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Comparison of the surface properties of the metal–oxygen cluster compounds, 12-tungstophosphoric acid and ammonium 12-tungstophosphate from the sorption of benzene, nitrogen and pyridine

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Abstract

The surface properties of ammonium 12-tungstophosphate and its parent acid, 12-tungstophosphoric acid have been evaluated from measurements of the adsorption of benzene, nitrogen and pyridine. Ammonium 12-tungstophosphate prepared from a number of different ammonium salts is found to have different surface areas, benzene sorption capacities and diffusivities and numbers of Brønsted acid sites, the latter as estimated from the sorption of pyridine. The surface areas, sorption capacities and acidity distributions of both the parent acid and ammonium 12-tungstophosphate show significant differences and are strongly influenced by duration calcination of its temperature and environment.

Key words: acidic properties; ammonium 12-tungstophosphate; heteropoly oxometalates; metal-oxygen cluster compounds; sorption, surface properties, 12-tungstophosphoric acid

Introduction

Metal–oxygen cluster compounds form a unique class of materials that possess both unusual and interesting catalytic properties [1–9]. The heteropoly oxometalates of Keggin structure, probably the most studied of these cluster compounds, have bifunctional catalytic capabilities in the sense that, depending on their elemental composition, they are active as either acidic or oxidation–reduction catalysts. The conversion of methanol to hydrocarbons has been shown to be catalyzed by the acidic forms of the metal–oxygen cluster compounds [5a,5b], the copper and silver salts of 12-tungstophosphoric acid [5c], by other metallic salts of the acid [5d] as well as the ammonium salt [5e,5f]. In contrast, 12-molybdophosphoric acid supported on silica converts methane to formaldehyde [6] and various salts of this acid are effective in the production of methacrylic acid from isobutyric acid [7–9].

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The anion of 12-tungstophosphoric acid ($H_3PW_{12}O_{40}$ abbreviated to HPW) has twelve octahedra with oxygen atoms at their vertices surrounding a central PO_4 tetrahedron (Fig. 1). A tungsten atom is positioned approximately at the centre of each octahedron. The four oxygen atoms of the central tetrahedron serve as bridges between the central phosphorus atom and the peripheral metal (tungsten) atoms. Twenty-four oxygen atoms bridge the pairs of peripheral metal atoms. Twelve oxygen atoms are bonded only to the tungsten atoms and protrude from the anions. As is evident from Fig. 1 these anions are large, high molecular weight, approximately spherical species. These are packed structures and consequently no atomic or molecular species are able to penetrate these anions.

Neutron and X-ray diffraction studies have shown that each proton in the hexahydrate of HPW is surrounded by four, approximately coplanar positions for the two water molecules (Fig. 2) [10]. As a consequence of a two-fold thermal disorder only two water molecules are hydrogen-bonded to the proton at a given time. The crystallographic structure of HPW is cubic (*Pn*3*m*) with the hydrogen atoms of the aforementioned water molecules hydrogen-bonded to the terminal oxygen atoms of the anions.

In the solid acidic forms of the heteropoly oxometalates, where protons serve as cations, the surface areas are of the order of 10 $m^2\,g^{-1}$ [5b]. Although the cagelike structures of the anions are packed and unable to receive foreign molecules, polar molecules such as ammonia, pyridine, and methanol can penetrate into the secondary or bulk structure of 12-tungstophosphoric acid, for example, and evidently form ammonium ions, pyridinium ions and protonated

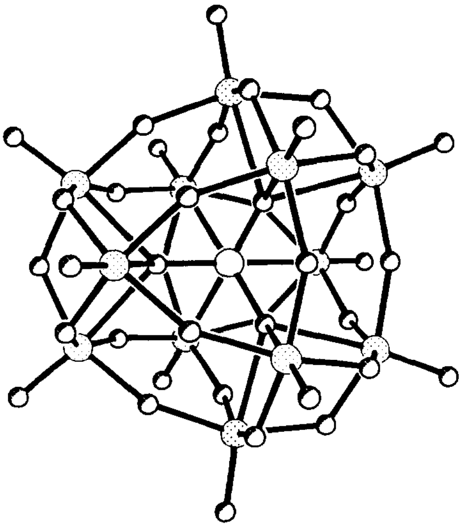

Fig. 1. Heteropoly oxometalate anion of Keggin structure; large circles: central atom (P) and peripheral metal atoms (W); small circles: oxygen atoms.

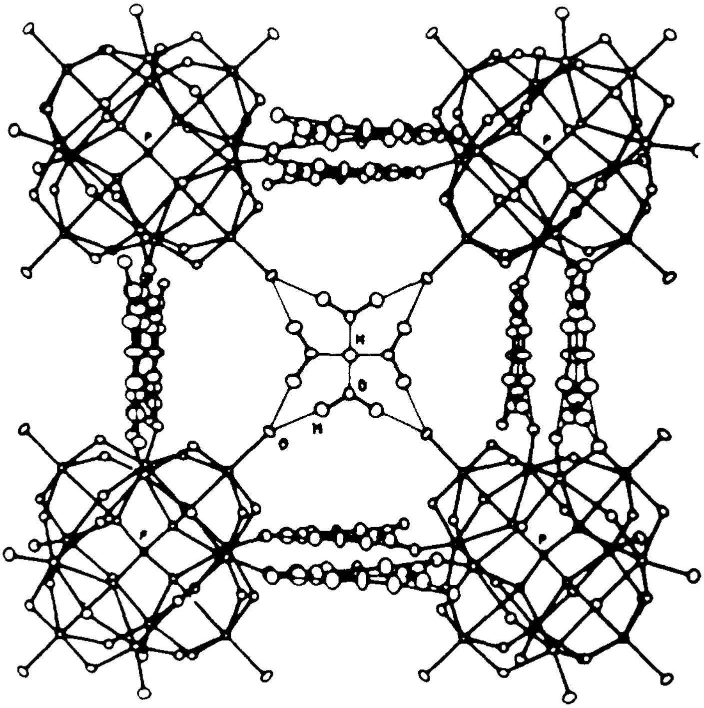

Fig. 2. Anion–cation configuration in $H_3PW_{12}O_{40} \cdot nH_2O$ [10].

methanol with the protons both on the surface and within the bulk structure [3,11–15].

Heteropoly oxometalates with microporous structures can be formed from the reaction of the acidic forms with some of the monovalent cations, such as NH_4^+ [14]. The ammonium salts have been shown to be nonstoichiometric in the sense that protons provide the charge balance for a deficiency in ammonium cations [11]. It is believed that these residual protons are the source of activity in the catalysis by ammonium 12-tungstophosphate [$(NH_4)_3PW_{12}O_{40}$ abbreviated to NH_4PW] of reactions such as the conversion of methanol [5] and of methylethylbenzene [16] and the alkylation of toluene [17]. Differential thermal analysis has shown that the salts of the metal–oxygen cluster compounds are of higher thermal stability than the parent acids [18a,18b]. Decomposition of the cation in NH_4PW has been shown to proceed by elimination of nitrogen, water and ammonia beginning at approximately 823 K [19] while the maximum in the TPD peak does not occur until 923 K.

Evidence exists to suggest that the distributions of acid strengths in ammonium 12-tungstophosphate and its parent acid are not identical [20]. The activities and selectivities of these two catalysts in the conversion of methanol are significantly different although the surface areas are also much larger with the former solid [5e,5f].

The present work is concerned with a comparison of the acidic and sorption properties of ammonium 12-tungstophosphate and its parent acid by studying the physisorption of benzene and the chemisorption of pyridine for samples of NH_4PW prepared from the parent acid and a number of different ammonium salts and calcined under various conditions. Additional information on the morphological and textural consequences of the preparative method has recently been reported [21]. Although the adsorption of pyridine on HPW has been studied previously in both this [12] and other laboratories [3] no detailed studies of the chemisorption and desorption of pyridine on NH_4PW have been reported previously.

Experimental

High purity chemicals, benzene (BDH-AnalaR), pyridine (Baker Analyzed), ammonium carbonate (Baker Analyzed), ammonium nitrate (Baker Analyzed) and ammonium sulphate (Baker Analyzed) were used without further purification. 12-Tungstophosphoric acid $H_3PW_{12}O_{40}$ (BDH AnalaR) was recrystallized before use. The ammonium salt of 12-tungstophosphoric acid, $(NH_4)_3PW_{12}O_{40}$, was prepared from different sources of NH_4^+ cation by treating an aqueous solution of $H_3PW_{12}O_{40}$ with stoichiometric quantities of aqueous solutions of different ammonium salts *viz.*, ammonium carbonate, ammonium chloride, ammonium nitrate, and ammonium sulphate. The resulting precipitates were washed several times with distilled water and dried in an air oven at 383 K for 3 h. $(NH_4)_2HPW_{12}O_{40}$ and $(NH_4)H_2PW_{12}O_{40}$ were prepared by treating aqueous solutions of HPW with two thirds and one third of stoichiometric quantities, respectively, of aqueous ammonium carbonate solution, evaporating to dryness over a steam bath and heating in an air oven at 383 K for 3 h. The morphology of the ammonium salts of HPW prepared by using different NH_4^+ sources was determined from scanning electron microscopy (JEOL-JSM-840). Sorption of pyridine and benzene were measured by a gravimetric method using a Cahn electrobalance fitted to a high vacuum system.

Approximately 25–30 mg of heteropoly oxometalates were used for sorption of pyridine, nitrogen, and benzene. In order to reduce the resistance to the external mass transfer and to the transfer of heat liberated upon sorption the solid samples were spread to form a single layer of crystals over the wide surface of an aluminum sample holder. The system could be evacuated to 10^{-4} mbar by the use of a Balzers mechanical pump and two mercury diffusion pumps connected in series. Any desired atmosphere could be maintained in the system by connecting to the respective storage bulbs (N_2, H_2 or air). The pressure in the system was measured with a Texas Instruments fused quartz precision pressure gauge.

The $(NH_4)_3PW_{12}O_{40}$ samples prepared by using different NH_4^+ sources and the partially ammoniated $(NH_4)_2HPW_{12}O_{40}$ samples were calcined at 523

K under vacuum for 2 h, prior to the adsorption of either nitrogen at 78 K or benzene at 323 K. For the adsorption of pyridine (323–723 K) all samples were pretreated at 723 K under vacuum for 2 h.

For studies of the effect of pretreatment temperature on surface area, sorption and diffusion of benzene and acidity distribution, the samples were heated at the required temperature under vacuum for 2 h. The effect of pretreatment duration was measured with samples heated at 723 K under vacuum for different required periods. The influence of pretreatment atmosphere was observed with calcined samples at 723 K for 2 h under different atmospheres.

The data on irreversible adsorption of pyridine were collected by first contacting the (pretreated) solid sorbent with pyridine vapour at 298 K and 20 mbar and degassing at the same temperature after the solid sorbent is completely saturated with pyridine, until no further decrease in weight of the solid samples occurs. The temperature of the sample was then increased in discrete temperature steps from 298 K to 323, 423, 523, 623, and 723 K allowing sufficient time after each temperature is attained to desorb the reversibly adsorbed pyridine (which was irreversibly adsorbed at 298 K) at that temperature.

Results

The anion accompanying the NH_4^+ ion in the preparation of the ammonium salt of HPW appears to have a marked influence on the properties of the resulting ammonium salt. The BET surface areas as measured by N_2 adsorption show that the NH_4PW sample prepared by NH_4Cl possesses maximum surface area when compared to other NH_4PW samples (Table 1). Regardless of the source of the ammonium ion, the surface areas of the NH_4PW samples are at least a factor of ten higher than those of the parent acid [5e,5f,14]. The order of surface areas of NH_4PW prepared from different sources of NH_4^+ is $NH_4Cl > NH_4NO_3 > (NH_4)_2CO_3 > (NH_4)_2SO_4$. The sorption of benzene on the

TABLE 1

Comparison of the properties of NH_4PW prepared from various anions

NH_4PW preparation source	BET surface area ($m^2\,g^{-1}$)[a]	Average crystal diameter (μm)	Characteristic length, L (μm)	Benzene sorption capacity[b] ($mmol\,g^{-1}$)	Diffusivity of benzene, D ($cm^2\,s^{-1}$) $\times 10^{11}$
$(NH_4)_2CO_3$	112	0.70	0.117	0.22	4.1
NH_3Cl	162	0.80	0.133	0.50	3.2
NH_4NO_3	143	0.90	0.155	0.49	3.4
$(NH_4)_2SO_4$	85	1.2	0.200	0.30	3.8

[a] After calcination at 523 K for 2 h.
[b] At 50 mbar and 323 K.

different NH_4PW samples at 323 K is almost reversible (Fig. 3). The benzene sorption capacities (total amount of benzene adsorbed at the stated temperature and pressure) of NH_4PW samples prepared from NH_4Cl and NH_4NO_3 are much higher than those of NH_4PW samples prepared from $(NH_4)_2CO_3$ and $(NH_4)_2SO_4$ (Table 1). The sorption capacity of NH_4PW prepared from NH_4Cl is only slightly higher than that of NH_4PW prepared from NH_4NO_3. The order of sorption capacities of NH_4PW samples for benzene at 343 K is $NH_4Cl \approx NH_4NO_3 > (NH_4)_2SO_4 > (NH_4)_2CO_3$. The sorption capacities of the NH_4PW samples for benzene, regardless of their source, are approximately tenfold those of the parent acid [22].

The diffusivities of benzene calculated by application of a method described previously [22] are listed in Table 1. It is interesting to note that the orders of magnitude of the diffusivity of benzene on NH_4PW samples are similar regardless of the source of NH_4^+. As expected, the diffusivity (D) of benzene on the parent acid (HPW) (2.5×10^{-11} cm^2 s^{-1}) is smaller than those measured for the ammonium salts [22], although it should be noted that the value for HPW was obtained at 293 K.

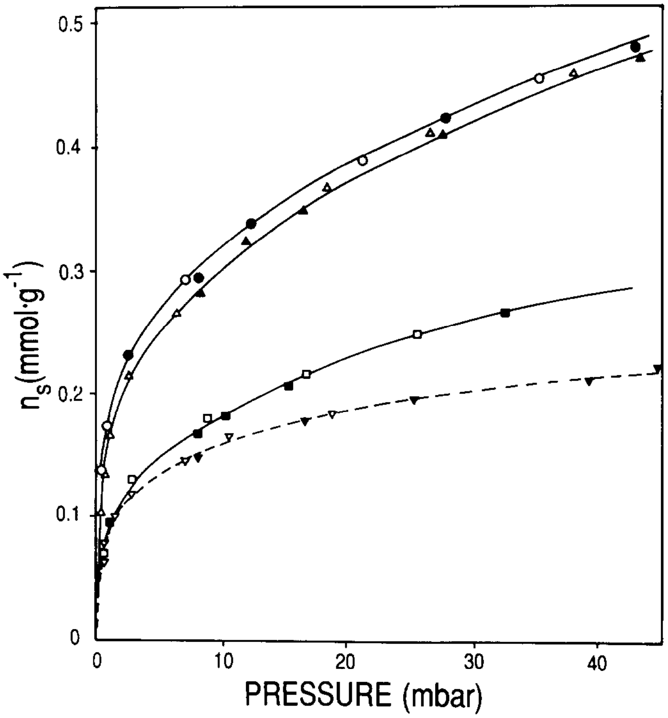

Fig. 3. Adsorption isotherms of benzene at 323 K on $(NH_4)_3PW_{12}O_{40}$ prepared from different sources of ammonium ions (●, ○) NH_4Cl; (▲, △) NH_4NO_3; (■, □) $(NH_4)_2SO_4$; (▼, ▽) $(NH_4)_2CO_3$. Closed symbol: adsorption; open symbol: desorption.

The amounts of irreversibly held pyridine on NH_4PW samples, prepared from different NH_4^+ sources and pretreated at 723 K under vacuum for 2 h at different temperatures are shown in Fig. 4. As expected, the number of irreversibly adsorbed pyridine molecules decreases with increase in temperature in all cases. Earlier work has shown that the acid sites of NH_4PW and HPW are Brønsted in nature [11,12] and consequently in the present work one chemisorbed pyridine molecule is assumed to be equivalent to one Brønsted acid site. In order to provide estimates of the numbers and strengths of acidic sites on and in the catalyst, the total number of Brønsted acid sites and the number of strong acid sites are assumed to be equal to the numbers of pyridine molecules remaining on and in the catalyst at 389 K (the boiling point of pyridine) and 623 K, respectively.

The number of Brønsted acid sites on the ammonium salts ranges from 1.3 to 1.6 per heteropoly anion (KU) with NH_4PW prepared from the sulfate and the carbonate having the largest number followed by those made from the chloride and the nitrate ($(NH_4)_2SO_4 \sim (NH_4)_2CO_3 > NH_4Cl > NH_4NO_3$) where the formulae represent the reagents from which NH_4PW was prepared. In contrast, the number of strong acid sites falls in the order $(NH_4)_2CO_3 > NH_4Cl > NH_4NO_3 > (NH_4)_2SO_4$.

In contrast to the observations with $(NH_4)_3PW_{12}O_{40}$, the surface areas

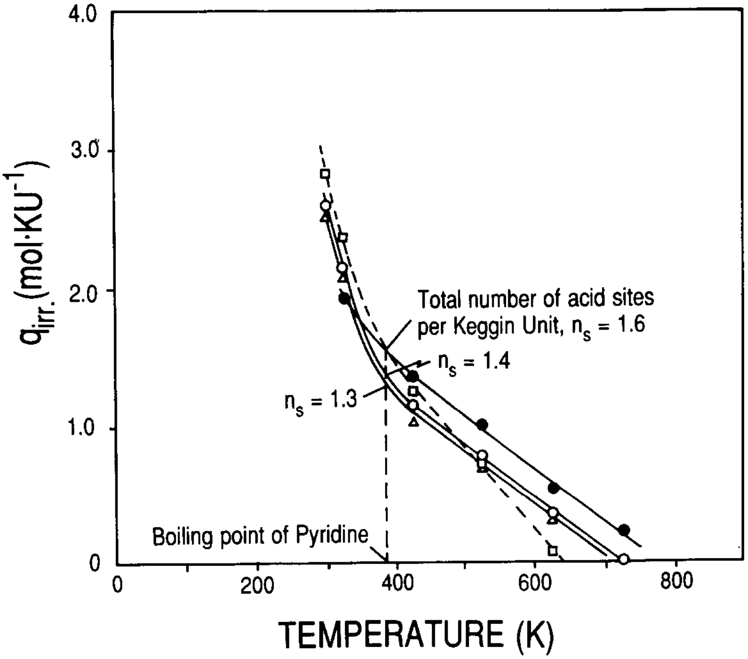

Fig. 4. Dependence of number of irreversibly adsorbed pyridine molecules on temperature for $(NH_4)_3PW_{12}O_{40}$ calcined at 723 K under vacuum for 2 h and prepared from different sources of NH_4^+ (○) NH_4Cl; (△) NH_4NO_3; (□) $(NH_4)_2SO_4$; (●) $(NH_4)_2CO_3$.

for $(NH_4)_2HPW_{12}O_{40}$ and $NH_4H_2PW_{12}O_{40}$ are similar to that for the parent acid $H_3PW_{12}O_{40}$ and are thus indicative of the absence of explicit microporosity (not shown). As expected, small but similar sorption capacities for benzene at 323 K are found for the latter three solids, again in contrast with that for $(NH_4)_3PW_{12}O_{40}$.

The amounts of sorbed pyridine on the $(NH_4)_{3-x}H_xPW_{12}O_{40}$ ($x=0, 1, 2$) and the parent acid show a wider spread in values than found with the four $(NH_4)_3PW_{12}O_{40}$ salts prepared from the different ammonium sources (compare Figs. 4 and 5). At 389 K, for example, the number of sorbed pyridine molecules ranges from 1.6 to 2.8 (Fig. 5) with, not surprisingly, the parent acid possessing the largest number followed by $NH_4H_2PW_{12}O_{40}$. The two salts $NH_4HPW_{12}O_{40}$ and $(NH_4)_3PW_{12}O_{40}$ both sorb approximately 1.6 pyridine molecules at 389 K. The amounts of sorbed pyridine remaining with the catalysts at temperatures higher than approximately 400 K again decrease approximately linearly with increase in temperature.

The surface area of NH_4PW increases from 102 to 112 $m^2\ g^{-1}$ as the pretreatment temperature increases from 423 to 523 K, but decreases to 30 $m^2\ g^{-1}$ as the temperature is raised to 923 K (Table 2). The surface area is also altered

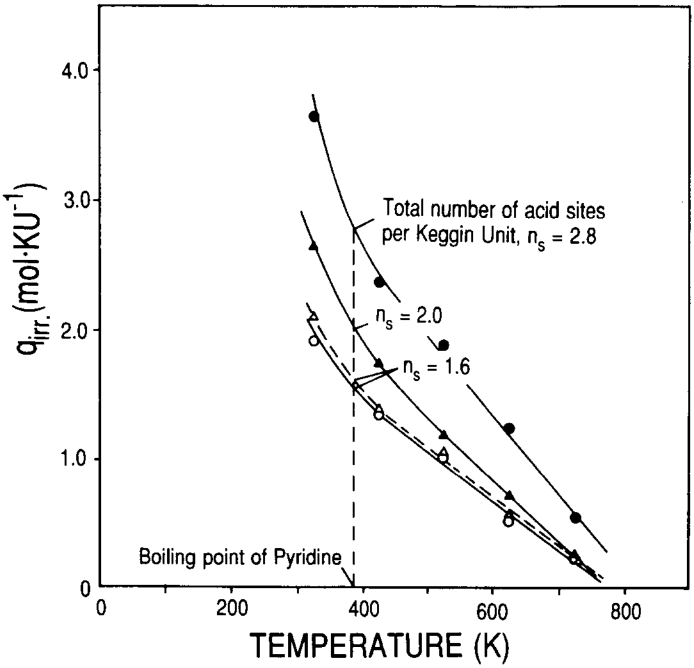

Fig. 5. Dependence of amount of irreversibly adsorbed pyridine on temperature for $H_3PW_{12}O_{40}$ and its ammonium salts with different degrees of NH_4^+ exchange (●) $H_3PW_{12}O_{40}$; (▲) $NH_4H_2PW_{12}O_{40}$; (△) $(NH_4)_2PW_{12}O_{40}$; (○) $(NH_4)_3HPW_{12}O_{40}$ after calcining at 723 K under vacuum for 2 h.

TABLE 2

Effect of calcination temperature and atmosphere on surface area, benzene sorption capacity and diffusivity of NH_4PW

Temperature (K)	BET surface area ($m^2 g^{-1}$)	Benzene sorption capacity ($mmol\ g^{-1}$)[a]	Diffusivity of benzene[b] D ($cm^2 s^{-1}$) $\times 10^{11}$
423	102[c]	0.207	4.0
523	112[c]	0.212	4.1
623	81[c]	0.182	4.0
723	66[c]	0.165	3.9
823	55[c]	0.147	3.4
923	30[c]	0.110	3.0
723	44[d]	0.14	3.4
723	28[e]	0.10	2.7
723	21[f]	0.08	2.7

[a] At $P = 50$ mbar and $T = 323$ K.
[b] At 323 K.
[c] In vacuum for 2 h.
[d] In air for 2 h.
[e] In nitrogen for 2 h.
[f] In hydrogen for 2 h.

by a change in the atmosphere in which the heating takes place. For a temperature of 523 K the highest surface area is obtained after a pretreatment in vacuum for 2 h, while use of air, nitrogen, and hydrogen yield smaller values in that order. Earlier temperature-programmed desorption studies showed no loss of NH_3 up to 823 K.

The adsorption isotherms of benzene measured at 323 K on NH_4PW preheated in vacuum for 2 h at temperatures from 423 to 923 K are reversible (not shown). The sorption capacities and diffusivities correlate, as expected, with the surface areas (Table 2) for changes in the pretreatment temperature, although the differences observed in the former are much greater than those of the latter.

The quantities of pyridine remaining sorbed on NH_4PW and HPW after heating to various temperatures depend on the pretreatment temperature (Figs. 6A and 6B). For 389 K, for example, the amount of pyridine sorbed on NH_4PW increases from approximately 0.15 molecules KU^{-1} after a pretreatment at 423 K to 1.5 molecules KU^{-1} after a pretreatment at 723 K and for further increase in pretreatment temperature to 823 K decreases to approximately 0.4 KU^{-1}. A similar maximum in the amount of sorbed pyridine at 389 K is observed with HPW after pretreatment at 723 K but the quantity remaining is considerably higher (2.8 molecules KU^{-1}) than is found under the same conditions with NH_4PW.

The quantities of pyridine remaining sorbed on HPW and NH_4PW at various temperatures after pretreatment of the catalysts at 723 K for various

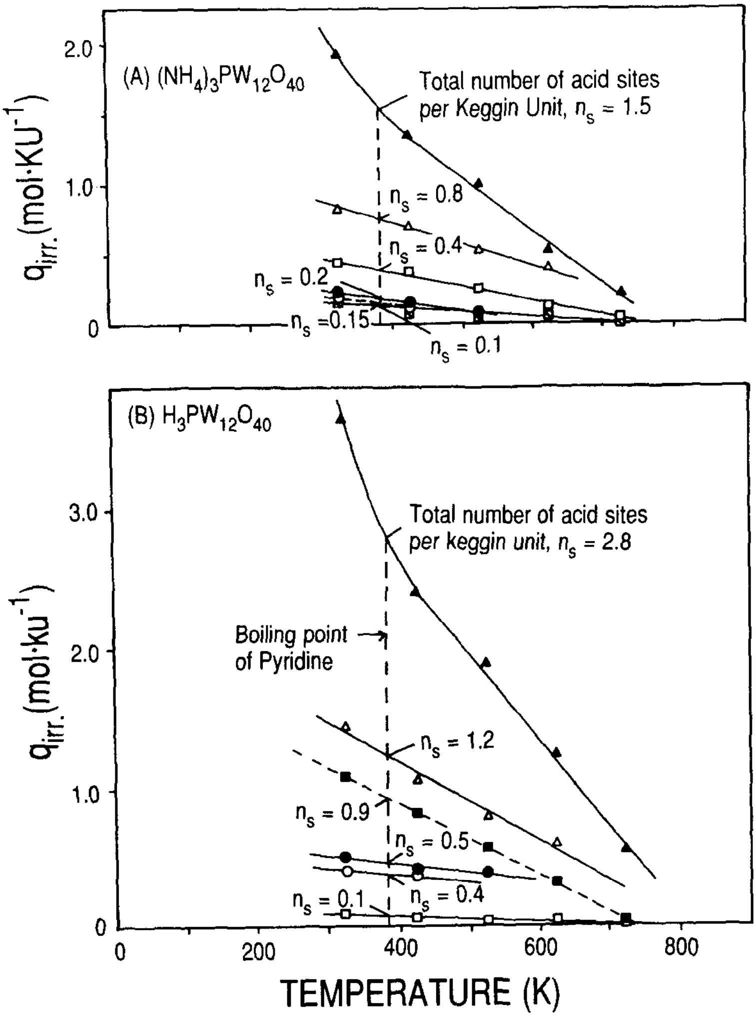

Fig. 6. Effect of calcination temperature on the acidity distributions of $(NH_4)_3PW_{12}O_{40}$ (A) and $H_3PW_{12}O_{40}$ (B) (○) 423; (●) 523; (△) 623; (▲) 723; (□) 823; (■) 923 K for NH_4PW and (■) 823 K for HPW treated with water vapour, after calcining under vacuum for 2 h.

lengths of time are shown in Tables 3 and 4. With HPW and at any given temperature the quantities of pyridine remaining sorbed decrease with increasing length of pretreatment time, from 3.1 KU^{-1} after 1 h to 2.0 KU^{-1} after 70 h at a desorption temperature of 389 K, the decrease becoming less substantial with increasing pretreatment duration. Approximately linear decreases of quantities of pyridine sorbed with increasing desorption temperatures above 400 K are observed for all pretreatment durations.

In contrast to the observations with HPW, with NH_4PW the quantity of

TABLE 3

Effect of calcination period at 723 K on acidity distribution of $H_3PW_{12}O_{40}$

Calcination period[a] (h)	Amount of pyridine irreversibly adsorbed, q_{irr} (molecules KU^{-1}) at different temperatures (K)					
	323	389[b]	423	523	623	723
1	4.28	3.1	2.75	2.15	1.45	0.62
2	3.64	2.7	2.37	1.90	1.25	0.54
4	3.31	2.5	2.23	1.74	1.12	0.48
7	3.14	2.4	2.10	1.71	1.09	0.48
24	2.74	2.2	1.90	1.49	0.95	0.38
70	2.43	2.0	1.71	1.25	0.83	0.29

[a] At 723 K.
[b] n_s by interpolation.

TABLE 4

Effect of calcination period at 723 K on acidity distribution of $(NH_4)_3PW_{12}O_{40}$

Calcination period[a] (h)	Amount of pyridine irreversibly adsorbed, q_{irr} (molecules KU^{-1}) at different temperatures (K)					
	323	389[b]	423	523	623	723
1	1.62	1.2	1.07	0.78	0.43	0.14
2	1.93	1.5	1.34	1.02	0.53	0.23
4	2.45	2.0	1.82	1.30	0.91	0.44
7	3.94	2.8	2.44	1.93	1.35	0.64
24	4.48	3.1	2.69	2.17	1.50	0.71
70	3.65	2.6	2.26	1.88	1.37	0.66

[a] At 723 K.
[b] n_s by interpolation.

pyridine sorbed increases with pretreatment duration up to 24 h and, for times of 70 h decreases.

The gaseous environment in which the pretreatment takes place also appears to have a substantial effect on the properties of NH_4PW and HPW (Tables 5 and 6). The surface areas and benzene sorption capacities and diffusivities of NH_4PW pretreated in different atmospheres decrease in the order: vacuum > air > nitrogen > hydrogen. The total number of acid sites and the number of strong acid sites for NH_4PW follows the order: vacuum > air > hydrogen > nitrogen whereas for HPW the order is: air > nitrogen > vacuum > hydrogen. Evidently, hydrogen is the least favourable atmosphere for the pretreatment of HPW, as the total number of acid sites and the number of strong acid sites of HPW pretreated in a hydrogen

TABLE 5

Effect of calcination atmosphere at 723 K on acidity distribution of $H_3PW_{12}O_{40}$

Calcination atmosphere	Amount of pyridine irreversibly adsorbed, q_{irr} (molecules KU^{-1}), at different temperatures (K)					
	323	389[b]	423	523	623	723
vacuum	3.64	2.8	2.37	1.90	1.25	0.54
nitrogen	3.74	2.9	2.61	2.04	1.46	0.78
air	4.20	3.3	3.04	2.35	1.71	0.94
hydrogen	0.38	0.3	0.28	0.22	0.19	0.15

[a] At 723 K.

[b] n_s by interpolation.

TABLE 6

Effect of calcination atmosphere at 723 K on acidity distribution of $(NH_4)_3PW_{12}O_{40}$

Calcination atmosphere[a]	Amount of pyridine irreversibly adsorbed, q_{irr} (molecules KU^{-1}), at different temperatures (K)					
	323	389[b]	423	523	623	723
vacuum	1.93	1.6	1.34	1.02	0.53	0.23
nitrogen	0.31	0.25	0.20	0.15	0.04	0.00
air	0.86	0.5	0.43	0.22	0.06	0.00
hydrogen	0.35	0.3	0.24	0.16	0.05	0.00

[a] At 723 K.

[b] n_s by interpolation.

atmosphere are much lower than those of HPW pretreated in other atmospheres.

Discussion

Interest in a comparison between 12-tungstophosphoric acid and its ammonium salt arises from a number of contrasting features of these two solids. The parent acid HPW has a low surface acid (approximately 10 $m^2 g^{-1}$) and no explicit porosity while its ammonium salt (NH_4PW) has a significantly larger surface area and microporosity [14]. As has been suggested earlier [14] the microporosity in NH_4PW appears to result from a rotation and translation of the metal–oxygen cluster anions so that the barriers separating the interstitial voids which are present in the parent acid are at least partially removed, thus permitting the formation of channels between the cations and anions.

In addition both the parent acid and the ammonium salt have been shown to catalyze the conversion of methanol to hydrocarbons, thus indirectly demonstrating the presence of acid sites, but both the activity and selectivity of the ammonium salt are superior to that of the parent acid [5e]. Photoacoustic FT-IR has been employed to show that ammonium 12-tungstophosphate, although prepared to be stoichiometric, contains nonstoichiometric quantities of the ammonium and tungstophosphate ions, the charge balance being established by residual protons [11]. The presence of protons will reduce, but not eliminate, the porosity and thereby reduce both the sorption capacity and the surface area. Thus, in the present work, the dependence of the surface areas on the source of the ammonium ion may be related, in part, to the presence of residual protons.

Since the ammonium salts of HPW can be conveniently prepared by precipitation from an aqueous solution of the parent acid and a water-soluble ammonium salt, the dependence of the properties of the resulting precipitate on the source of the ammonium cation, that is, the accompanying anion, is of considerable interest. The present work has examined four different ammonium salts, the carbonate, chloride, nitrate and sulphate. While the surface areas, benzene sorption capacities and diffusivities of NH_4PW prepared from the chloride and the nitrate are similar, those of the samples precipitated from the carbonate and the sulphate are significantly different from each other and the former two preparations.

While it is not possible from the data available to fully interpret such results, it appears that the preparative anion has an influence on the pore structure of the resulting solid. Since the equilibrium associated with the preparative process is, in practice, shifted by the precipitation, the solubility product will indirectly be related to the concentration of the preparative anions, which itself will be determined by any secondary equilibrium process in which these anions can participate. In the present system no such secondary equilibrium process (involving protons) appears to be possible for the chloride and nitrate anions, in contrast to the carbonate and sulphate anions. Thus the primary equilibrium process, in which NH_4PW is produced and precipitated may be retarded when the latter two anions are present, resulting in precipitates which contain additional residual protons and hence, less microporosity. The observation that the diffusivities of benzene are virtually independent of the preparative anion suggests that the reduction in microporosity results from the closing of pores rather than changes in pore diameters and is consistent with the aforementioned rationalizations. The observations (Fig. 4) that the total number of pyridine molecules held at 398 K on NH_4PW prepared from the carbonate and sulphate are similar (1.6 per anion) while those on NH_4PW from the chloride and nitrate are smaller (1.4 and 1.3 per anion, respectively), provides additional support for these conclusions.

The surface area and sorption capacity data on partially and completely neutralized $H_3PW_{12}O_{40}$ samples show that only $(NH_4)_3PW_{12}O_{40}$ is highly microporous. This is consistent with the aforementioned hypothesis concerning the source of the microporosity. The presence of residual quantities of protons is evidently sufficient to allow some of the anions to relax to the positions and orientations found in the acidic structure thus severing the connection between the interstitial voids. PAS FT-IR studies have shown that the relative amounts of NH_3/H are 2.6/0.4 in NH_4PW [11]. Thus the similarity in the amounts of irreversibly adsorbed pyridine at various temperatures for $(NH_4)_3PW_{12}O_{40}$ and $(NH_4)_2HPW_{12}O_{40}$ can be at least partially related to residual protons in the former material.

With the increase in pretreatment temperature of NH_4PW the surface area and the sorption capacity increase. Earlier temperature-programmed desorption studies on HPW have shown the existence of two peaks, one with a maximum at approximately 473 K the other at 773 K [19]. Both peaks were shown to be due to water; that appearing at the lower temperature due to molecularly adsorbed water, the upper to water resulting from the abstraction of oxygen atoms from the heteropoly anions by the acidic protons. Consequently, it appears that the initial increase in surface area and sorption capacity found for NH_4PW is due to the removal of residual water molecules from the pores. With further increase in pretreatment temperature above 523 K the surface area and benzene sorption capacity decrease presumably due to either pore shrinkage or peripheral sintering effects. However, with increase in the pretreatment temperature of HPW, the number of Brønsted sites increases markedly, presumably as a result of removal of the water molecules blocking approach to the protons. The decrease in the number of Brønsted sites on HPW at temperatures higher than 723 K is consistent with the results from the temperature-programmed desorption studies.

As noted earlier one chemisorbed pyridine molecule has been assumed, in the present report, to be equivalent to one Brønsted acid site. It should be recalled parenthetically, that all Brønsted sites, both those on the surface and the bulk, are available to the pyridine molecules. Some amplification of the basis for this assumption is relevant and appropriate. PAS FT-IR studies have shown that, at room temperature, HPW sorbs up to 6 pyridine (py) molecules per Keggin unit to form the dimer cation $(pyHpy)^+$ [12] and further, exchange studies show that the pyridine molecules in the dimer cation are equivalent. Above 373 K the dimer cation is converted to the pyridinium ion $(pyH)^+$ with, of course, loss of pyridine to the gas phase. Although the aforementioned assumption is strictly valid only for temperatures below 373 K it is convenient to retain the same py/H^+ ratio throughout the present discussion since most of the presently reported results have been obtained at temperatures above this latter value. It may be noted that values for the total number of irreversibly sorbed pyridine molecules greater than 3 (the stoichiometric number for 12-tungstophosphoric acid) are found only for temperatures of 300 K, consistent with the previous observations.

With either HPW or NH_4PW, the total number of acid sites per Keggin unit (that is, the number of irreversibly adsorbed pyridine molecules) remaining at 389 K are less than or equal to 3, the stoichiometric number. With NH_4PW, not surprisingly, this value is generally less than that found with HPW under otherwise identical conditions. With both solids the apparent number of acid sites decreases with increasing temperature, as expected.

As the calcination temperature is increased by 100 degree increments with either HPW or NH_4PW, the number (n_s) of pyridine molecules per KU remaining adsorbed at 389 K increases. At a calcination temperature of 723 K, with either HPW or NH_4PW, n_s reaches a maximum, 2.8 or 1.5, respectively, and for further increases in calcination temperature, decreases. The similarity of these temperatures for both HPW and NH_4PW suggests that the processes leading to the increase and decrease in the number of acid sites are similar for both solids, namely, the loss of water molecules guarding the protons and the loss of protons as water, respectively. However, after calcination at 823 K, values of n_s equal to 0.4 and 0.1 for NH_4PW and HPW, respectively, are observed, indicative of a larger number of acid sites with the former solid, at least under these conditions.

The quantities of irreversibly held pyridine after various durations of calcination at 723 K change in markedly different fashions for HPW and NH_4PW. With HPW, n_s decreases steadily with increasing calcination duration from 3.1 after 1 h to 2.0 after 70 h. In contrast, with NH_4PW, n_s increases with increasing calcination duration at 723 K from 1.2 after 1 h to 3.1 after 24 h and subsequently decreases to 2.6 after 70 h. As noted earlier TPD studies have shown that decomposition of the cation in NH_4PW begins to occur at approximately 823 K. The conditions under which the effect of the duration of calcination was measured were chosen to be sufficiently severe as to remove protons as water through the previously described process. It should be noted that the earlier TPD studies employed a stream of helium whereas reduced pressures were employed in the present calcination experiments to remove any desorbed gases and consequently the latter conditions are expected to be more severe than the former. It is therefore possible to visualize, with NH_4PW, the partial elimination of ammonia, but not necessarily as ammonia, in the earlier stages of the calcination, followed by the removal of protons as water at later periods. It is interesting to note however that, after a calcination at 723 K for 70 h, the quantity of pyridine remaining adsorbed at 723 K on NH_4PW is more than twofold that on the parent acid.

Pretreatment of NH_4PW at 723 K in a hydrogen atmosphere results in a decrease in surface area, benzene sorption capacity and Brønsted acidity. Earlier temperature-programmed reduction and exchange experiments showed that hydrogen is sorbed by the catalyst with production of water at temperatures similar to those at which oxygen was stripped from the heteropoly anions in the TPD experiments [19]. Thus the results of pretreatment in hydrogen as found in the present work may also be due to removal of lattice oxygen to form water. When the pretreatment is carried out in air the extraction of terminal oxygen atoms may be reduced resulting in higher values of surface area, benzene sorption capacity and Brønsted acidity than those of NH_4PW pretreated in hydrogen. However, with the pretreatment of NH_4PW in nitrogen the oxidation of desorbed ammonia will presumably involve the extraction of terminal anionic oxygen atoms to a greater extent than that observed with pretreatment in air but to a lesser extent than found in hydrogen. Earlier PAS FT-IR studies have shown that Keggin structures remain with HPW even after heating in vacuo at 723 K, although the intensities of the characteristic bands are diminished somewhat [11–13]. With NH_4PW even at 773 K the detail in the spectrum indicates some retention of the anion structure although the appearance of a shoulder at 1260 cm^{-1} and an increase in background absorption below 1200 cm^{-1} are characteristic of WO_3. Consequently, in the present work, the

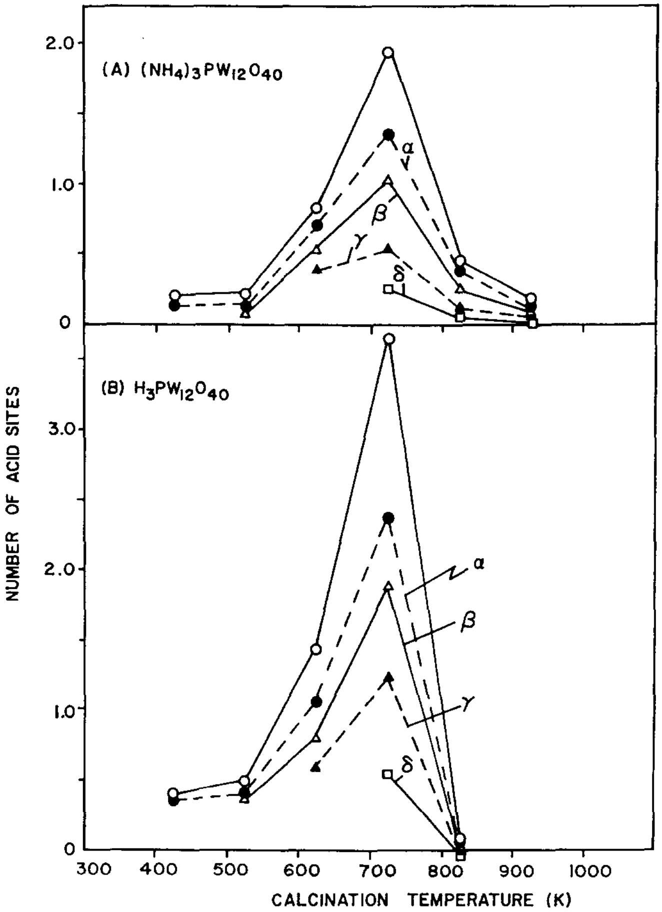

Fig. 7. Dependence of acid site strength distribution of $(NH_4)_3PW_{12}O_{40}$ (A) and $H_3PW_{12}O_{40}$ (B) on calcination temperature. ○, ●, △, ▲ and □ represent number of acid sites which can adsorb pyridine irreversibly at 323, 423, 523, 623, and 723 K, respectively.

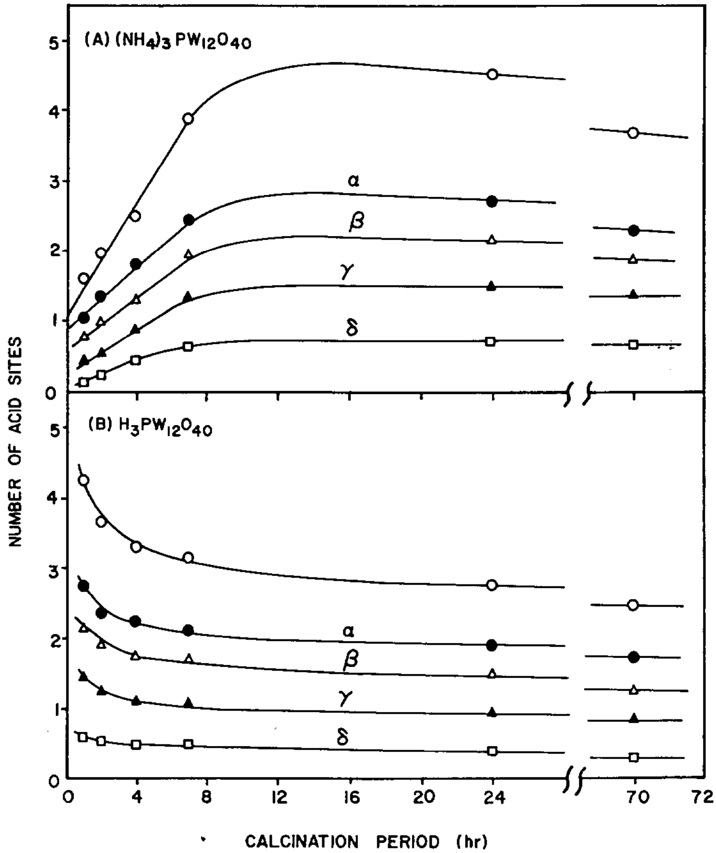

Fig. 8. Dependence of acid site strength distribution of (A) $(NH_4)_3PW_{12}O_{40}$ and (B) $H_3PW_{12}O_{40}$ on calcination period at 723 K under vacuum. ○, ●, △, ▲, and □ represent number of acid sites which can adsorb pyridine irreversibly at 323, 423, 523, 623, and 723 K, respectively.

possibility that application of temperatures of 673 K produces some degradation of the Keggin structures cannot be dismissed.

While the number of acid sites can, in the present work, be equated at least approximately to the number of pyridine molecules irreversibly sorbed on and in the metal–oxygen cluster compounds, it is also useful to have some measure of the strengths of the acid sites. With the reasonable assumption that the acidic strength increases with the temperature at which pyridine molecules are irreversibly sorbed, sets of acidic strengths can be classified. For convenience, the number of sites which can sorb pyridine irreversibly at 423, 523, 623 and 723 K will be labelled as $\alpha, \beta, \gamma, \delta$, respectively. It should be noted that a particular group contains, by definition, all those acidic sites in the groups referring to higher temperatures. With both NH_4PW and HPW the numbers of acid sites within each group increase exponentially with pretreatment temperature (PT) up to approximately 723 K (Fig. 7) and decrease with further increase in PT. By 823 K the numbers of acidic sites on HPW have diminished to a small fraction of the values at 423 K while those on NH_4PW remain appreciable for PT up to 923 K.

The data shown in Tables 3 and 4 are partitioned into the groups α, β, γ, δ and plotted versus calcination period in Fig. 8. With HPW the number of acid sites belonging to the four groups decreases sharply at 723 K during the initial pretreatment periods, and then decrease slowly after approximately 12 h. It is important to note that, for example, after a calcination at 723 K for 70 h, the quantitites of pyridine remaining sorbed on NH_4PW at the temperatures ranging from 323 to 723 K are at least 50% higher than those on HPW under the same conditions. Thus the superior catalytic properties of NH_4PW, relative to those of HPW are, at least in part, attributable to both a larger number of acid sites as well as a larger number of stronger acid sites. It is, of course, not possible from the present data to determine which of these two factors is the more important in the methanol process.

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