Phosphates and Hydrogeno-Phosphates as Materials for Catalysts and Humidity Sensors

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Abstract

Phosphates as surface-functional materials were investigated. Boron phosphate (BPO_4), which is known to be a solid acid catalyst, showed prominent activity for the oligomerization of light olefins giving a liquid fuel, although other phosphates were inactive. Its activity was enhanced by grinding before use or by adopting a new preparation method characterized by supercritical drying. As a catalyst support, AlPO_4 was examined for selective catalytic reduction of NO in exhaust gas to N_2 by hydrocarbon in the presence of excess oxygen. It was found that the activity of $\text{Pt}(0.5\text{wt\%})/\text{AlPO}_4$ catalyst was higher than that of conventional $\text{Pt}(0.5\text{wt\%})/\text{Al}_2\text{O}_3$ catalyst, although AlPO_4 alone was hardly inactive. Next, metal phosphates were examined as humidity-sensing materials, and several new candidates including $\text{Ti}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ were found. The humidity-sensing characteristics of $\text{Ti}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ was considerably improved by treating with a NaOH solution. In addition, we found that Cu-P-Y-O ceramics, which were produced by the solid-state reaction between $\text{Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ and Y_2O_3 , showed good humidity-sensitive characteristics; its electric resistance decreased by three orders in magnitude as the surrounding relative humidity increased from 0% to 96%.

INTRODUCTION

Phosphates are utilized for detergents, food additives, fertilizers, corrosion inhibitors, etc. as bulk materials, and for adsorbents, catalysts, chemical sensors, etc. as surface-functional materials. The interaction of some guest molecules with the surface of a host functional phosphate results in (1) adsorption on the surface, (2) activation of the adsorbed molecules, (3) chemical reaction on the surface, (4) change in electric or electronic properties of the host phosphate, etc. The present paper describes several surface-functional phosphates exemplified below.

PHOSPHATES AS THE MATERIALS FOR CATALYST

Boron phosphate, BPO_4 , as a solid acid catalyst

Light olefins can be converted to a liquid fuel by their oligomerization over acid catalysts. There are a number of oligomerization catalysts [1] such as liquid acids, solid phosphoric acid, clays, and silica-alumina. In 1981, one of the authors [2] has reported the potentiality of high-temperature outgassed boron phosphate catalyst. Recently, zeolites, particularly H-Fe-silicate [3] and H-Co-silicate [3] have been found to be very effective. The products of the oligomerization of light olefins depend on catalysts, reaction conditions, kind of olefins, and so on. In order to develop an effective olefin oligomerization process fitting one's purpose, it is necessary to understand comprehensively the activities and selectivities of various oligomerization catalysts.

Boron phosphate, $\text{BPO}_4(\text{RP})$ was prepared by heating an equimolar mixture of boric acid and phosphoric acid at 40 °C in a rotary evaporator followed by drying in situ at that temperature, heating at 150 °C for 24 h, and finally calcining at 360 °C for 12 h [4]. Another boron phosphate, $\text{BPO}_4(\text{SC})$ was prepared by adding acetic anhydride to a mixture of boric acid, phosphoric acid, acetic acid and methyl acetate [5]. The grinding of BPO_4 sample was performed with a FRITSCH planetary micro mill pulverisette [6]. The oligomerization of olefins was carried out using a closed recirculation reactor (volume = 600 ml).

Figure 1 shows the results of propene oligomerization over $\text{BPO}_4(\text{RP})$ at 0 - 200 °C. The progress of the reaction is expressed as a rate of decrease in total pressure, $100 \cdot (P_0 - P)/P_0$, where P_0 is the initial (total) pressure of the monomer and P is total pressure at any reaction time. At 0 - 100 °C, the activities of various catalysts for the oligomerization of propene decreased in the order, $\text{BPO}_4(\text{RP}) > \text{SiO}_2\text{-Al}_2\text{O}_3 > \text{HY-zeolite} > \text{H-ZSM-5}, \text{SO}_4/\text{ZrO}_2$. Figure 2 summarizes the product distributions of propene oligomerization at 0 - 200 °C for 20 h over BPO_4 . At 0 °C the products were rich in relatively higher molecular weight substances such as C_{12-15} compounds. With a rise in temperature, the percentage of such substances decreased and that of C_6 compound increased. At 100 °C, both C_8 and C_9 were formed in abundance. Figure 3 shows the products of propene oligomerization at 50 - 200 °C for 20 h over $\text{SiO}_2\text{-Al}_2\text{O}_3$. With increasing temperature, the percentages of C_6 and C_7 compounds increased. As can be seen in Figure 4, the products of propene oligomerization at 150 °C over HY were similar to those over $\text{SiO}_2\text{-Al}_2\text{O}_3$. However, at 100 °C, C_{10-15} compounds were appreciably produced.

Figure 1: Oligomerization of propene over $\text{BPO}_4(\text{RP})$ at various temperatures. Initial pressure (P_0) of propene = 600 Torr, total pressure at any time = P , weight of catalyst = 0.5 g, calcination 500 °C, 2 h; evacuation 500 °C, 2 h

Figure 2: Products of the oligomerization of propene over $\text{BPO}_4(\text{RP})$ at various temperatures. Reac. time = 20 h

Figure 3: Products of the oligomerization of propene over silica-alumina at various temperatures.
Reac. time = 20 h

Figure 4: Products of the oligomerization of propene over HY zeolite at various temperatures.
Reac. time = 20 h

Table 1 The specific surface area and the activity of BPO₄(RP) for the oligomerization of *cis*-2-butene before and after grinding

Grinding time / h	Surface area / m ² ·g ⁻¹	Oligomerization / % at reac. time (min) of					
		2	5	10	20	30	60
0	15	6.2	8.6	10.5	12.9	14.0	15.9
6	22	9.5	12.7	15.5	18.9	20.6	23.7
9	25	9.2	12.3	15.1	18.5	20.2	23.5
12	25	9.2	12.0	14.8	18.3	20.0	22.6
18	27	8.6	11.6	14.2	18.3	20.4	23.4
24	25	9.5	11.6	14.0	17.0	18.3	21.3

Amount of *cis*-2-butene = 70 Torr, 0.5 l; weight of catalyst = 0.20 g; reac. temp. = 0 °C

Generally the catalytic activity (per weight) of a solid catalyst depends on its specific surface area. As seen in Table 1, the specific surface area of $\text{BPO}_4(\text{RP})$ was increased by grinding it and as a result its activity for the oligomerization of *cis*-2-butene was also increased [6]. In order to prepare highly porous BPO_4 , a new preparative method has been developed. The method is characterized by both the reaction of H_3PO_4 and H_3BO_3 in a mixture of acetic acid and methyl acetate and the subsequent supercritical drying [5]. Clearly, the activity of $\text{BPO}_4(\text{SC})$ was much higher than that of $\text{BPO}_4(\text{RP})$ for propene oligomerization at 50 °C (Figure 5).

Figure 5: Oligomerization of propene over $\text{BPO}_4(\text{SC})$ and $\text{BPO}_4(\text{RP})$. Pressure of propene = 600 Torr, weight of catalyst = 0.5 g, calcination 500 °C, 2 h; evacuation 500 °C, 2 h; reac. temp. = 50 °C

Aluminum phosphate (amorphous), AlPO_4 , as a catalyst support

Selective catalytic reduction of NO_x to N_2 by a hydrocarbon (HC) in the presence of excess oxygen, HC-SCR, has been investigated over various catalysts such as zeolites, metal oxides, and noble metals as one of important reactions for purifying the automotive exhaust gas of a diesel engine or a lean-burn engine [7]. One of the most extensively studied metal oxides is alumina and it is often used as a metal-loaded alumina ($\text{M}/\text{Al}_2\text{O}_3$) [8-10]. Aluminum phosphate, however, has seldom been used as a catalyst material for HC-SCR catalysts.

Aluminum phosphate was prepared by neutralizing a solution containing an equal molar ratio of aluminum nitrate and phosphoric acid with ammonia solution [11]. Catalytic reactions were carried out with a fixed bed flow reactor by passing a reactant gas mixture at a total flow rate of $130 \text{ ml} \cdot \text{min}^{-1}$ over a catalyst (0.40 g). The gas mixture contained 1000 ppm NO_x , 2.0% O_2 , 500 ppm C_2H_4 or C_3H_6 as a reductant and balance helium.

Contrary to our expectation, AlPO_4 alone was inactive for both C_2H_4 -SCR and C_3H_6 -SCR, while Al_2O_3 was considerably active. As a result of examining many metal-loaded catalysts, it was found that the activity of $\text{Pt} (0.5\text{wt}\%) / \text{AlPO}_4$ catalyst was higher than that of conventional $\text{Pt} (0.5\text{wt}\%) / \text{Al}_2\text{O}_3$ catalyst for both C_2H_4 -SCR and C_3H_6 -SCR as shown in figure 6. In C_2H_4 -SCR, the maximal NO conversion value of $\text{Pt} (0.5\text{wt}\%) / \text{AlPO}_4$ is similar to that of $\text{Pt} (0.5\text{wt}\%) / \text{Al}_2\text{O}_3$, but the temperature window of $\text{Pt} (0.5\text{wt}\%) / \text{AlPO}_4$ shifts to lower temperature by 50 °C compared with that of $\text{Pt} (0.5\text{wt}\%) / \text{Al}_2\text{O}_3$. The superiority in activity of $\text{Pt} (0.5\text{wt}\%) / \text{AlPO}_4$ is more evident for C_3H_6 -SCR.

Figure 6: Temperature dependence of the catalytic activities over Pt (0.5 wt%)/Al₂O₃ and Pt (0.5 wt%)/AlPO₄. a) NO (1000 ppm) + C₂H₄ (500 ppm) + O₂ (2%), W/F=0.18 g·s·cm⁻³, total flow rate=130 ml·min⁻¹. b) NO (1000 ppm) + C₂H₄ (1000 ppm) + O₂ (5%), W/F= 0.30 g·s·cm⁻³, total flow rate=80 ml·min⁻¹.

PHOSPHATES AS THE MATERIALS FOR CHEMICAL SENSORS

Humidity-Sensitive Characteristics of Various Metal Phosphates

A ceramic humidity sensor has advantages of both chemical and thermal stability; thus, many metal oxides such as ZnCr₂O₄/LiZnVO₄ [12], niobia [13], Al₂O₃-TiO₂-SnO₂ [14] have been used as suitable materials. Needless to say, humidity-sensor materials should be insoluble in water, because they must be durable for adsorption/desorption cycles of water vapor. From this viewpoint, metal phosphate can be another candidate. Actually, hydroxyapatite [15], AlPO₄ [16], and Zr(HPO₄)₂ [17,18] have been investigated as a ceramic humidity-sensing material. However, there still seems to be room for finding of other metal phosphates as a ceramic humidity-sensing material.

All metal phosphates were prepared by the methods given in the literature [19]. Sodium cation exchanged metal phosphates were also prepared [19]. Every precalcined sample was pulverized, pressed into a disc with 13 mm in diameter and 0.5-1 mm in thickness. Finally every disc was sintered at 800 °C for 3 h in air. An OS-type element was prepared by painting the comb-pattern electrodes shown in figure 7 on the one side of a disc with a silver paste and then by heating at 700°C for 10 min. A sensor element was placed in a test chamber (200 ml) containing a suitable saturated salt solution (40 ml), which gives a specified relative humidity. The four-point resistance measurements of sensor elements were performed at 25 °C by using a LCR meter (YHP4261A) under a applied voltage of 1 V AC (1 kHz).

Figure 7: Schematic view of OS-type sensor element

Figure 8: Humidity-sensitive characteristics of various metal phosphate elements

As can be seen in figure 8, $\text{Mg}_3(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$, YPO_4 , $\text{Ce}(\text{HPO}_4)_2 \cdot 1.33\text{H}_2\text{O}$, $\text{Ti}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$, $\text{Zr}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$, $\text{Co}_3(\text{PO}_4)_2$, $\text{Ni}_3(\text{PO}_4)_2$, and SiP_2O_7 showed good humidity-sensing characteristics; the electric resistance changed by two or three orders of magnitude in the humidity range 33 to 94% rh. Among them, $\text{Mg}_3(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$, SiP_2O_7 , and $\text{Ti}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$ seem to be superior materials in terms of resistance variation with relative humidity and the linearity between resistance and relative humidity. As seen in figure 9, $\text{Zr}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$ showed better humidity-sensing characteristics than those of $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ and AlPO_4 . In addition, it is noted that $\text{Ce}(\text{HPO}_4)_2 \cdot 1.33\text{H}_2\text{O}$ and $\text{Ti}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$ exhibited similar humidity-sensing characteristics to those of $\text{Zr}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$.

Figure 9: Humidity-sensitive characteristics of selected metal phosphate elements

Figure 10: Humidity-sensitive characteristics of $\text{Ti}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ -based elements

For a good humidity-sensitive characteristic, the resistance or conductance of the sensor must be low in a low relative humidity range. In the case of $\text{Ti}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$, NaOH-treatment made the resistance lower, especially in the middle relative humidity range. Contrary to these results, in NaOH-treated $\text{Ti}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$, considerably improved humidity-sensing characteristics were observed (Figure 10); the resistance decreased from 10^6 to 10^4 in the whole relative humidity range. The linearity was also improved greatly.

Cu-P-Y-O Based Ceramic Humidity Sensor

A variety of materials including several metal phosphates have been examined as humidity-sensitive element. Among metal phosphates particular attention has been paid to zirconium phosphate [20-23]. Humidity sensors are based on variation in impedance or capacitance with the environmental humidity, and the impedance type is further divided into the two types, ionic and electronic [24]. The humidity sensor using zirconium phosphate can be grouped into the ionic type, because the impedance is inversely proportional to the concentration of the acidic hydrogen [20]. Some metal phosphates other than zirconium phosphate can be used as humidity-sensing material, provided they have acidic property and can be molded into porous disc. Recently, we incidentally noticed that a composite compound containing Cu, P, and Y (denoted as CPY-number, where the number indicates a Cu/Y atomic ratio multiplied by ten) was produced by the solid-state reaction between $\text{Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ and Y_2O_3 , and its resistivity was affected by the environmental humidity. A preliminary experiment revealed that the CPY involved YPO_4 which had been known to exhibit weak surface acidity. Thus the CPY can be expected to have humidity-sensitive property.

The CPY samples were prepared from calculated amounts of $\text{Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ and Y_2O_3 by the method given in the literature [25]. Figure 11 shows the schematic view of a sensor element, which was made by painting a silver paste on both faces of a disk-shaped sample and by heating at 700°C for 10 min. The resistance measurement of the sensor elements was performed in a manner similar to the experiment described above (3.1).

Figure 12 shows the humidity-sensitive characteristics of the CPY sensor elements prepared by sintering at 950°C . Most of the CPY elements, except for the CPY-15 and CPY-20, showed lower resistivities, which decreased almost linearly with the increase in relative humidity. Among the sensor elements tested the CPY-10 or CPY-13 element is considered to be a promising sensor material for the wide resistivity change of three orders in magnitude over the whole range. Four kinds of crystalline phases YPO_4 , Y_2O_3 , CuO , and $\text{Cu}_2\text{Y}_2\text{O}_5$ were observed in most CPY samples. YPO_4 and Y_2O_3 elements exhibited comparable resistivity to that of the CPY-10 element, and YPO_4 was found to play more important role in those elements. In addition, it was suggested that a critical point for the excellent humidity-sensitivity of the CPY-10 and CPY-13 elements at least in the lower relative humidity range will be the synergistic effect of CuO (and/or Cu_2O) as an electronic conductor and YPO_4 as an ionic conductor.

CONCLUSION

A number of useful surface-functional materials can be obtained from phosphates by finding means best fitted to make the most of their peculiar characteristics.

Figure 11: Schematic view of sensor element

Figure 12: Humidity-sensitive characteristics of CPY compounds

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