

ACIDITY AND CATALYTIC ACTIVITY OF PHOSPHORIC ACID MODIFIED TITANIUM OXIDE SURFACE

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By refluxing the anatase form of TiO_2 powder in phosphoric acid, the surface acidity was observed to increase. The amount of acid was determined by *n*-butylamine titration in *n*-heptane media, and was found to be proportional to the reflux period in phosphoric acid. XRD patterns and IR spectra revealed that the products contained a mixture of the anatase form of TiO_2 and titanium phosphate phases. Based on the calculated acid density on the surface, part of the titrant, *n*-butylamine penetrated into the titanium phosphate layers. Further investigations using TGA, FT-IR and TEM techniques along with surface area measurements indicated that the titanium phosphate phase was coated over the TiO_2 phase. The surface acidity of the phosphoric acid treated anatase increased due to the substitution of Ti-OH groups by phosphate groups. Nevertheless, the chemical properties of the resultant surfaces were found to be influenced by the internal anatase phase. The kinetic data on the 2-propanol dehydration reaction, where the activation energies were found to decrease gradually with an increase in phosphate content, also support these conclusion.

INTRODUCTION

A great number of supported and unsupported catalysts are used in industry. Typical catalyst supports in common use are Al_2O_3 , SiO_2 , zeolites and active carbon. In the 1970's, a TiO_2 -based catalyst was first applied commercially in air pollution control equipment and became a subject of many scientific studies. The TiO_2 -based catalyst was found to be the best catalyst for the selective catalytic reduction of NO_x with NH_3 (SCR process),¹ which is used to remove NO_x contained in flue gas from a stationary combustion facility. On the other hand, because of the reducibility of TiO_2 , the strong-metal-support-interaction (SMSI) was first reported for noble metals supported on TiO_2 .² This subject has also attracted great attention in the field of catalysis.

Titania has several significant and distinctive properties compared with conventional supports such as Al_2O_3 and SiO_2 . Because sulfates of TiO_2 such as $\text{Ti}(\text{SO}_4)_2$ and TiOSO_4 are not stable at temperatures above 300°C , TiO_2 -based catalysts show high resistance to SO_x poisoning. In contrast, Al_2O_3 reacting with SO_x to form $\text{Al}_2(\text{SO}_4)_3$, which is stable up to 770°C , results in a decrease of catalyst

surface area and pore volume. In addition, TiO_2 is easily reduced to form various stoichiometric and non-stoichiometric lower oxides and shows properties of *n*-type semiconductivity. Therefore, it is expected that some distinguishing catalytic properties will be obtained when titanium oxide is used as a catalyst or catalyst support.

One of the disadvantages that limit titania from wide applications to catalytic reactions is that titania has relatively low acidity and very few acid sites on the surface compared with Al_2O_3 and SiO_2 . In order to improve the surface acidity, our approach in this experiment is to reflux commercially available TiO_2 of the anatase powder in concentrated phosphoric acid for various periods of time and to compare the acidities and catalytic activities of the resultant materials. Similar phosphorus modification has been reported for ZSM-5 zeolites.³⁻⁵ Surface phosphate groups were found to affect the acidity and selectivity in toluene disproportionation and methanol conversion reactions. There, similar mechanisms were proposed by Kaeding et al.⁴ and Vedrine et al.⁵ that phosphate groups present in the zeolites reduced the dimensions of pore openings and channels sufficiently to favor the formation and outward diffusion of the

isomer or products with the smallest dimension. Changes in acid strength were neglected. On the other hand, Lercher and Rumlpmayr³ reported that phosphorus treatment created weak acid sites at the expense of the strong acid sites. These results are based on temperature programmed desorption of ammonia and pyridine. Furthermore, the surface-OH groups were proposed to be replaced by $-H_2PO_4$ groups. The effect of phosphorus treatment on titania will be compared with that reported for zeolites.

EXPERIMENTAL

Reagents. Reagent grade chemicals were used without further purification. TiO_2 (anatase), $TiCl_4$ and H_3PO_4 were purchased from Merck. *N*-butylamine and *n*-heptane were from Riedel-deHaen. Before use as a solvent for acidity titration, *n*-heptane was dehydrated with 5A-molecule sieve.

Catalysts. Anatase powder(115g) was refluxed with 100mL of 10M H_3PO_4 acid for 0.5, 3, and 10 hours. The resultant materials were filtered and washed with deionized distilled water until the pH value reached 5, followed by drying at 100°C in air. The catalysts were denoted as compound 0.5h, compound 3h and compound 10h according to their reflux periods. Pure titanium phosphate, $Ti(HPO_4)_2 \cdot H_2O$ was also prepared in order to compare its acidity and catalytic activity. $TiOCl_2$ solution was added into an excess amount of 10M H_3PO_4 solution, and the titanium phosphate gel formed immediately. The gel was then refluxed in the mother liquid for one day, followed by filtering, washing and drying. The XRD pattern and IR spectra were confirmed by comparison with that reported for α -titanium phosphate in the literature.⁶

Apparatus. X-Ray powder diffraction patterns were obtained using a Phillips 1792 X-ray diffractometer with $CuK\alpha$ radiation. Infrared spectra were obtained with a Perkin-Elmer 983 spectrometer and a

Bomen DA 3.02 FT-IR spectrometer. The wafers used for examining the stretching modes of surface hydroxyl groups were of thickness 0.1mg/cm². Thermal gravimetric analysis was carried out with a Du Pont 9900 thermal analysis system programmed for a heating rate of 20°C/min under a nitrogen atmosphere. The morphologies of the catalysts were examined by taking transmission electron micrographs of the samples with a Hitachi 600 TEM system. The measurement of the surface area of the catalysts was based on the physical adsorption of nitrogen at liquid N_2 temperature using a volumetric system. The surface acidities were determined by *n*-butylamine titration in *n*-heptane media. Indicators used were phenylzonnaphthylamine (pKa = +4.0), dimethyl yellow (pKa = +3.3), benzene azodiphenylamine (pKa = +1.5), and dicinnamalacetone (pKa = -3.0). The concentration of the indicator in *n*-heptane was about 0.01g/mL.

Procedures for the 2-propanol dehydration reaction. The reaction was carried out in an ordinary plug-flow type reactor at atmospheric pressure. The catalyst, 0.1g in powder form, was packed into a U-shape pyrex glass reactor. A thermocouple well was fixed at the center of the catalyst bed to register the temperature in the reaction zone. Catalysts were preheated at 280°C for 2h under vacuum. 2-Propanol was kept in a 3-stage bubbling trap and the flow-rate of the diluent, N_2 gas, was controlled by a tubular flow-meter (Kofloc Inc.). The N_2 gas was passed through the bubbling trap and carried saturated 2-propanol vapor into the catalyst bed. The products were analyzed by a Hewlett-Packard 5890A gas chromatograph. A porapak Q column coupling with a OV-1 column was used for separating the product mixture.

RESULTS AND DISCUSSION

Structural changes in the TiO_2 samples after refluxing in phosphoric acid were examined with X-

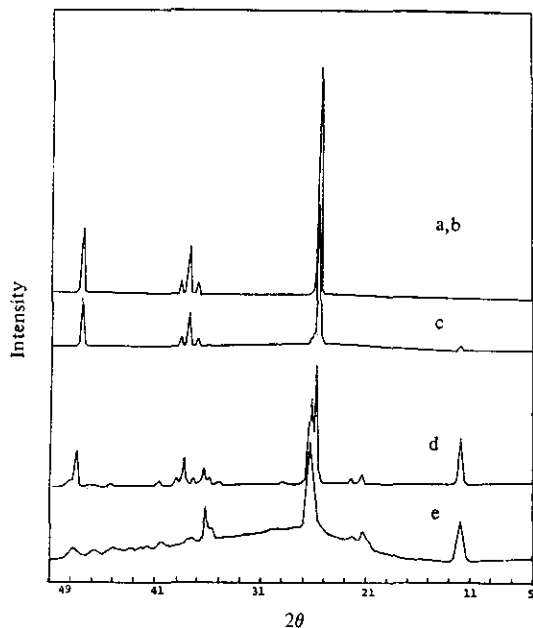


Fig. 1 XRD spectra for phosphoric acid treated TiO_2 samples, (a) original TiO_2 , (b) compound 0.5h, (c) compound 3h, (d) compound 10h, (e) titanium phosphate.

ray powder diffraction and infrared spectroscopy. Fig. 1 shows the XRD patterns of the refluxed samples compared with those of the original TiO_2 and pure $\text{Ti}(\text{HPO}_4)_2$. The 0.5h reflux period does not make a detectable change in the structure of anatase TiO_2 . Compound 3h shows that a small amount of titanium phosphate was formed in addition to the original anatase phase. Moreover, peaks corresponding to α -titanium phosphate grew stronger as the refluxing period was increased. On the other hand, peaks corresponding to anatase are gradually weakened. Infrared spectra also demonstrate similar results (Fig. 2). Peaks at 685, 518, and 354cm^{-1} corresponding to Ti-O stretching are retained on compound 0.5h, but become weaker when the reflux period is increased. On the other hand, peaks in the region of $1300\text{--}900\text{cm}^{-1}$ corresponding to P-O stretching become stronger as the refluxing period is lengthened.

The effect of phosphoric acid treatment on the surface acidity of TiO_2 powder was determined by

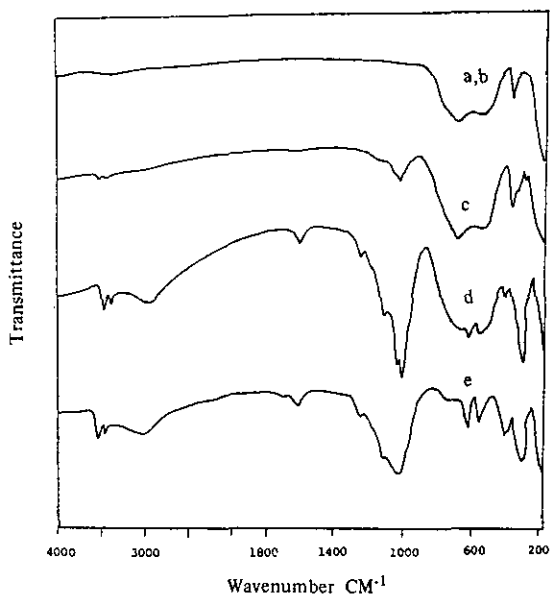


Fig. 2 IR spectra of KBr pellets of phosphoric acid treated TiO_2 samples calcinated at 100°C , (a) original TiO_2 , (b) compound 0.5h, (c) compound 3h, (d) compound 10h, (e) titanium phosphate.

n-butylamine titration in *n*-heptane media. Fig. 3 shows the acid density in units of equivalents/ \AA^2 versus the Hammett constants. The original TiO_2 surface was found to have acidity weaker than $\text{H}_0 = 4.0$, and is not shown in the figure. For the phosphoric acid treated surfaces, however, the acidity significantly increased in the range of $\text{H}_0 = -3.0$ to $+4.0$. For example, for compound 0.5h, the surface acidity increased to $0.03\text{ eq}/\text{\AA}^2$, with $\text{H}_0 = 4.0$, although there was no detectable change in the structure. Moreover, the acid strength and amount were retained up to a heating temperature of 500°C . Overall, the acid amount was found to increase as the reflux period was lengthened. However, a great portion of the acid sites were lost when the samples were heated at 500°C due to the condensation of phosphate groups. This even though the surface acidities of the treated materials were much higher than those of the original anatase surface. This is opposite to what has been reported for zeolites. The different affects on acidity for titanium oxide and

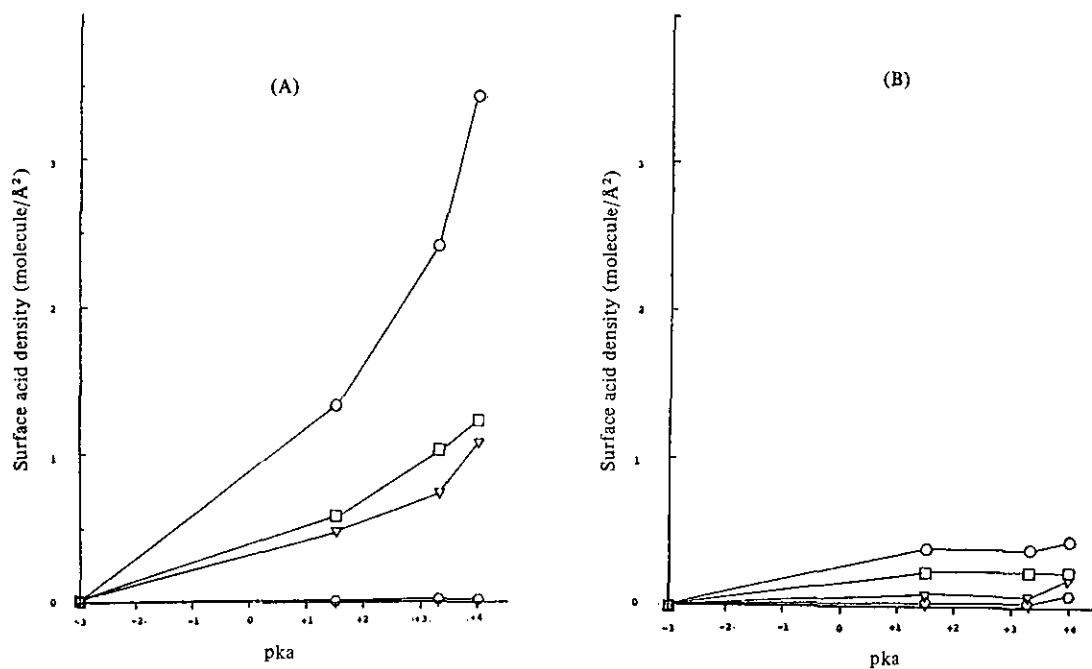


Fig. 3 Surface acid density of phosphoric acid treated TiO₂ samples, (A) after calcination at 100°C (B) after calcination at 500°C

○ : compound 10 h
◇ : compound 0.5h

□ : compound 3h
▽ : titanium phosphate

zeolites after phosphorus treatment are apparently the result of different starting materials having original surfaces with different acidic nature.

When phosphoric acid treated materials were used as catalysts in the 2-propanol decomposition reaction, propylene was found to be the main product. The kinetic data were analyzed according to first order kinetics in a plug flow reactor. Fig. 4 shows the Arrhenius plot for various samples. The calculated rate constants, activation energies and Arrhenius constants are tabulated in Table 1. Phosphoric acid treatment has lowered the activation energy from 30 Kcal/mol down to around 20 Kcal/mol. However, variation in the reflux period does not seem to change the activation energy too much. Comparing with pure titanium phosphate, a rise of approximately 4 Kcal/mol in activation energy is still obtained for compound 10h in which the titanium phosphate phase was quite dominant.

The titanium phosphate phase may be formed through two pathways. One is that the titanium species dissolving from the oxide surfaces react with phosphoric acid and forms titanium phosphate crystallites in separate particles. The other is that titanium phosphate is formed by attaching to the surface of titanium oxide particles. If the former were the case, the total surface area should increase due to the formation of additional small particles. However, Table 1 shows that BET surface areas of various samples were similar and independent of the reflux period. The difference in morphologies of anatase and titanium phosphate crystallites is quite distinguishable. Anatase particles are almost spherical while titanium phosphate particles have the shape of a hexagonal platelet. Fig 5 shows TEM photographs of phosphoric acid treated TiO₂ samples comparing with that of original TiO₂ and pure titanium phosphate. It is found that com-

Table 1 Kinetic data and surface area measurements for H₃PO₄ treated TiO₂ samples.

Catalyst	TiO ₂	Compound 0.5h	Compound 3h	Compound 10h	Ti(HPO ₄) ₂ ·H ₂ O
S.A. (m ² /g)	9	9.4	8.2	10.5	40
rxn. Temp (°C)	rate const. k(ml/g.min)				
210	—	6.5	13.9	17.1	37
240	—	30.9	63	60.8	114
280	0.81	54.9	85	96.4	189
310	5	119	179	182	233
330	10.1	—	—	—	—
350	16.8	—	—	—	—
Arrhenius const.	7.94 × 10 ¹¹	4.37 × 10 ¹⁰	1.61 × 10 ⁹	5.34 × 10 ⁹	1.46 × 10 ⁸
Ea (Kcal/mole)	30	21.7	17.7	18.8	14.6

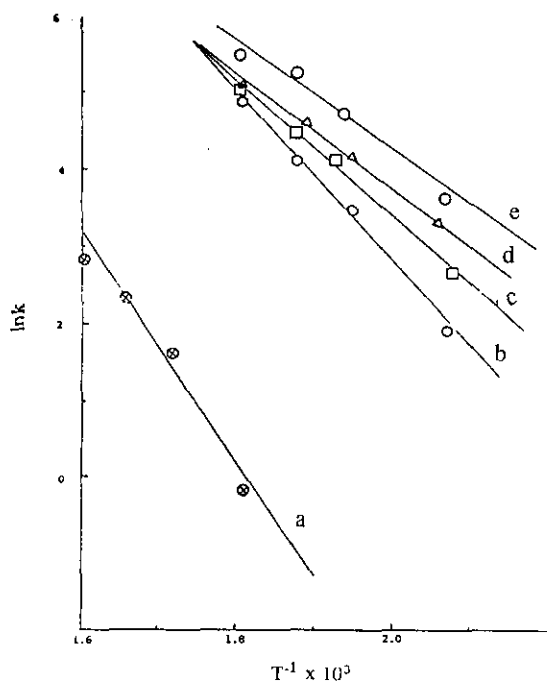


Fig. 4 Arrhenius plots for the 2-propanol dehydration reaction over phosphoric acid treated TiO₂ catalysts, (a) original TiO₂, (b) compound 0.5h, (c) compound 3h, (d) compound 10h, (e) titanium phosphate.

pounds 0.5h and 3h basically have the same spherical shape as the original TiO₂ powders. Moreover, no small hexagonal platelets were observed. This indicates that the titanium phosphate phase is not formed in separate particles. Instead, the titanium phosphate phase is attached to the original TiO₂ particles. When the phosphate layers have grown to a certain thickness, the particles take on the shape of hexagonal phosphate platelets as is seen in compound 10h in Fig. 5(d).

The thermal stability of modified TiO₂ samples was examined with thermal gravimetric analysis. Fig. 6 shows that compound 0.5h, similar to original TiO₂, has a negligible weight loss through the heating temperature range. Compounds 3h and 10h have shown weight losses in three stages, while pure titanium phosphate demonstrates weight loss in two distinctive stages. For the latter, weight loss in the temperature range of 100–300°C (region A in Table 2) is due to the escape of lattice water molecules, and weight loss at 450–700°C (region C) is due to the condensation of phosphate groups. Moreover, the amount of weight loss in these two regions is the

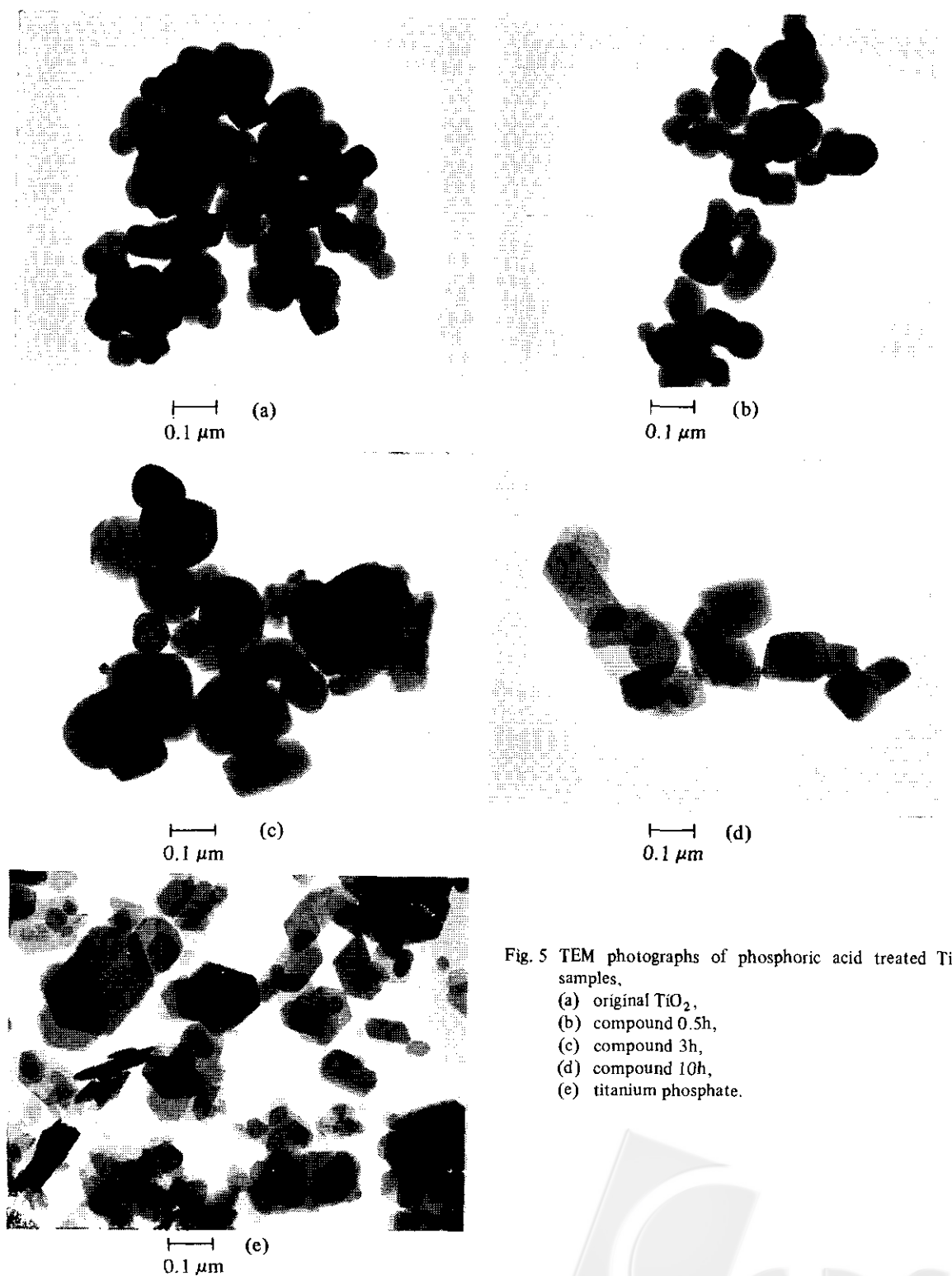


Fig. 5 TEM photographs of phosphoric acid treated TiO_2 samples,
(a) original TiO_2 ,
(b) compound 0.5h,
(c) compound 3h,
(d) compound 10h,
(e) titanium phosphate.



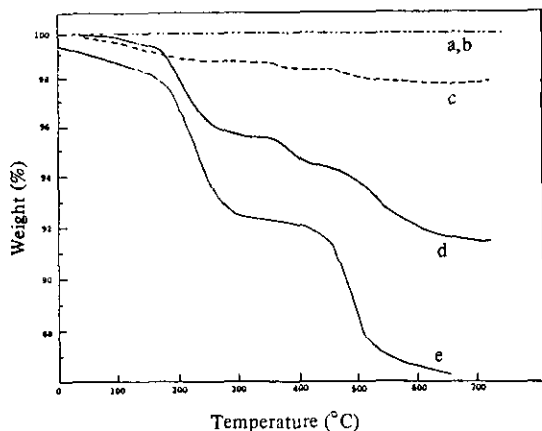


Fig. 6 TGA curves for phosphoric acid treated TiO_2 samples, (a) original TiO_2 , (b) compound 0.5h, (c) compound 3h, (d) compound 10h, (e) titanium phosphate.

same as expected theoretically. Compounds 3h and 10h show weight loss in an extra region (region B) at 300–450°C. Since TiO_2 has negligible weight loss through the whole temperature range, region B should have the character of titanium phosphate layers. It is interesting to note that the sum of the weight loss percentage over regions B and C gives values very close to that of region A. It indicates

Table 2 Weight loss data obtained from the TG analysis of H_3PO_4 treated TiO_2 samples.

Catalyst	Temp. range (°C)	Weight loss %			
		Region A	Region B	Region C	Region B+C
TiO_2	100–300	—	—	—	—
Compound 0.5h	300–450	—	—	—	—
Compound 3h	450–700	1.0	0.28	0.52	0.80
Compound 10h	300–700	4.12	1.04	2.85	3.89
$\text{Ti}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$	100–300	6.1	0	6.1	6.1

that the excess weight loss region probably is also due to the process of phosphate condensation. It is possible that titanium phosphate existing in the interface region and close to TiO_2 phase is not as stable as that in the bulk structure and decomposes at a relatively lower temperature.

FT-IR absorption spectra of the wafers of phosphoric acid treated TiO_2 samples after evacuation at 300 and 500°C are shown in Fig. 7 in order to compare the O-H stretching frequencies. The

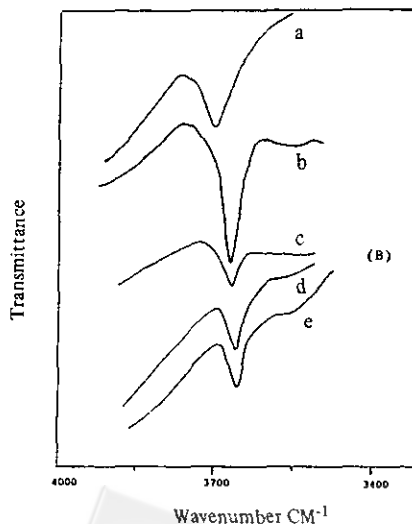
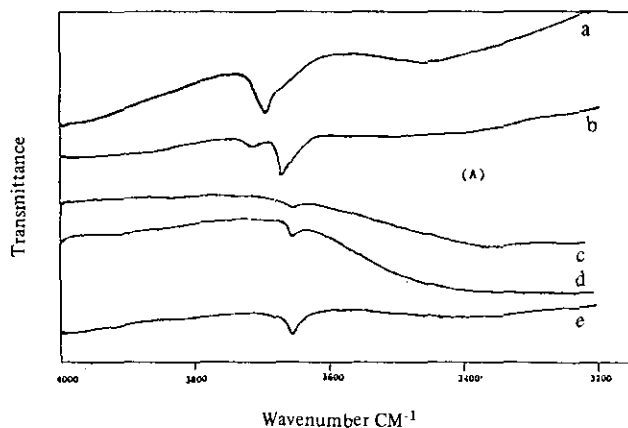


Fig. 7 FT-IR spectra of the wafers of phosphoric acid treated TiO_2 samples (A) evacuated at 500°C for 2 hrs, (B) evacuated at 100°C for 2 hrs, (a) original TiO_2 , (b) compound 0.5h, (c) compound 3h, (d) compound 10h, (e) titanium phosphate.

lattice water molecules are expected to disappear completely at 300°C. The original TiO₂ sample has a peak at 3696cm⁻¹ corresponding to TiO-H stretching on the surface. Although the XRD and TGA data show that compound 0.5h has no significant changes in structure, the O-H stretching frequency is shifted to 3672cm⁻¹ with only a small absorption remaining at 3696cm⁻¹. As the reflux period is lengthened, the O-H stretching is observed to shift further to lower frequencies and close to 3653cm⁻¹, which corresponds to free PO-H stretching on a pure titanium phosphate surface. The wafers evacuated at 500°C show similar trends in the O-H stretching frequencies. This shifting indicates that the PO-H stretching is affected by the bulk composition and even the thickness of the phosphate layers plays a role in the strength of the Brönsted acid sites. This conclusion is also consistent with the activation energy obtained in the 2-propanol dehydration reaction.

CONCLUSIONS

The present work shows that the phosphoric acid treated anatase form of TiO₂ demonstrates increased acidity on the surface due to the formation of the phosphate phase. The titanium phosphate layers seem to grow on the outer sphere of the TiO₂ crystallites. The thickness of the phosphate layers is increased as the reflux period is lengthened. The thermal stability of the resultant materials is affected by the thickness of the phosphate layers. However, the strength of the Bronsted acidity obtained in these samples is weaker than that of pure titanium phos-

phate. Experimental results show that the interior titanium oxide phase still affects the chemical properties of the surface phosphate layers.

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