepare phosphate-modified titania from titanium oxysulphate solution at a temperature of about 98 °C using a seed. The particle size range of 4–20 nm shows that they fall in the nanomaterial class. The composition of the 10P-TiO<sub>2</sub> analysed on XRF showed 9.8 % P<sub>2</sub>O<sub>5</sub>. The adsorption of phosphate ions from aqueous solution onto titania has been studied by XRD, XPS, and DRIFT spectra which showed strong adsorption of phosphate on the surface of titania. While there was a decrease in the

surface area, there was an increase in crystallinity, with calcination temperature. XPS results suggest a pentavalent oxidation state for P and the presence of Ti-O-P linkage (only  $\text{PO}_4^{3-}$ ) in 10P-TiO<sub>2</sub>-700. Furthermore, a comparison of the binding energy for Ti2P<sub>1/2</sub> and Ti2P<sub>3/2</sub> with anatase reveals the substitution of P for oxygen. The calcination at 900 °C for 4 h showed the formation of stable titanium pyrophosphate. The calcination of 10P-TiO<sub>2</sub> in the range of 500–900 °C showed its stability towards porosity and moderate retention of surface area, the properties essentially required for its application as a catalyst and active support.

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