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Influence of Thermal, Hydrothermal, and Acid–Base Treatments on Structural Stability and Surface and Catalytic Properties of $AlPO_4^{5-}$

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Effects of thermal treatment (at 813–1433 K), hydrothermal treatment [low-pressure water vapor (35 Torr) at 773 K for 0–168 h, high-pressure steam (16 atm), and water (at autogenous pressure) at 473 K for 12 h], and acid–base (pH 1–12.5) treatment (at 303 K for 20 h) on the structural stability, physical properties (viz., size and morphology of crystals, relative surface concentrations of Al and P, and N_2 sorption capacity at 78 K), acidity, and catalytic activity (in the cumene cracking and *o*-xylene isomerization reactions at 673 K) of $AlPO_4^{5-}$ have been investigated. Although $AlPO_4^{5-}$ has good thermal stability, calcination at higher temperatures (≥973 K) causes a small decrease in its crystallinity and N_2 sorption capacity and a large decrease in its acidity and catalytic activity. The crystallinity, surface properties, acidity, and catalytic properties of $AlPO_4^{5-}$ are affected significantly by hydrothermal treatment, particularly treatment with high-pressure steam or water at autogenous pressure at 473 K. These treatments lead to a complete collapse of the channel structure. $AlPO_4^{5-}$ dissolves completely in both HCl and NaOH solutions at concentrations of 0.1 mol cm^{-3} or greater. The pH of the acid or alkali solutions has a pronounced effect on its structural stability, as well as its surface and catalytic properties and acidity.

INTRODUCTION

$AlPO_4^{5-}$, a novel crystalline molecular sieve aluminophosphate introduced recently by Wilson *et al.* (*1, 2*), is a zeolite-like material. It has a unique three-dimensional structure (*3*) with hexagonal symmetry (cell constants: $a = 1.373$ nm and $c = 0.848$ nm, $\gamma = 120°$). It contains one-dimensional cylindrical channels of uniform cross section (pore diameter = 0.8 nm) oriented parallel to the *c* axis and bounded by 12-membered rings composed of alternating AlO_4 and PO_4 tetrahedra. Its framework is neutral; therefore, there are no extra framework cations.

In our earlier studies (*4*), the site energy distribution and catalytic properties of $AlPO_4^{5-}$ were investigated. $AlPO_4^{5-}$ contains both Lewis and protonic acid sites (*4, 5*) and possesses considerable catalytic activity in hydrocarbon cracking, isomerization, and disproportionation reactions and also in conversion of methanol and ethanol to aromatics (*4*). Thus, from the point of view of its application as an adsorbent, catalyst, and/or catalyst support, a knowledge of the influence of various thermal, hydrothermal, and acid–base treatments on its structural stability and its surface and catalytic properties and acidity is of great interest. The present investigation was undertaken with the goal of studying these properties.

EXPERIMENTAL

Preparation of $AlPO_4^{5-}$

$Pr_3N-AlPO_4^{5-}$ (an $AlPO_4^{5-}$ precursor) was synthesized by the hydrothermal procedure described by Wilson *et al.* (*2*). According to this procedure, it is crystallized from a gel of composition $1.5Pr_3N \cdot 1.0Al_2O_3 \cdot 1.0P_2O_5 \cdot 40H_2O$ at 423 K over a period of 24 h in a stainless-steel (316 type) pressure bomb. The sources of P_2O_5 and Al_2O_3 were orthophosphoric acid and boehmite, respectively. Crystals were washed thoroughly with deionized distilled water, filtered, and

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dried in an air oven at 373 K for 16 h. The XRD pattern of the aluminophosphate thus prepared was found to be very similar to that of $AlPO_4^{5-}$ reported earlier (*2, 3*). Examination by scanning electron microscopy (SEM) showed that the material was highly crystalline and that the crystals had a hexagonal cross section.

$AlPO_4^{5-}$ was obtained from Pr_3N–$AlPO_4^{5-}$ by heating the latter in air at 813 K for 12 h to remove the organic template. Detailed characterization of $AlPO_4^{5-}$ for its crystalline nature, crystal size and morphology, acidity, and site energy distribution has already been reported (*4*). The material was pressed binder free, crushed to particles of about 0.2 mm, and subjected to various thermal, hydrothermal, and acid–base treatments.

Thermal Treatment

$AlPO_4^{5-}$ was heated at different temperatures (813–1433 K) for 12 h in a muffle furnace with air flowing over it at the rate of 100 cm^3 min^{-1}.

Hydrothermal Treatment

Low-pressure steam treatment. A mixture of water vapor (partial pressure = 35 Torr) and nitrogen at a flow rate of 100 cm^3 min^{-1} was passed through a bed of $AlPO_4^{5-}$ particles at 773 K for periods ranging from 0 to 160 h.

High-pressure steam treatment. The $AlPO_4^{5-}$ particles were placed in a wire-mesh (stainless-steel) basket and suspended in a stainless-steel pressure bomb containing water at the bottom in such a way that there was considerable clearance between it and the water level. The closed bomb was then heated in an air oven at 473 K for 12 h. The aluminophosphate was then calcined at 773 K for 4 h.

Water treatment. $AlPO_4^{5-}$ was immersed in water and heated in a pressure bomb at 473 K for 12 h at autogenous pressure. After treatment, the aluminophosphate was filtered, dried in a vacuum oven at 373 K for 12 h, and calcined at 773 K for 4 h.

Acid–Base Treatment

To determine the influence of various acid–base treatments, the aluminophosphate (1.0 g) was treated with acid/alkali solution (400 cm^3) of pH from 1.0 to 12.5 at 303 K for 12 h. The pH of the treatment solution was adjusted to the required value using hydrochloric acid and sodium hydroxide solutions.

After the acid–base treatment, the aluminophosphate was dried in a vacuum oven at 373 K for 12 h and calcined in air at 773 K for 4 h.

Characterization of Treated $AlPO_4^{5-}$

Treated $AlPO_4^{5-}$ samples were chemically analyzed for their Al and P content.

The crystalline nature and crystallinity of the treated $AlPO_4^{5-}$ were determined with a Holland Philips PW/1730 X-ray diffractometer fitted with a Ni-filtered Cu*Kα* radiation source and a scintillation counter. The XRD spectra of the treated samples of $AlPO_4^{5-}$ are given elsewhere (*6*).

Changes in the size and morphology of the crystals of $AlPO_4^{5-}$ after treatment were studied with a Cambridge Stereoscan Model 150 scanning electron microscope.

The relative concentrations of Al and P on the surface of the aluminophosphate were studied by X-ray photoelectron spectroscopy (XPS) using a VG Scientific ESCA-3 MK II electron spectrometer.

The sorption capacity of the treated samples for nitrogen at 78 K [relative pressure (p/p_s) = 0.3] was measured by determining the adsorption of nitrogen at a concentration of 30 mol% (balance, helium) using a Quantasorb adsorption meter (Quantachrome Corp., U.S.A.) by the dynamic adsorption/desorption technique. This measurement may, however, give the relative N_2-sorption capacity of the treated $AlPO_4^{5-}$ samples, because of the possibility of competitive sorption between N_2 and He.

Changes in the acidity of $AlPO_4^{5-}$ as a result of the various treatments were investigated by measuring the chemisorption of pyridine at 673 K by the GC pulse method (*7*) and measuring the temperature-programmed desorption (TPD) of pyridine under chromatographic conditions (*8, 9*). TPD data were collected using a Sigma 3B Perkin–Elmer gas chromatograph with a flame ionization detector under the following experimental conditions: amount of treated $AlPO_4^{5-}$, 0.1 g; N_2 flow rate, 10 cm^3 min^{-1}; initial temperature of TPD, 373 K; final temperature of TPD, 673 K; heating rate, 10 K min^{-1}; amounts of pyridine injected at the start of TPD, 4.0 μl (for $AlPO_4^{5-}$ calcined at different temperatures) and 6.0 μl (for other aluminophosphate samples). The procedure for obtaining the TPD data is given elsewhere (*9, 10*).

Measurement of Catalytic Activity

The catalytic activity of the treated $AlPO_4^{5-}$ in the cumene cracking and *o*-xylene isomerization reactions was measured in a pulse microreactor (i.d. = 4 mm) connected to the gas chromatograph. The reported values are, for the first pulse of the reactants, measured under the following conditions: amount of catalyst, 0.1 g; N_2 flow rate, 60 cm^3 min^{-1}; temperature, 673 K; pulse size, 1.0 μl; total pressure, 180 kPa. Before the activity test, all the catalyst samples were heated in situ at 673 K in a flow of nitrogen (60 cm^3 min^{-1}) for 1 h.

The details of the microreactor, procedures for measuring catalytic activity, and product analysis by gas chromatography are reported elsewhere (*4, 10, 11*).

RESULTS AND DISCUSSION

Effect of Thermal Treatments

The data in Table 1 indicate that the increase in the calcination temperature of $AlPO_4^{5-}$ from 813 to 1433 K results in a significant decrease in its crystallinity, as indicated by the decrease in the height (intensity) of the XRD peaks. Also, at and above 973 K, there appears a tridymite phase (in trace amounts), the concentration of which increases with increasing temperature. The N_2 sorption capacity (at 78 K and relative pressure of 0.3) and relative surface concentrations of Al and P [measured in terms of the $I_{Al(2p)}/I_{P(2p)}$ ratio, where $I_{Al(2p)}$ and $I_{P(2p)}$ are the intensities of the XPS spectra for Al(2*p*) and P(2*p*) electrons] of $AlPO_4^{5-}$ are affected only to a small extent.

A comparison of the scanning electron micrograph of $AlPO_4^{5-}$ calcined at 1433 K (Fig. 1b) with that calcined at 813 K (Fig. 1a) indicates that the calcination temperature has no significant effect on the size and morphology of the crystals of the alumino-

TABLE 1

Effect of Calcination Temperature on Crystallinity and Surface Properties of $AlPO_4^{5-}$

Calcination temperature (K)	Crystalline phase[a]	Crystallinity (as $AlPO_4^{5-}$) (%)	N_2 adsorbed at 78 K (mmol g^{-1})	$\frac{I_{Al(2p)}}{I_{P(2p)}}$	q_i (pyridine at 673 K) (μmol g^{-1})
813	5	100	4.73	0.55	2.5
973	5 (major) T (trace)	87	4.51	0.61	1.0
1273	5 (major) T (trace)	84	4.33	0.57	<0.5
1433	5 (major) T (trace)	82	4.30	0.55	<0.5

[a] 5 = $AlPO_4^{5-}$ and T = tridymite.

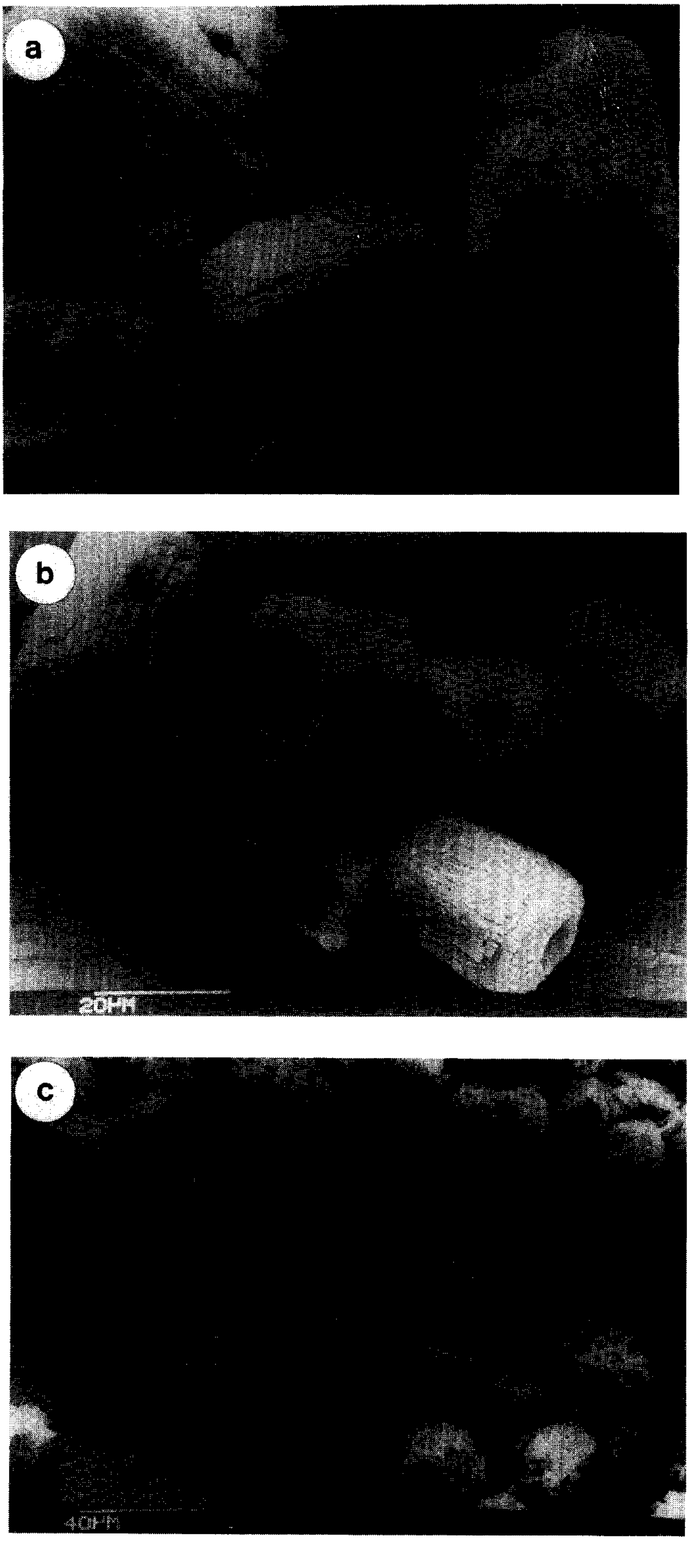

FIG. 1. Scanning electron micrographs of $AlPO_4^{5-}$ (a) calcined at 813 K, (b) calcined at 1433 K, and (c) treated with liquid water at 473 K (at autogenous pressure) for 12 h.

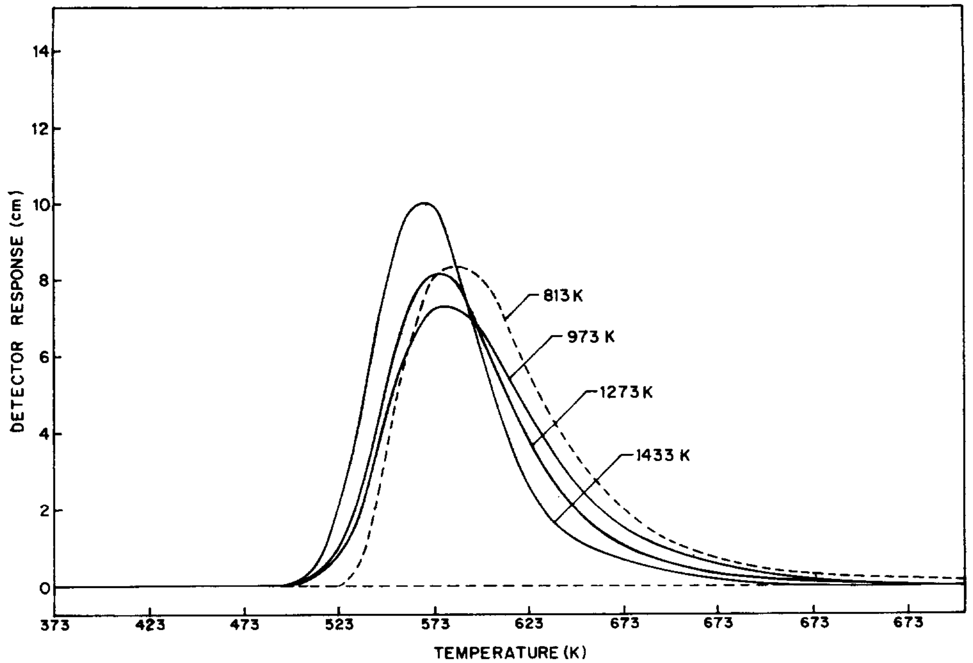

FIG. 2. TPD chromatograms of pyridine on AlPO$_4^{5-}$ calcined at different temperatures (amount of catalyst, 0.1 g; pyridine pulse size, 4.0 μl; heating rate, 10 K min^{-1}).

phosphate. The results (Table 1, Fig. 1) lead to the conclusion that like mordenite and pentasil zeolites, AlPO$_4^{5-}$ too has a high thermal stability. Its crystal structure and morphology remain in tact up to 1433 K. There is, however, a small decrease in crystallinity and a minor transformation to the tridymite phase at or above $\geq$973 K.

With the increase in the calcination temperature, the acidity of AlPO$_4^{5-}$ [measured in terms of the chemisorption of pyridine at 673 K (q_i(pyridine at 673 K))] decreases sharply (Table 1) and the site energy distribution of the pyridine adsorption sites, as shown by the TPD curves in Fig. 2, shifts toward the low-energy region.

Figure 3 shows that the increase in the calcination temperature causes a sharp decrease in the catalytic activity of AlPO$_4^{5-}$ in the cumene cracking and *o*-xylene isomerization reactions.

The decrease in acidity with increasing calcination temperature (Table 1 and Fig. 2) is expected, mainly as a result of the dehy-

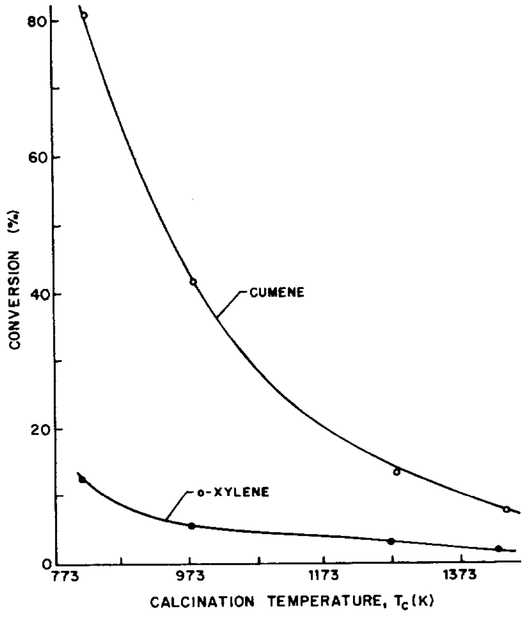

FIG. 3. Effect of calcination temperature on catalytic activity of AlPO$_4^{5-}$ in cumene cracking and *o*-xylene isomerization reactions at 673 K (amount of catalyst, 0.1 g; N$_2$ flow rate, 60 cm^3 min^{-1}; pulse size, 1.0 μl).

TABLE 2

Effect of Hydrothermal Treatment on Crystallinity and Surface and Catalytic Properties of AlPO$_4^{5-}$

Hydrothermal treatment			Crystalline phase[a]	Crystallinity as AlPO$_4^{5-}$ (%)	$\frac{I_{Al(2p)}}{I_{P(2p)}}$	N_2 adsorbed at 78 K (mmol g^{-1})	q_i (pyridine at 673 K) (μmol g^{-1})	Total conversion (%)	
Temperature (K)	P_{H_2O} (Torr)	Period (h)						o-Xylene isomerization	Cumene cracking
Untreated AlPO$_4^{5-}$			5	100	0.55	4.73	2.5	12.6	81.3
773	35	6	5	87	0.51	4.65	1.3	2.9	29.2
773	35	48	5	67	0.57	4.58	1.5	4.5	35.0
773	35	168	5	63	0.52	4.50	1.4	6.3	35.2
473	16 (atm)	12	T(major) 5(minor)	—	—	0.08	0.0	0.3	3.8
473[b]	Water	12	T and amorphous	—	2.20	0.12	0.0	0.4	4.1

[a] 5 = AlPO$_4^{5-}$ and T = tridymite.

[b] Sample immersed in water and treated at the autogenous pressure.

droxylation of AlPO$_4^{5-}$ and, to a small extent, the decrease in its crystallinity. The sharp decrease in catalytic activity in the cumene cracking and *o*-xylene isomerization reactions with increasing calcination temperature (Fig. 3) suggests the involvement of protonic acid sites in these reactions.

Effect of Hydrothermal Treatment

The data in Table 2 indicate that when AlPO$_4^{5-}$ (precalcined at 813 K for 12 h) is treated with water vapor (P_{H_2O} = 35 Torr) at 773 K, there is no phase transformation, even when the treatment is extended for 7 days, but the crystallinity of the aluminophosphate decreases with increasing time of treatment. On the other hand, the high-pressure steam (16 atm) treatment at 473 K results in extensive phase transformation; AlPO$_4^{5-}$ is almost completely transformed to tridymite. The treatment with water at 473 K (under autogenous pressure) also causes a complete structural collapse of AlPO$_4^{5-}$ followed by its recrystallization to tridymite. The low-pressure water vapor (35 Torr) treatment at 773 K does not cause a significant change in the morphology of the crystals of AlPO$_4^{5-}$, even when it is carried out for an extended period of 7 days. In contrast, crystals of AlPO$_4^{5-}$ treated with water at 473 K (Fig. 2c) degrade and become amorphous, as revealed by the scanning electron micrograph. Thus, AlPO$_4^{5-}$ has very poor hydrothermal stability compared with ZSM-5 (*12*).

Apparently, the structural collapse of AlPO$_4^{5-}$ is due mainly to the hydrolysis of the structural Al; the precipitation of Al on the surface is indicated by the large increase in the surface concentration of Al following the water treatment (Table 2) [$I_{Al(2p)}/I_{P(2p)}$ increases from 0.55 to 2.20]. The N_2 sorption capacity of the treated AlPO$_4^{5-}$ samples (Table 2) is quite consistent with the structural changes, viz., change in crystallinity or structural collapse followed by recrystallization.

The chemisorption of pyridine and the catalytic activity (in the cumene cracking and *o*-xylene isomerization reactions) of AlPO$_4^{5-}$ (Table 2) decrease as a result of the different hydrothermal treatments, depending upon the severity of the treatment. As expected, this decrease is drastic when the aluminophosphate is treated with high-pressure steam or water at 473 K.

Comparison of the TPD chromatograms in Fig. 4 shows that the strength distribution of the pyridine adsorption sites of AlPO$_4^{5-}$ is significantly affected by the hydrothermal treatments. The TPD curves

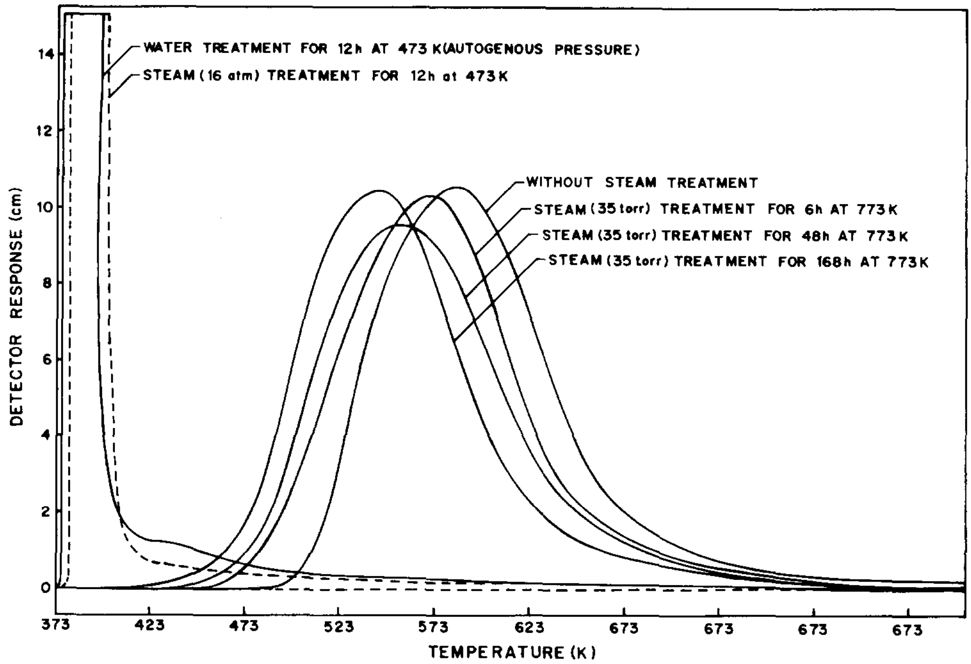

FIG. 4. TPD chromatograms of pyridine on $AlPO_4^{5-}$ hydrothermally treated under different conditions (amount of catalyst, 0.1 g; pyridine pulse size, 6.0 μl, heating rate, 10 K min^{-1}).

shift more and more toward the lower energy region with increasing length of the low-pressure water vapor treatment. TPD chromatograms for the high-pressure steam- and water-treated $AlPO_4^{5-}$ shift very close to the lowest temperature of the TPD, indicating that these two treatments almost completely destroy the pyridine adsorption sites on $AlPO_4^{5-}$.

Effect of Acid–Base Treatments

The results in Fig. 5a reveal that the solubility of $AlPO_4^{5-}$ in the aqueous treatment depends strongly on the pH of the solution. At pH ≤ 1 and ≥ 12.5 there is a complete dissolution of $AlPO_4^{5-}$. It may be noted that the aluminophosphate dissolves completely in HCl and NaOH solutions at a concentration ≥ 0.1 mol dm^{-3}. Its dissolution in the pH range 5.0–9.5 is, however, negligibly small. The difference between the electronegativities of Al and P, which is supposed to cause the hydrophilicity of the alumino-

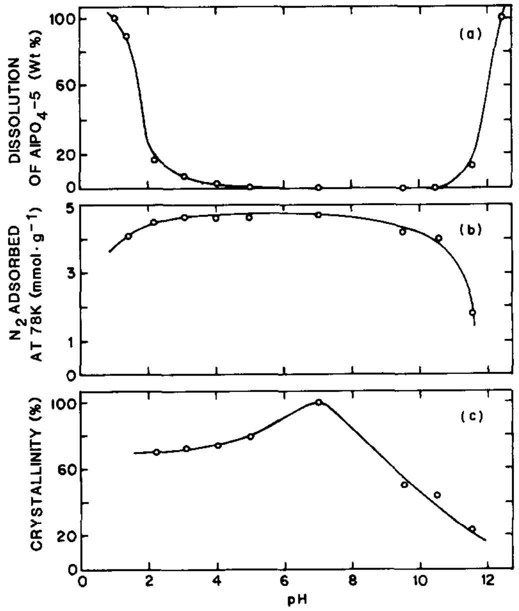

FIG. 5. Influence of pH of treatment solution on (a) dissolution, (b) N_2 adsorbed at 78 K ($p/p_s = 0.3$), and (c) crystallinity of $AlPO_4^{5-}$.

TABLE 3

Effect of Acid–Base Treatments[a] on Bulk and Surface Properties of $AlPO_4^{5-}$

pH of treatment solution		Properties of treated $AlPO_4^{5-}$			q_i (pyridine at 673 K) (μmol g^{-1})
Initial	Final	Bulk Al/P ratio	Crystalline phase	$\frac{I_{Al(2p)}}{I_{P(2p)}}$	
1.0	1.0	—	—	—	—
1.4	1.5	—	—	0.54	—
2.2	2.3	1.07	5	0.55	—
3.1	3.2	1.10	5	0.51	1.1
4.0	4.2	1.09	5	0.51	1.3
5.0	5.9	1.06	5	0.52	1.7
7.0	7.0	1.03	5	0.55	2.4
9.5	7.4	1.05	5	0.55	<0.5
10.5	8.6	1.12	5	0.61	0.0
11.5	9.6	1.20	5	0.77	—
12.4	12.1	—	—	—	—

[a] 1 g $AlPO_4^{5-}$ was treated with 400 ml aqueous solution at 303 K for 20 h.

phosphate (*2*) and the polar nature of its structure (*3*) might be responsible for the strong interaction of polar species (such as water molecules) with the structural Al and P in the $AlPO_4^{5-}$ samples that have been subjected to hydrothermal and acid–base treatments under severe conditions. This is expected to cause a weakening of Al–O and P–O bonds and lead to the structural collapse of $AlPO_4^{5-}$.

When the pH of the acid/base treatment solution is increased from 1.4 to 11.5, the N_2 sorption capacity of the resulting solid (Fig. 5b) increases until the pH reaches 3.1, remains almost unaltered in the pH range 3.1–7.0, and thereafter decreases sharply. This decrease is drastic in the higher pH (≥10.5) region.

Variation of the pH from 2.2 to 11.5 does not result in the phase transformation of $AlPO_4^{5-}$ (Table 3), but the crystallinity of the treated $AlPO_4^{5-}$ (Fig. 5c) is strongly dependent on the pH of the treatment solution. The crystallinity of treated $AlPO_4^{5-}$ is highest at pH 7.0, but decreases above and below pH 7.0. The influence of pH on the crystallinity of $AlPO_4^{5-}$ becomes very pronounced at higher pH. Scanning electron microscopic examination of the $AlPO_4^{5-}$ treated at pH 11.5 indicates the development of cracks on the external surface of the crystals due to leaching during treatment.

The data in Table 3 show that both the bulk and surface concentrations of Al and P are affected by the pH of the treatment solution and the effect is more pronounced at higher pH (≥10.5).

The acidity of $AlPO_4^{5-}$ is strongly affected, particularly at higher pH (≥9.5) (Table 3). Figure 6 shows that the strength distribution of the pyridine adsorption sites shifts more and more toward the low-energy region as the pH of the treatment solution increases above 7.0 or decreases below 7.0.

Figure 7 shows the effects of the acid–base treatments of aluminophosphate on its cumene cracking and *o*-xylene isomerization activities at 673 K. The catalytic activity in both reactions passes through a maximum corresponding to pH 7.0 of the treatment solution. It may be noted that the catalytic activity is very adversely affected by treatment at higher pH (≥9.5). These results are consistent with those for N_2 sorption capacity, crystallinity, and acidity of the treated $AlPO_4^{5-}$.

CONCLUSIONS

Calcination of $AlPO_4^{5-}$ at higher temperatures (≥973 K) results in a small decrease in its crystallinity and also causes a phase transformation to tridymite to a very small extent. Its channel structure is stable even at 1433 K in spite of these minor changes. Its acidity and catalytic activity, however, decline sharply with the increase in calcination temperature from 813 to 1433 K.

Low-pressure water (35 Torr) treatment at 773 K for a prolonged period causes a significant decrease in the crystallinity, acidity, and catalytic activity of $AlPO_4^{5-}$. Its N_2 sorption capacity is, however, affected only to a very small extent. These properties, however, undergo a drastic change when $AlPO_4^{5-}$ is treated with high-pressure steam (16 atm) and liquid water at 473 K,

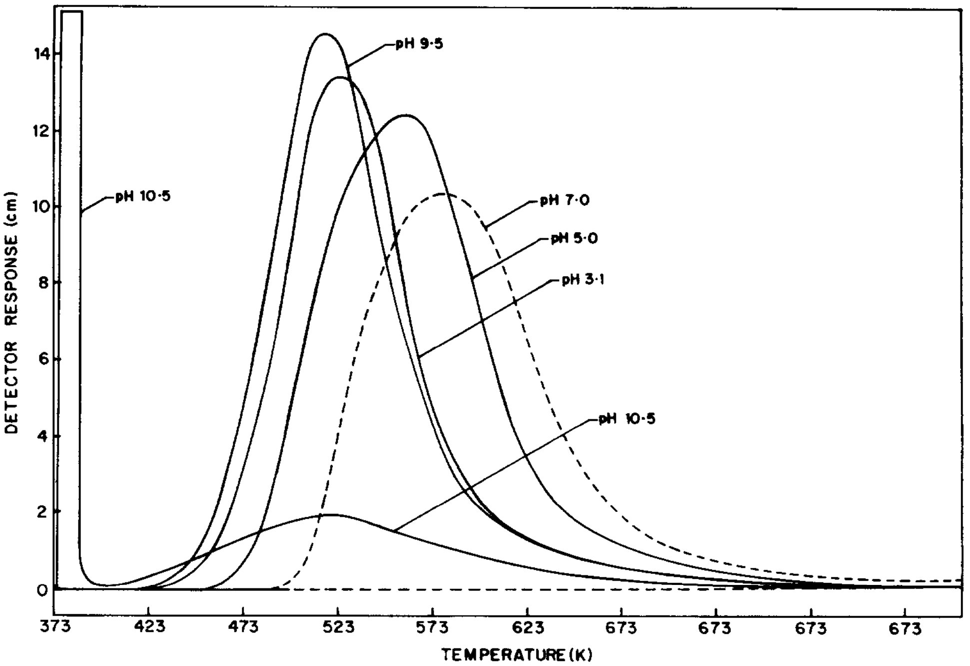

FIG. 6. TPD chromatograms of pyridine on $AlPO_4^{5-}$ treated with aqueous HCl or NaOH solution of different pH (amount of catalyst, 0.1 g; pyridine pulse size, 6.0 μl; heating rate, 10 K min^{-1}).

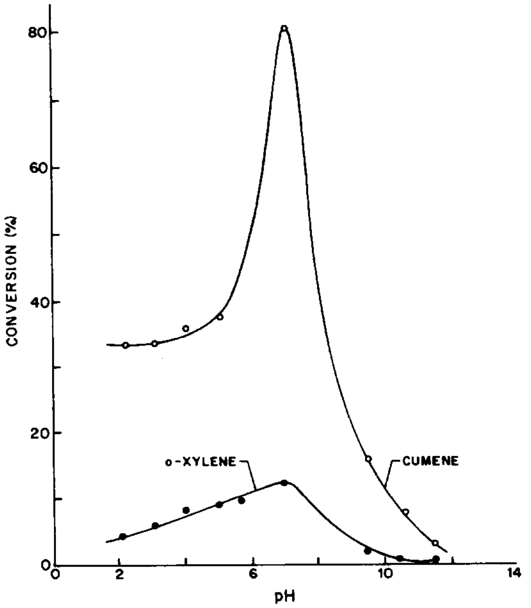

FIG. 7. Effect of pH (initial) of treatment solution on the catalytic activity of treated $AlPO_4^{5-}$ in cumene cracking and o-xylene isomerization reactions at 673 K (amount of catalyst, 0.1 g; N_2 flow rate, 60 cm^3 min^{-1}; pulse size, 1.0 μl).

because of the total collapse of the channel structure.

The structure and other properties of $AlPO_4^{5-}$ are very sensitive to acid–base treatment (that is, the pH of the treatment solution). $AlPO_4^{5-}$ dissolves completely in highly acidic ($pH \leq 1.0$) and highly basic ($pH \geq 12.5$) solutions. When treated with acid–base solutions in the pH range 2.2–11.5, it only partially dissolves at the higher ($pH > 9.5$) and lower ($pH < 5.0$) pH. Its crystallinity, surface properties, acidity, and catalytic activity are affected to a very significant extent by treatment with solutions of pH higher or lower than 7.0, and the effect is more pronounced for the treatment at higher pH.

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