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MIXED TITANIUM AND PHOSPHORUS OXIDES. II. --
The Effect of pH Values of Solutions on Surface Acidity

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A series of mixed oxides of titanium and phosphorus were prepared by co-precipitation method accompanying refluxing treatment. The effect of the pH values of the solutions on the structures, compositions, and surface acidities of the resultants compounds was determined. The samples were characterized by BET surface area measurement, X-ray powder diffraction (XRD) for structural analysis and amine-titration for surface acidities. After calcinating the oxides at 773 K, the surface acidities were attributed mainly to Ti(OH)PO$_4$ structure. Elemental analysis revealed that the P/Ti ratios in the samples decreased with increasing the pH value of the preparative solution. When the mixed oxides were used as catalysts for 2-propanol decomposition reaction, the highest activities were obtained over the samples prepared in the solutions with the pH values being 2 or 3. That result was in agreement with the variation in surface area and acid amount of the catalysts.

INTRODUCTION

In 1970's, a TiO$_2$-based catalyst was first applied commercially in air pollution control equipment. It was found to be the best catalyst for the selective catalytic reduction of NO$_x$ with NH$_3$ (SCR process).[1] Since then, interest has increased in the catalytic materials containing TiO$_2$.[2,3] The latter compound captivated great attention when the so-called strong metal-support interaction (SMSI) was first reported for noble metals supported on titanium oxide.[4] This pioneering work has stimulated numerous studies and has forced chemists to change their views on supported metal catalysts.[5]

Different from commonly used catalyst supports such as commercially available Al$_2$O$_3$ and SiO$_2$, titanium oxide itself is reducible,[6,7] but has relatively low acidity and very few acidic sites on the surface.[8] In order to improve the acidity, Shibatta *et al.*[9] synthesized a series of binary metal oxides containing titanium by the co-precipitation method. The resultant oxides were found to show higher acid strength than each component oxide. Similarly, we observed in a previous study that the acidity of mixed oxides of titanium and phosphorus were higher than that of pure titanium oxide.[10] In addition, the structures and acidities

were found to be a function of preparative variables. In this article, we report that pH values of the solutions where the oxides of titanium and phosphorus precipitate also play an important role in determining the composition and the structure of the resultant mixed oxides. Because the surface behaviors of the oxides are correlated with their structural variation, the pH values of the preparative liquids were in turn affecting the surface acidities.

In the present studies, a series of mixed oxides of phosphorus and titanium were synthesized by the co-precipitation method with the P/Ti mole ratios in the starting materials being kept at 1, but the pH values of the solutions being varied from 1 to 4. The structures, physico-chemical properties and catalytic activities of the resultant compounds were examined.

EXPERIMENTAL

Reagents

Reagent grade chemicals were used without further purification. Titanium oxide, TiCl$_4$ and H$_3$PO$_4$ were purchased from Merck. N-butylamine and n-heptane were purchased from Riedel-deHaen. Ammonium molybdate was

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purchased from Janssen. Monopotassium phosphate was purchased from Kanto. Before use as a solvent for acidity titration, n-heptane was dehydrated with 5Å-molecular sieve.

Catalyst preparation

A 10 mL portion of 5 M $TiOCl_2$ solution prepared by dissolving $TiCl_4$ in 1M HCl solution was added to a weighted amount of H_3PO_4 solution, where the P/Ti mole ratio was equal to one. At that time, a 1 M NaOH solution was added dropwise with stirring until the desired pH value of the solution was reached. Amorphous solid was precipitated. Four samples were prepared with the pH values of the solutions kept at 1, 2, 3, and 4, respectively. The amorphous precipitates were then poured into round bottom flasks and refluxed in their mother liquors at 373 K for 14 days. After filtration, the solids were stirred in excess amount of 1 M NH_4Cl solutions overnight at room temperature, followed by filtering, washing, drying and calcination at 773 K. The resultant samples are designated as R-bS, where the first letter "R" indicates that refluxing was the method of heat treatment, the numbers at the letter "b" indicate the pH values of the solutions, and the last letter "S" indicates that the base used was NaOH.

Apparatus

X-Ray powder diffraction patterns were obtained using a Philips 3390 and a Rigagu Dmax-IIC X-ray diffractometer with Cu $K\alpha$ radiation (λ = 1.5418 Å). 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 phenylazonaphthylamine (pKa = +4.0), dimethyl yellow (pKa = +3.3), benzeneazodiphenylamine (pka = +1.5) and dicinnamalacetone (pKa = -3.0). The concentrations of the indicators in n-heptane were about 0.01 g/mL.

Procedures of elemental analysis

The phosphorus and titanium contents in the samples were determined by photospectroscopy according to the methods mentioned by Alberti et al.[11] and Berhart et al.[12] 100 mg of sample were refluxed with 25 mL of concentrated H_2SO_4 containing 10 grams of $(NH_4)_2SO_4$, until completely dissolved. The solution was diluted to 100 mL with distilled water. 25 mL of the diluted solution was added with 25mL of 50% sodium hydroxide solution and 100 mL of water. The solution was covered with a watch glass, placed on a hot plate and boiled for 45 minutes to concentrate to about 50 to 80 mL. After cooling to room temperature, the solution was diluted to 100 mL with a volumetric flask. A 10-mL aliguot was then transferred to a 50-mL flask in an ice bath. In the meantime, a mixture containing 100 mL of the ammonium molybdate solution, 150 mL of acetone, and 150 mL of water was made up and chilled in the ice bath. The sample was diluted to 50 mL with this acetone-ammonium molybdate-water solution, mixed well, and the absorbance at 430 nm was determined after 1 minute. The titanium content was determined by adding 10 mL of 9M H_2SO_4, 10 mL of 3% H_2O_2 and 25 mL of water successively to 5 mL of sampling solution and the absorbance at 420 nm was determined.

Ammonium Molybdate Solution was prepared by dissolving 18.75 grams of ammonium molybdate in 300 mL of water, adding carefully 150 mL of concentrated sulfuric acid , cooling, and diluting to 500 mL.

Standard Phosphate Solution was prepared by dissolving 0.9578 gram of monopotassium phosphate, previously dried for 1 hour at 383 K, in water and diluted to 500 mL; 1 mL = 1.0 mg of phosphorus pentoxide.

Standard Titanium Solution was prepared by refluxing 0.1000 gram of titanium oxide (99 % of purity) in 25 mL of concentrated sulfuric acid containing 10 grams of $(NH_4)_2SO_4$ until completely dissolved and dilute to 100 mL with water.

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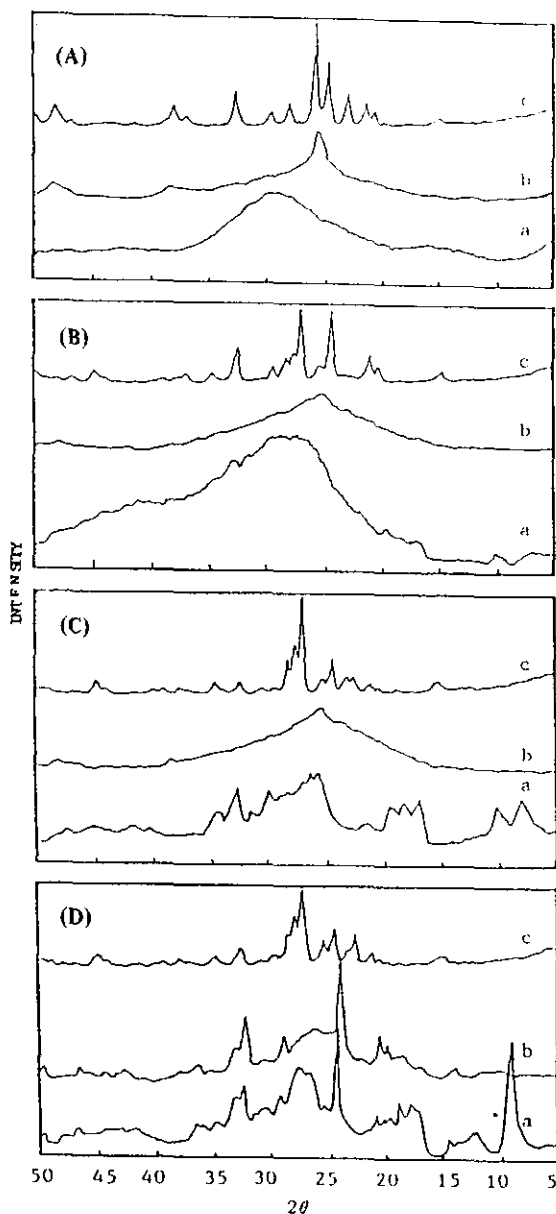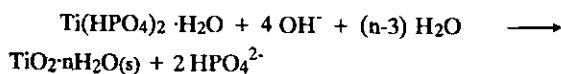
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Fig. 1. XRD profiles of the refluxing samples (P/Ti = 1) with various pH values. (A)R-4S (B)R-3S (C)R-2S (D)R-1S. where a: before cacination; b: calcination at 773 K; c: calcintion at 1073 K.

Procedures for 2-propanol dehydration reaction

The reaction was carried out in an ordinary plug-flow type reactor at atmospheric pressure. The catalyst, 0.1 g in powder form, was packed into an U-shaped 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 623 K for 3 hours 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 flowmeter (Kofloc Inc.). The N_2 gas passed through the bubbling trap and carried saturated 2-propanol vapor into the catalyst bed. The products were analyzed by a Hitachi 163 gas chromatography. A Porapak S column was used for the product separation.

RESULTS AND DISCUSSION

The results of elemental analyses and BET surface areas of the refluxing samples prepared in the solution of various pH values are tabulated in Table 1. Samples R-2S and R-3S were found to have higher surface areas compared with the other two. The phosphorus contents relative to that of titanium expressed as P/Ti ratios in the samples were found to decrease with the increase in pH values of the solutions. It was attributed to that α-titanium phosphate compound which was unstable and easily decomposed in the presence of OH^- groups while TiO_2 precipitation preferred to form in a basic solution.[13] The reaction can be expressed in the following equations:

$$Ti(HPO_4)_2 \cdot H_2O + 4\ OH^- + (n-3)\ H_2O \longrightarrow$$
$$TiO_2 \cdot nH_2O(s) + 2\ HPO_4^{2-}$$

or

$$Ti(HPO_4)_2 H_2O + 2\ OH^- + (n-1)\ H_2O \longrightarrow$$
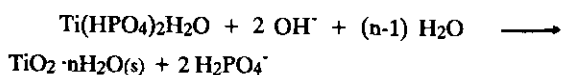$$TiO_2 \cdot nH_2O(s) + 2\ H_2PO_4^-$$

Fig. 1 shows the XRD patterns of the samples calcined at different temperatures. Before calcination (curve a), the crystallinity of the samples decreases with increasing the pH

Table 1   The data of elemental analysis and surface areas over P-Ti mixed oxides.

Sample	P/Ti	S.A (m^2/g)
R-4S	1.04	92
R-3S	1.51	152
R-2S	1.59	155
R-1S	2.08	105

Table 2   Identified phases for XRD patterns.

Sample	Before calcination	Calcination at 773K	Calcination at 1073 K
R-4S	Amorphous	Anatase	Anatase, TiP_2O_7, $Ti_2Na(PO_4)_3$
R-3S	$Ti(OH)PO_4$ $TiNaxH_2.x(PO_4)_2 \cdot H_2O$.	Amorphous	$Ti_2O(PO_4)_2$, $Ti_2Na(PO_4)_3$,
R-2S	$Ti(OH)PO_4$, $TiNaH(PO_4)_2 \cdot 4H_2O$, $TiNaH(PO_4)_2 \cdot H_2O$	Amorphous	$Ti_2O(PO_4)_2$, $Ti_2Na(PO_4)_3$, TiP_2O_7
R-1S	$TiNa_2(PO_4)_2 \cdot 3H_2O$, $Ti(OH)PO_4$, $Ti_2Na(PO_4)_3$, $TiNa_{0.8}H_{1.2}(PO_4)_2$, $Ti(HPO_4)_2 \cdot H_2O$	$Ti_2Na(PO_4)_3$ $Ti(OH)PO_4$, $TiNa_{0.8}H_{1.2}(PO_4)_2$	$Ti_2O(PO_4)_2$, $Ti_2Na(PO_4)_3$, TiP_2O_7

values of the solutions. Peaks at low diffraction angles (2θ = 7-12°) corresponding to d-spacings of 12.6-7.3Å referred to that layered structures were possibly included in samples R-1S, R-2S and R-3S, however, R-3S had very low crystallinity. Crystalline phases in the samples were identified by peak search and comparison with the known phases. Table 2 lists all the possible phases contained in the samples. For the samples consisting of mixed crystalline phases, the identified phases are tabulated according to the order of decreasing the intensity of the XRD peaks. Among these crystalline phases, compounds $TiNaxH_{2-x}(PO_4)_2$, x = 0-2, have layered structures and are the derivatives of α-titanium phosphate. Since all the samples were stirred with NH_4Cl solutions overnight during the preparative procedures, the fact that Na^+ ions still retained in the samples revealed that Na^+ ions are very difficult to be substituted by NH_4^+ ions. Besides the layered structures, $Ti(OH)PO_4$ was the main crystalline structure observed on samples R-1S, R-2S and R-3S. After calcination at 773 K for 5h, the layered structure observed on sample R-1S almost disappeared, while samples R-2S and R-3S became amorphous, and sample R-4S showed anatase TiO_2 phase. Further calcination at 1073 K for 5h, crystalline structures appeared again for all samples. The $Ti(OH)PO_4$ phase was found to convert to $Ti_2O(PO_4)_2$ phase through the condensation of hydroxyl groups.

The surface acidity of the calcined samples (at 773 K) was determined by n-butylamine titration. Fig. 2 shows the acid density as a function of Hammett constant. The acid strength distributes through weak ($H_o = +4$) to relative

strong ($H_o < -3$) sites. Among them, samples R-2S and R-3S had larger amount of acid sites. The acidities can be explained based on the structural changes observed on the XRD patterns. Since α-titanium phosphate undergoes condensation and transfers to pyrophosphate at temperatures around 723 K,[14] it is expected that the hydroxyl groups in the layered phosphate phases are dehydrated at the calcination temperature of 773 K. The resultant TiP_2O_7 and $Ti_2Na(PO_4)_3$ phases will contribute very little to surface acidities. But very weak peaks corresponding to $TiN_{0.8}H_{1.2}(PO_4)_2$ were still observed on the calcined sample R-1S. Therefore, the protons on the latter compound might contribute to some of the surface acidities. On
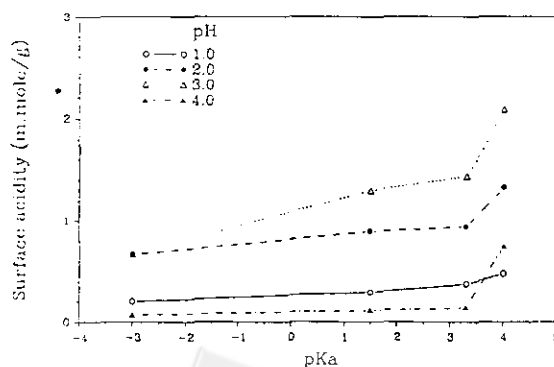

Fig. 2. Surface acidities of the samples with various pH values. ○ R-4S, • R-3S, △ R-2S, ▲ R-1S

the other hand, Ti(OH)PO$_4$ structure was proposed to survive through the calcination at 773 K since its crystalline phase was observed on sample R-1S with relative strong intensity. Although samples R-2S and R-3S were amorphous after calcination at 773 K, the Ti(OH)PO$_4$ structure still be expected to play the main role in contributing the surface acidities of samples R-1S, R-2S and R-3S. The acid amount seems to be proportional to the surface area. On the contrary, sample R-4S did not contain Ti(OH)PO$_4$ phase, its acidity was attributed to the anatase structure. In a previous report, anatase TiO$_2$ doped with small amount of phosphorus was found to demonstrate moderate acidity.[10] Nevertheless, the acid strength of these series of
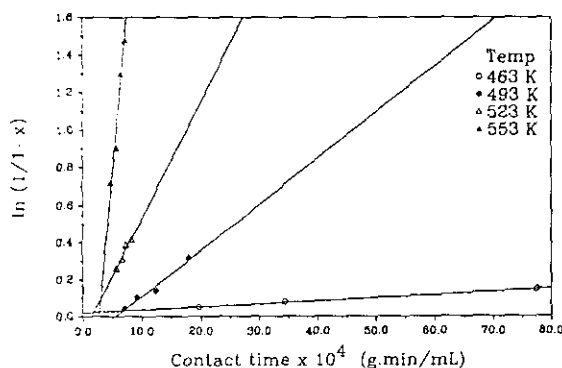

Fig. 3. Polt of ln(1/1-x) vs. τ for sample R-1S.
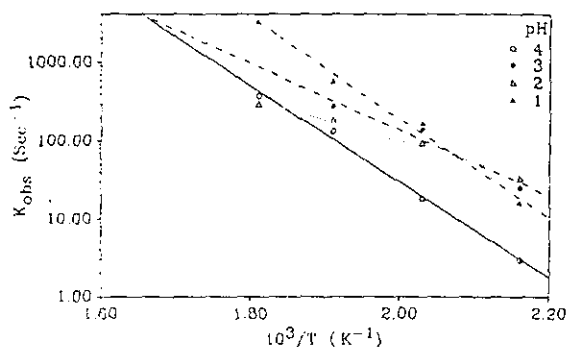

Fig. 4. Arrhenius polt for 2-propanol dehydration reaction over the samples with various pH values. ° R-4S, • R-3S, Δ R-2S, ▲ R-1S.

samples which were prepared by co-precipitation of the oxides of Ti and P was stronger than that of samples prepared by refluxing anatase particles with phosphoric acid.[15]

The decomposition of 2-propanol was studied over the calcined samples (at 773 K) in the temperature range of 463 - 553 K. The reaction was proved to be first order by obtaining a straight line when plotting ln(1/1-x) against τ(Fig. 3), according to the first-order rate equation:

$$\ln \frac{1}{1-x} = kt$$

where τ is the space time in g.min.mL^{-1} and x is the conversion of 2-propanol. The rate constants "k" were calculated from the slopes of the straight lines. Linear plots of log k against 1/T were obtained, showing that the Arrhenius equation, k = A exp(-Eapp/RT), adequately describes the effect of the temperature on k (Fig. 4). In comparison of the k values of different catalysts at the same reaction temperature, the highest activities were found over the mixed oxides prepared in the solutions with pH values being 2 and 3. That was in consistent with the variation in acid amount determined by amine titration. Values of the apparent activation energy (Eapp), the pre-exponential factor (A), and the correlation coefficient (r) of log k against 1/T are given in Table 3. The activation energies obtained were in the range of 13-29 Kcalmol^{-1}. These values were lower than the values of 31-34 Kcalmol^{-1} obtained with pure and doped rutile TiO$_2$ by Gentry.[16] Compensation effect,[17] which was com-

Table 3   Kinetic data for 2-propanol decomposition over P-Ti mixed oxides.

Sample	Eapp(Kcal/mol)	A	r*
R-4S	28.10	5.70 x 10^{13}	0.997
R-3S	20.02	8.04 x 10^{10}	0.991
R-2S	12.53	3.02 x 10^{7}	0.991
R-1S	29.08	9.98 x 10^{14}	0.995

r*: correlation coefficient for ln k vs. 1/T.
Reaction temperature range: 463 K − 553 K.

monly observed on heterogencous catalysis, was found on the mixed metal oxides as well. Fig. 5 shows that linear plots were obtained for E*app* against log A. It implies that the activation energy is dependent on both the acidic character and the surface area of the catalyst. Therefore, the E*app* value itself cannot reflect the catalytic activity.

CONCLUSION

The structures and compositions of the mixed oxides of titanium and phosphorus were found to be affected by the pH values of the preparative solutions. A comparison among samples prepared with the pH values of the solution varying from 1 to 4, the P/Ti ratios of the resultant oxides were found to increase with the decrease in the pH values of the solutions. That was attributed to the solubility of titanium phosphate in solutions containing hydroxyl groups, while titanium oxide was stable in the basic solutions. The samples prepared under pH values of 2 or 3 showed higher surface areas, higher acidic amounts and higher catalytic activities toward 2-propanol decomposition reaction. The $Ti(OH)PO_4$ structure was proposed to be the most important phase in contributing the acidity. Furthermore, the acidities of these series of compounds were higher than that of the samples prepared by modifying anatase TiO_2 surface

Fig. 5. Compensation effect shown by plotting Log A vs. Ea for the samples with various pH values.

with phosphoric acid.

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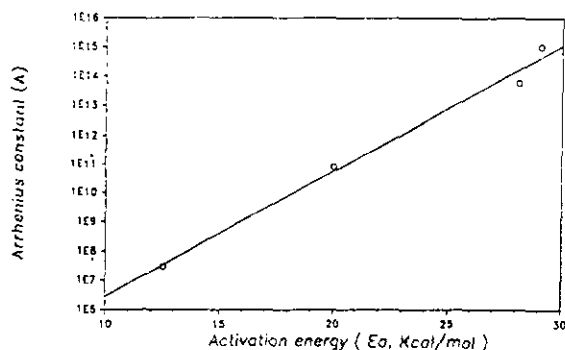12. Bernhart, D.N.; Wreath, A.R. *Anal. Chem.* **1955,** *27,* No.

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