

# Photo-oxidation of 4-nitrophenol in aqueous suspensions, catalysed by titania intercalated zirconium phosphate (ZrP) and titanium phosphate (TiP)

Kulamani Parida\*, Dipti Prakasini Das

*Regional Research Laboratory (CSIR), Bhubaneswar 751013, Orissa, India*

Received 30 June 2003; received in revised form 15 January 2004; accepted 13 February 2004

## Abstract

Titania pillared zirconium phosphate and titanium phosphate samples were prepared by intercalating titanium(IV) isopropoxide sol inside the phosphate layer. The sol-intercalated samples were calcined at various temperatures and characterised by different techniques. Basal spacing and surface area revealed that highest amount of pillaring in interlayer has taken place with 2 and 4 wt.% TiO<sub>2</sub> loading for ZrP and TiP, respectively. These pillared samples are stable up to 500 °C and exhibit highest surface area in the range of 70–172 m<sup>2</sup> g<sup>-1</sup>, basal spacing in the range of 15.5–25.9 Å, which is greater than that of neat ZrP and TiP. These materials also showed greater activity towards photo-oxidation of 4-nitrophenol under solar radiation. The low crystallite size, low p*H*<sub>pzc</sub>, high surface area, higher acid sites and larger basal spacing might be responsible for highest activity shown by 2 and 4 wt.% pillared ZrP and TiP, respectively.

© 2004 Elsevier B.V. All rights reserved.

*Keywords:* ZrP and TiP; TiO<sub>2</sub> pillared; Surface area; Acid sites; Photodegradation

## 1. Introduction

Nitrophenols are some of the refractory pollutants, which can be present in the industrial wastewater. The 4-nitrophenols and its derivatives result from the production process of pesticides, herbicides [1] and synthetic dyes [2]. Photocatalysis plays an important role in the degradation of these pollutants into the components that are nontoxic and safe for air and water. In other words, photocatalysis is a system, which operates at room temperature and being used for the purification of polluted water and decomposition of toxic organic pollutants. Heterogeneous photocatalysis is one of the techniques used for this purpose. Photochemical and photocatalytic properties of semiconductor microcrystallites in solution have become popular due to quantum size effects [3–5]. Recently, it has been reported about the photochemical properties of modified ZrP [6] and zirconia incorporated titania [7]. Semiconductor photocatalysis appears to be a promising technology that has a number of applications towards air and water purification, water disinfection and hazardous waste remediation. In addition, the basic re-

search underlies the application of these technology is forgoing a new understanding of the complex heterogeneous photochemistry of metal oxide system in multiphasic environments where semiconductor photosensitizers like TiO<sub>2</sub> act as catalyst for irreversible oxidation of impurities present in the wastewater using sunlight.

The current work deals with the photocatalytic degradation of 4-nitrophenol in aqueous solution using titania pillared ZrP and TiP under solar radiation. The activities of titania intercalated ZrP and TiP were determined by varying reaction conditions such as TiO<sub>2</sub> load, catalyst dose, substrate concentration, time, pH etc. A correlation has also been derived between photocatalytic activity and surface properties of the intercalated material.

## 2. Experimental

### 2.1. Materials

Titania intercalated ZrP and TiP were prepared by following the procedure reported by Yamanaka and co-workers [8] using Na-form of montmorillonite and mono sodium form of ZrP and TiP. First titania sol was prepared by drop wise addition of titanium(IV) isopropoxide to a vigorously stirred

\* Corresponding author.

*E-mail addresses:* [kmparida@rllbhu.res.in](mailto:kmparida@rllbhu.res.in), [kmparida@yahoo.com](mailto:kmparida@yahoo.com) (K. Parida).

1 M HCl solution to give a molar ratio of 0.25, between alkoxide and HCl solution. The resulting slurry was stirred for 3 h to get a clear titania sol. Then aqueous suspension of sodium exchanged ZrP or TiP was added slowly to the sol. The resultant suspension was further stirred for 3 h at 50 °C. It was then filtered and washed thoroughly with deionised water and dried at different temperatures for further studies.

Degussa P25 titania has also been used as a reference material for comparison purpose. This titania is a 70:30 anatase:rutile mixture and possesses iron impurities. The existence of different phases of titania and the presence of iron in titania lattice has a strong effect on several other catalytic processes [9] and the use of this titania P25 does not appear to be advisable as a good reference material for research on photocatalysis [10]. The prepared samples were characterised by XRD, BET-surface area, FT-IR and UV-VIS DRS.

## 2.2. Physicochemical characterisation

The X-ray powder diffraction pattern was taken in Philips PW 1710 diffractometer with the automatic control. The patterns were run with a monochromatic Cu K $\alpha$  radiation, with a scan rate of 2° min<sup>-1</sup>.

The BET-surface area measurement was carried out using Quantasorb instrument (Quantachrome, USA) by nitrogen adsorption–desorption isotherms at liquid nitrogen temperature (–196 °C). Prior to adsorption–desorption measurements, samples were degassed at 110 °C and 0.00133322 Pascal for 5 h in vacuum.

The UV-VIS DRS was taken in Varian UV-VIS spectrophotometer in the range of 200–800 nm. The spectra were recorded against boric acid reflectance standard as base line. The computer processing of spectra with CARY 1E software consisted of calculation of Kubelka–Munk function  $F(R_{\infty})$  from the absorbance. This reflectance spectroscopy has been utilised to characterise the bulk structure. This is used to probe the band structure or molecular energy levels in the materials since UV-VIS light excitation creates photogener-

ated electrons and holes. The UV-VIS adsorption band edge is strong function of cluster size diameter less than 10 nm, which can be attributed to quantum size effect for these semiconductors.

The FT-IR spectra were taken using JASCO FT-IR-5300 in KBr matrix in the range 400–4000 cm<sup>-1</sup>.

## 2.3. Experimental procedures

The photo-oxidation of 4-nitrophenol (CDH) was performed in batch reactors by taking 0.05 g l<sup>-1</sup> of substrate (4-nitrophenol in water) and 0.2 g l<sup>-1</sup> of catalyst. The solution was exposed to sunlight in closed pyrex flasks at room temperature with constant stirring. All the experiments were performed in triplicate during the second week of May, 2002, in Bhubaneswar. The experiments were carried out at pH 3.0. The pH was adjusted by using sulfuric acid (Merck). The observations were compared with the blank, which was done in dark. After irradiation, the suspension was filtered and analysed for 4-nitrophenol quantitatively by measuring the absorbance at 315 nm using Cary 1E spectrophotometer (Varian). The detail method of measurement is available in [11].

## 3. Results and discussion

### 3.1. Physicochemical characterisation

It is seen from the XRD patterns that the crystallite size of titania intercalated ZrP decreases up to 2 wt.% loading and thereafter increases gradually with increase in the wt.% up to 10. The decrease in crystallite size in presence of TiO<sub>2</sub> species could possibly due to the interaction of titania species with ZrP layer and retards the growth of the particles. Similarly in case of TiP, with increase in the titania loading up to 4 wt.%, the crystallite size decreases and thereafter it increases up to 10 wt.%. An analysis of basal spacing (Table 1) shows that the basal spacing of titania pillared ZrP

Table 1  
Correlation of percentage of degradation with surface area, basal spacing and acid sites

Sample code	Sample surface area (m <sup>2</sup> g <sup>-1</sup> )	Basal spacing (Å)	Strong acid sites (μmol g <sup>-1</sup> )	Total acid sites (μmol g <sup>-1</sup> )	4-Nitrophenol degradation (%)
ZrP	60.83	7.56	21	35.62	19.2
TiO <sub>2</sub> /ZrP1	70.1	15.5	–	–	20.8
TiO <sub>2</sub> /ZrP2	116.95	19.3	61.9	89.55	86.6
TiO <sub>2</sub> /ZrP4	105.66	17.2	50.5	80.07	84
TiO <sub>2</sub> /ZrP8	50.02	16.4	30	56.38	78.4
TiO <sub>2</sub> /Zr10	30.92	14.3	20	37.9	37.6
TiP	63.83	7.6	104.02	120.28	17.6
TiO <sub>2</sub> /TiP2	100.56	17.3	106.89	180.68	40.2
TiO <sub>2</sub> /TiP4	172.33	25.9	120.9	300.29	96.6
TiO <sub>2</sub> /TiP8	66.58	18.2	99.2	282.97	60.9
TiO <sub>2</sub> /TiP10	40.92	15.5	77.9	152.04	66.8

TiO<sub>2</sub>/ZrP: titania pillared zirconium phosphate; TiO<sub>2</sub>/TiP: titania pillared titanium phosphate; TiO<sub>2</sub>/ZrP2: 2 wt.% titania pillared zirconium phosphate; TiO<sub>2</sub>/TiP2: 2 wt.% titania pillared titanium phosphate.

and TiP is more than that of the supporting material, i.e. ZrP and TiP. This confirms the effective pillaring of the material.

From BET-surface area, it has been found that the specific surface area of titania pillared ZrP and TiP is higher than that of sodium exchanged metal phosphates calcined at 500 °C, which also confirms the effective pillaring of the metal phosphates. ZrP and TiP loaded with 2 and 4 wt.% TiO<sub>2</sub>, respectively, possessed higher surface area compared to other samples. This shows that pillaring is most effective in these cases, i.e. the titania species are well oriented inside the layers of ZrP and TiP. In addition to this, small size of ZrP/TiP supported titania particle increases the surface area, increasing the chance for the electrons and holes to reach the surface and react with the organic substrate. The presence of the support, transparent to visible radiation, allows higher catalyst concentration with no loss of effectiveness of irradiation as in case of bulk titania [12,13].

From UV-VIS diffused reflectance spectrum of TiO<sub>2</sub> pillared ZrP and TiP, it has been found that there is an increase in the peak height, i.e. the absorbance increases from 0.5 to 1.2 due to pillaring. The spectrum shows a sharp peak at 220 nm [14–16] which correspond to Ti<sup>4+</sup> and some Ti<sup>5+</sup> (Fig. 1(c) and (d)). This species is responsible for the photo-oxidation of 4-nitrophenol. From the individual DRS spectrum of ZrP and TiP, it has been observed that for ZrP a peak at 240 nm and for TiP a peak at 205 nm were found (Fig. 1(a) and (b)). The broad peak in the range of 200–300 nm shows that different environment of titania present in the material. A band at 220–230 nm is considered as characteristic of the incorporation of titanium in the

lattice of ZrP or TiP. Due to this energy difference between the two phases, photoexcitation takes place and as a result of which the photodegradation occurred.

FT-IR spectra of materials heated at 383 K show that strong IR bands in the region of 1300–900 cm<sup>-1</sup> for ZrP and for TiP, a broad absorption containing a poorly resolved (PO<sub>3</sub>)<sub>asym</sub> and (PO<sub>3</sub>)<sub>sym</sub> is observed in the region 1300–1000 cm<sup>-1</sup> and several (PO<sub>3</sub>) deformation modes are in the region below 650 cm<sup>-1</sup>. The typical symmetrical mode characterising the P–O–P bridge is observed around 970 cm<sup>-1</sup>. The band at 1619 cm<sup>-1</sup> (ZrP), 1617 cm<sup>-1</sup> (TiP) is due to the bending vibrations of –OH of water associated PO<sub>4</sub><sup>3-</sup> group which supports the presence of water of crystallisation in the lamellar solid. A strong absorption band around 3148 cm<sup>-1</sup> (ZrP) and 3406 cm<sup>-1</sup> (TiP) is probably due to stretching vibration of –OH group and of physically adsorbed water and the broadness is due to the existence of hydrogen bond [17–19]. The appearance of two prominent bands at 3509, 3539 cm<sup>-1</sup> for ZrP and 3478, 3555 cm<sup>-1</sup> for TiP may be due to the stretching vibration of P–OH and Zr/Ti–OH, respectively.

A broad peak at 1099 cm<sup>-1</sup> for ZrP (Fig. 2(a)) and 1082 cm<sup>-1</sup> for TiP (Fig. 3(a)) was noticed at 500 °C calcination instead of splitted peaks for phosphate. After the pillaring and monolayer formation with TiO<sub>2</sub>, the PO<sub>4</sub><sup>3-</sup> peak has been broadened and two new peaks in the lower wave number region around at 480–450 cm<sup>-1</sup> were found which is due to TiO<sub>2</sub> for ZrP (Fig. 2(b)). For TiP the PO<sub>4</sub><sup>3-</sup> peak has been shifted to the lower wave number region

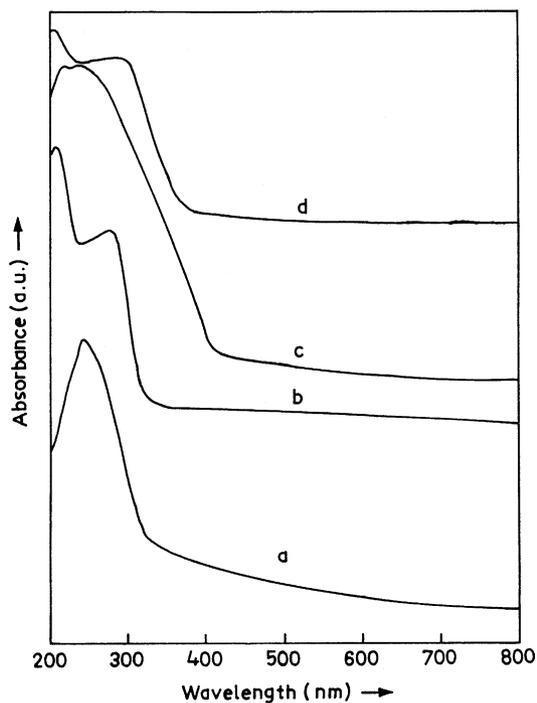


Fig. 1. UV-VIS DRS of (a) ZrP, (b) TiP calcined at 110 °C, (c) TiO<sub>2</sub>/ZrP2 and (d) TiO<sub>2</sub>/TiP4 calcined at 500 °C.

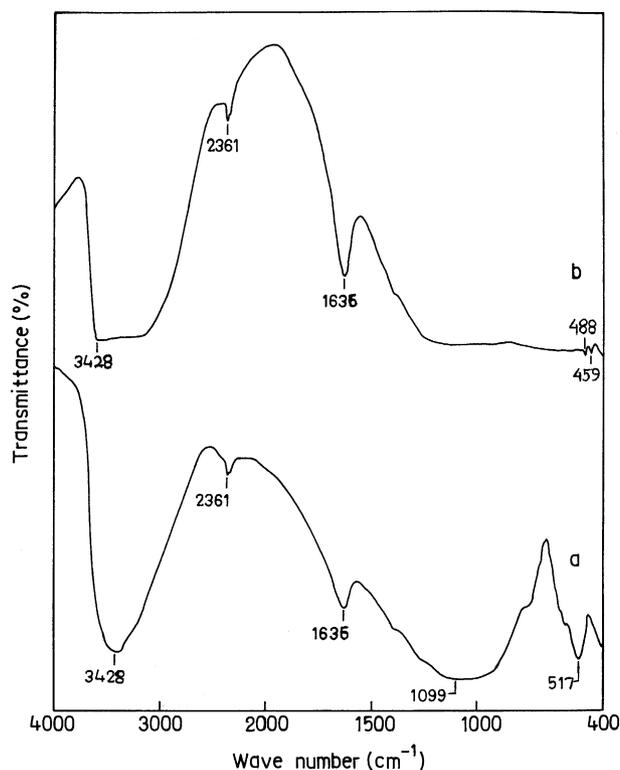


Fig. 2. FT-IR spectra of (a) ZrP and (b) TiO<sub>2</sub>/ZrP2 calcined at 500 °C.

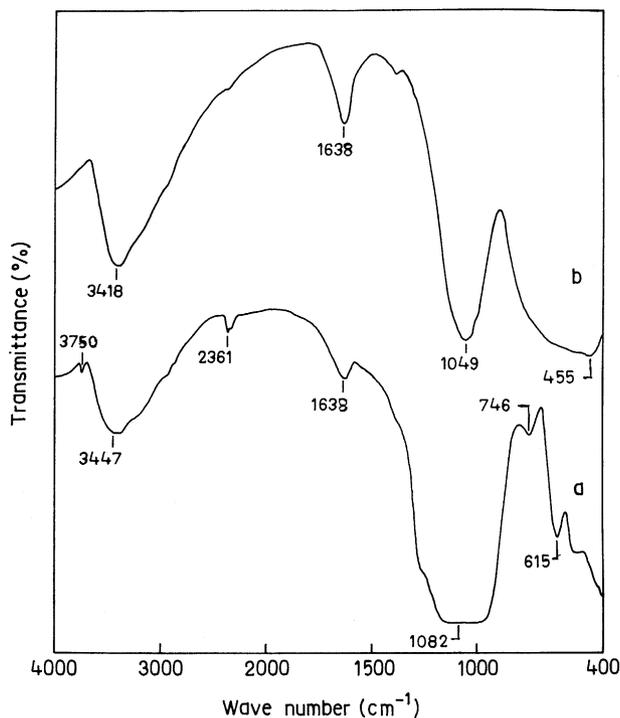


Fig. 3. FT-IR spectra of (a) TiP and (b)  $\text{TiO}_2/\text{TiP}_4$  calcined at  $500^\circ\text{C}$ .

from  $1082$  to  $1049\text{ cm}^{-1}$  and a new peak at  $455\text{ cm}^{-1}$  was found which is due to  $\text{TiO}_2$  (Fig. 3(b)) [20]. Due to pillaring of  $\text{TiO}_2$ , all other peaks due to  $(\text{PO}_3)_{\text{deformation}}$  overlaps with the peaks due to  $\text{TiO}_2$ . This also confirms pillaring is effective.

### 3.2. Photocatalytic activity

#### 3.2.1. Effect of pH

The pH of the solution determines the surface charge properties of the photocatalyst and therefore the adsorption behaviour towards the pollutants. No degradation of 4-nitrophenol is observed in absence of light and/or catalyst. On the other hand, around 15% of adsorption takes place in absence of light. Fig. 4 shows that the degradation (%) of 4-nitrophenol increases with increasing of pH up to 3 and thereafter it decreases gradually with increasing the pH of the solution. Since during the photocatalysis, the degradation of nitrophenol is maximum at pH 3.0 (around 90–96%), it can be concluded that reductive pathway is favoured in the acidic media. It is known that nitroaromatic compounds such as 4-nitrophenol are reduced in acidic media more easily than in alkaline solutions [21]. This can be explained on the basis of surface charge of titania pillared ZrP and TiP. For titania pillared ZrP and TiP, the point of zero charge ( $\text{pH}_{\text{pzc}}$ ) is around 5.0–6.0. At acidic medium, the surface will be positively charged. In case of  $\text{TiO}_2/\text{ZrP}$  or  $\text{TiO}_2/\text{TiP}$ , the optimum pH is 3.0. At that pH the surface can attract highest amount of negatively charged anion of nitrophenol as was explained by Fox and Dulay [22]. With increase in pH, negative charges predominate on the surface of titania pillared

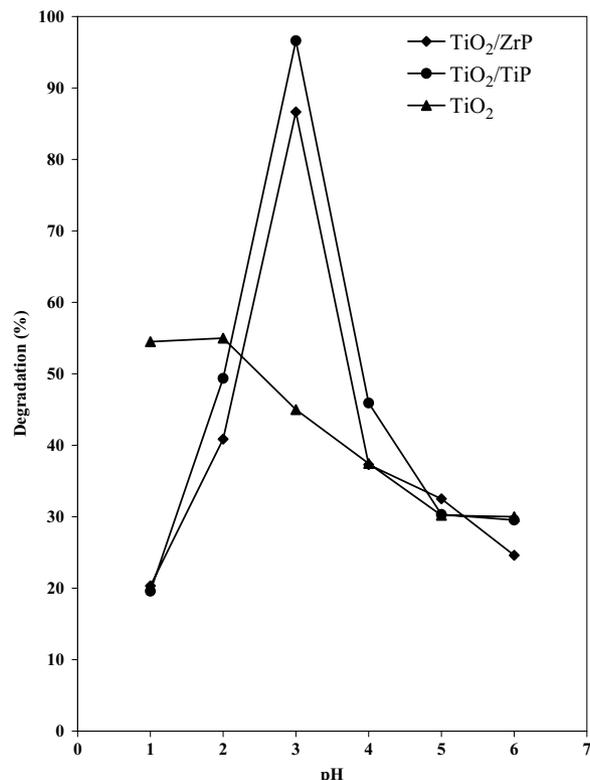


Fig. 4. Effect of pH of the solution on *p*-nitrophenol degradation at catalyst dose =  $0.6\text{ g l}^{-1}$  and substrate concentration =  $0.05\text{ g l}^{-1}$ .

samples which hinder the degradation of negatively charged nitrophenol and as a result the degradation of 4-nitrophenol decreases with increase in pH. The comparison plot of titania pillared ZrP and TiP with the commercial titania was presented in Fig. 4 which shows that highest percentage of 4-nitrophenol oxidation (55%) took place at pH 2.0. So it can be concluded that the titania pillared ZrP/TiP is an effective photocatalyst towards oxidation of 4-nitrophenol in comparison with commercial titania.

The photocatalytic oxidation is influenced by the acid sites [23]. Generally it is influenced by the strong acid sites. This might be due to increase in the adsorption strengths and therefore coverages of some organics, which consequently contributes to photocatalytic oxidation. The reason for the difference in coverages between titania pillared ZrP/TiP and neat ZrP/TiP is that the surface area of the former is greater than the latter. This explains the better photoactivity of titania pillared ZrP/TiP towards the oxidation of 4-nitrophenol. Again the 2 and 4 wt.% of titania pillared ZrP and TiP, respectively, have more acid sites as compared to other samples. Following the above explanation they showed greater photoreactivity towards the oxidation of 4-nitrophenol.

#### 3.2.2. Effect of $\text{TiO}_2$ loading on the photo-oxidation of 4-nitrophenol

ZrP loaded with 2 wt.% titania and TiP with 4 wt.% loading showed highest amount of degradation of nitrophenol;

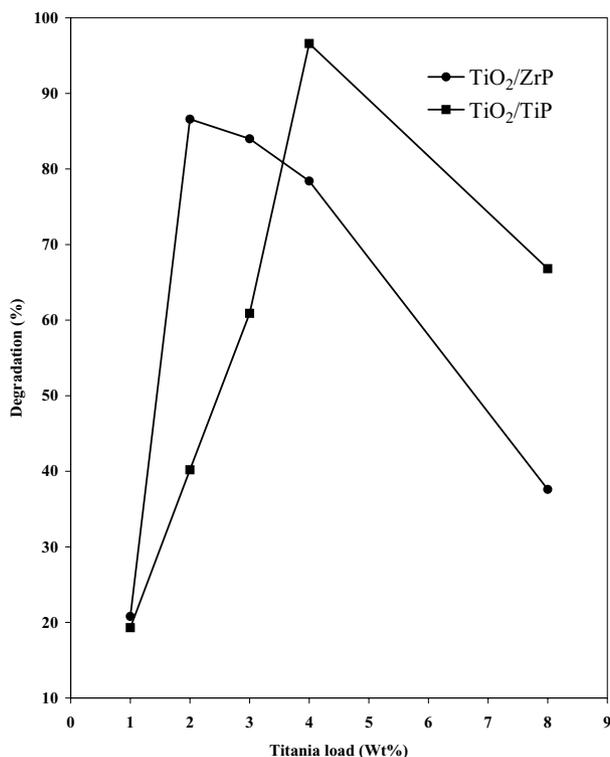


Fig. 5. Effect of titanium dioxide loading (wt.%) on the degradation process at catalyst dose =  $0.6 \text{ g l}^{-1}$ , substrate concentration =  $0.05 \text{ g l}^{-1}$  and pH = 3.0.

86.6 and 96.6%, respectively (Fig. 5). This might be due to highest amount of pillaring taking place which consequently decreases the crystallite size. This decrease in crystallite size facilitates quantum efficiency of the pillared material. These particles with smaller crystallite size provide larger surface area for the interaction of surface hydroxyl radicals with 4-nitrophenol. On the other hand, the surface area decreases with increase in the crystallite size and also hinders the exposure of substrate with the hydroxyl radical. With increasing titania loading surface coverage might be taking place leading to decrease in the percentage of degradation to 37.6 and 66.8 for ZrP and TiP, respectively.

### 3.2.3. Effect of substrate concentration and catalyst amount

Figs. 6 and 7 indicate that with increase in the substrate concentration at a fixed catalyst amount of  $0.6 \text{ g l}^{-1}$ , the percentage of degradation decreases. Because at higher concentration of substrate, the light absorbed by the substrate is more than that of the catalyst. The light absorbed by the substrate is not effective in bringing about the photodegradation. For a fixed catalyst dose the active sites remaining in the interlayer space increases. So there is a decrease in the percentage of degradation (Fig. 6).

With increase in the catalyst dose from 0.2 to  $0.8 \text{ g l}^{-1}$ , there is an increase in the number of active sites, which in turn helps in adsorption of more amount of 4-nitrophenol and

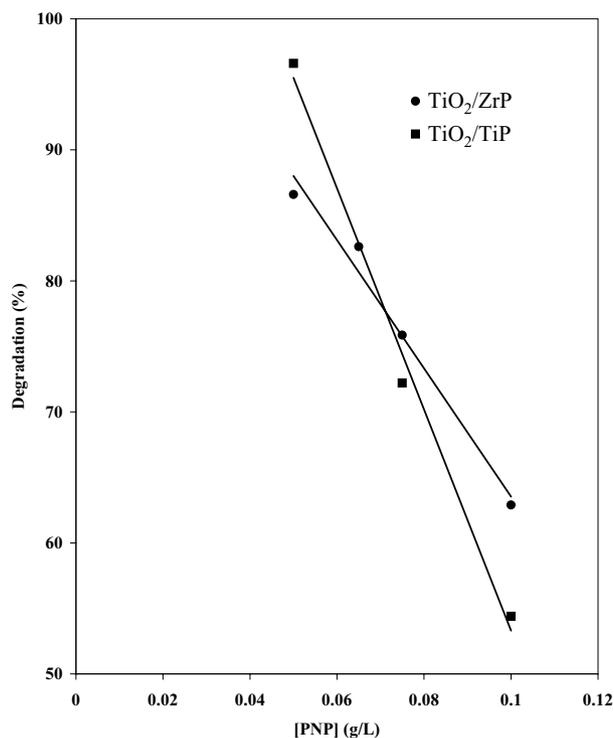


Fig. 6. Effect of substrate concentration on the degradation process at catalyst dose =  $0.6 \text{ g l}^{-1}$  and pH = 3.0.

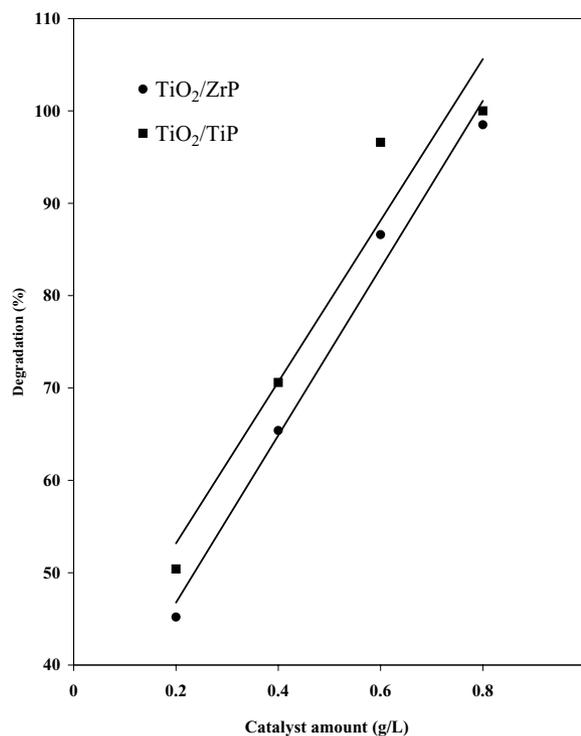


Fig. 7. Effect of catalyst dose on the percentage of degradation at substrate concentration =  $0.05 \text{ g l}^{-1}$  and pH = 3.0.

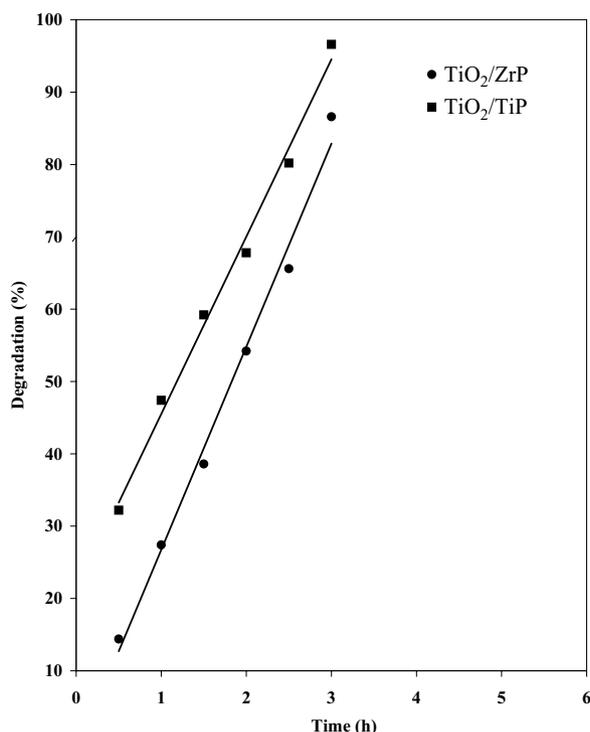


Fig. 8. Effect of time on the degradation process at substrate concentration =  $0.05 \text{ g l}^{-1}$ , catalyst dose =  $0.6 \text{ g l}^{-1}$  and pH = 3.0.

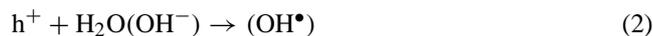
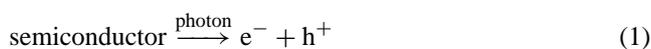
thereby facilitating the photodegradation of 4-nitrophenol (Fig. 7). The mechanism of which is explained in Section 4.

#### 3.2.4. Effect of time

With increase in time of irradiation, the percentage of photodegradation increases up to 3 h and thereafter it remains constant. This is because of the fact that with increase in the time of irradiation, the number of photons absorbed by the catalyst is more producing higher amount of  $\text{O}_2^{\bullet-}$  and  $\text{OH}^{\bullet}$  radicals. As a result of which more amount of 4-nitrophenol is absorbed by the titania pillared ZrP/TiP. So up to 3 h, the percentage of degradation increases and thereafter it remains constant due to surface saturation (Fig. 8).

## 4. Possible mechanisms

During the photocatalytic process, the adsorption of photon by semiconducting materials such as ZrP and TiP leads to the promotion of an electron from valence band to the conduction band producing electron–hole pair [22] (Eq. (1)). The electron in the conduction band is removed by oxidation reaction with oxygen dissolved in water (Eq. (3)). The resulting hole in the valence band can react with the  $\text{OH}^-$  ion present in aqueous solution producing hydroxyl radical ( $\text{OH}^{\bullet}$ ) (Eq. (2)). This OH radical promotes various oxidation reactions [24]:



The electron–hole recombination process explained by Venodgopal and Kamat [25] is in competition with the space charge separation of electron and hole. The photocatalytic activity can be increased by retarding the electron–hole recombination process. In case of titania pillared ZrP/TiP, due to their small crystallite size, high surface area and strong acid sites, they might be hindering the recombination of electron and hole pair.

Due to the band gap energy difference between  $\text{TiO}_2$  and ZrP or TiP, the electrons present in the conduction band of ZrP/TiP can be easily accepted by  $\text{Ti}^{5+}$  (confirmed by DRS) in  $\text{TiO}_2$ , which is then converted to  $\text{Ti}^{4+}$ . These reduced  $\text{Ti}^{4+}$  (in  $\text{TiO}_2$ ) immediately transferred the accepted electron to the oxygen molecules adsorbed on the surface of ZrP/TiP and returned to original form  $\text{Ti}^{5+}$  as in case of  $\text{WO}_3$ -loaded  $\text{TiO}_2$  [26]. According to Eq. (3) the  $\text{O}_2$  molecule accepts electron forming the superoxide radical and subsequently transformed to hydroxyl radicals contributing to oxidation reaction of 4-nitrophenol [27]:



Table 1 adds that samples with high surface area and basal spacing possess higher photoactivity than other samples. The samples having high surface area and larger basal spacing can provide more interlayer space for the interaction of 4-nitrophenol and  $\text{OH}^-$  radical produced during the reaction of electron from the conduction band and the dissolved oxygen.

## 5. Conclusions

Titania pillared ZrP and TiP can be prepared by stirring titanium(IV) isopropoxide sol with sodium exchanged respective metal phosphates at temperature 323 K. ZrP and TiP loaded with 2 and 4 wt.%  $\text{TiO}_2$ , respectively, possessed highest surface area, acid sites, low  $\text{pH}_{\text{pzc}}$ , smallest crystallite size and highest basal spacing and showed highest activity for the photo-oxidation of 4-nitrophenol. After optimisation of reaction conditions, it has been found that  $0.05 \text{ g l}^{-1}$  of 4-nitrophenol can be completely degraded by using  $0.6 \text{ g l}^{-1}$  of titania pillared ZrP (2 wt.%) and TiP (4 wt.%) in 3 h under solar light.

## Acknowledgements

The authors are thankful to Dr. S.N. Das, HOD, EMIC Department, for his co-operation and also thankful to Prof. Vibhuti. N. Misra, Director, Regional Research Laboratory, Bhubaneswar, for his constant encouragement and permission to publish this paper.

**References**

- [1] M.S. Dieckmann, K.A. Gray, *Water Res.* 30 (1996) 1169.
- [2] N. Takahashi, T. Nakai, Y. Satoh, Y. Katoh, *Water Res.* 28 (1994) 1563.
- [3] S. Rzesseti, S. Nakahara, L.E. Brus, *J. Chem. Phys.* 79 (1983) 1086.
- [4] T. Kanata, H. Murai, K. Kubota, *J. Appl. Phys.* 81 (1987) 969.
- [5] M. Abraham, G. Ptasch, A. Tadjeddine, N. Hakiki, *Solid State Commun.* 60 (1986) 397.
- [6] H. Miyoshi, M. Ieyasu, T. Yoshino, H. Kourai, *J. Photochem. Photobiol. A: Chem.* 112 (1998) 239.
- [7] G. Colon, M.C. Hidalgo, J.A. Navio, *J. Appl. Catal. A: Gen.* 231 (2002) 185.
- [8] H. Yoneyama, S. Haga, S. Yamanaka, *J. Phys. Chem.* 93 (1989) 4833.
- [9] M.R. Hoffman, S.T. Martin, W. Choi, D.W. Bahnemann, *Chem. Rev.* 95 (1995) 69.
- [10] L.J. Alemany, et al., *Appl. Catal. B: Environ.* 13 (1997) 289.
- [11] V. Auguglioro, L. Palmisano, M. Schiavello, A. Selafani, L. Marchese, G. Martra, F. Miano, *J. Appl. Catal.* 69 (1991) 323.
- [12] R.W. Matthews, *J. Catal.* 113 (1988) 549.
- [13] M. Trillas, J. Peral, X. Domenech, *Appl. Catal. B* 3 (1993) 45.
- [14] S. Klein, B.M. Weekhuysen, J.A. Martens, W.F. Maier, P.A. Jacobs, *J. Catal.* 163 (1996) 489.
- [15] D.P. Serrano, M.A. Uguina, G. Ovejero, P.V. Grieken, M. Camacho, *Micropor. Mater.* 7 (1996) 309.
- [16] H. Kochkar, F. Figueras, *J. Catal.* 171 (1997) 420.
- [17] H. Kim, S.W. Keller, T.E. Mallouk, *Chem. Mater.* 9 (1997) 1414.
- [18] C. Morterra, G. Magnacca, P.P. DeMacstri, *J. Catal.* 152 (1995) 384–395.
- [19] G. Busca, G. Ramis, V. Lorenzelli, A. Laginestra, P. Patrono, *Langmuir* 5 (1989) 911.
- [20] R. Lebeda, V.V. Turov, M. Marciniak, A.A. Malyagin, A.A. Malkov, *Langmuir* 15 (1999) 8441.
- [21] R. Dillert, I. Forneff, U. Siebers, D. Bahnemann, *J. Photochem. Photobiol. A: Chem.* 94 (1996) 231.
- [22] M.A. Fox, M.T. Dulay, *Chem. Rev.* 93 (1993) 341.
- [23] D.S. Muggli, L. Ding, *Appl. Catal. B: Environ.* 32 (2001) 181.
- [24] H. Gerischer, A. Heller, *J. Phys. Chem.* 95 (1991) 5261.
- [25] K. Venodgopal, P.V. Kamat, *Environ. Sci. Tech.* 29 (1995) 841.
- [26] Y.T. Kwon, K.Y. Song, W.I. Lee, G.J. Choi, Y.R. Do, *J. Catal.* 191 (2000) 192.
- [27] J.A. Navio, G. Colon, M. Trillas, J. Peral, X. Domenech, J.J. Testa, J. Padron, D. Rodriguez, M.I. Litter, *J. Appl. Catal. B: Environ.* 16 (1998) 187.