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Acidity of Heteropoly Compounds

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The acidity of 12-tungstophosphoric acid (HPW) and its salts of Na, Ca, Mg, Zn, Al, and Zr and of 12-tungstosilicic acids (HSiW) and its salts of NH_4 and Cs under different pretreatment conditions was determined by using an indicator method. The acid strength of the salts of HPW was found to increase with increase of the calculated charge on the peripheral oxygen atom of the anion, in the order of Zr > Al > Zn > Mg > Ca > Na. The number of acid sites decreases exponentially with the charge beginning with H and ending with Na. As the pretreatment temperature of HPW and HSiW is increased, the measured number of most strongly acidic sites ($H_0 = -5.6$) increases up to approximately 673 K, apparently due to the elimination of water molecules previously guarding the proton. With further heating above 673 K, the number of such strongly acidic sites diminishes abruptly to values of approximately zero, presumably as a result of deprotonation of the acids. The numbers of less strongly acidic sites remain relatively unchanged with pretreatment temperature up to 673 K. Changes in the pretreatment environment produced relatively few differences in the distributions of acidic sites.

INTRODUCTION

Heteropoly acids and their salts have been used as catalysts for reactions such as selective oxidation (*1–3*) and the conversion of methanol to hydrocarbons (*4–10*), the latter apparently involving carbocation intermediates which are formed and stabilized on surface acid sites. Infrared photoacoustic spectroscopic (PAS) investigations (*11–14*) of 12-tungstophosphoric acid and a number of its salts using ammonia and pyridine as probe molecules have shown, as expected, the presence of Brønsted acidity, consistent with their activity in the methanol conversion process (*7–10*). Although ammonia was readily sorbed on 12-tungstophosphoric acid, the sorption of pyridine was inhibited by hydrogen bonded water (*11–15*). The amount of pyridine taken up increased as the pretreatment temperature increased to 463–593 K, but thereafter decreased as the temperature was further increased, as a consequence of the loss of protons.

From temperature-programmed desorption (TPD) measurements (*13, 15, 16*) it has been found that water, apparently existing molecularly in the solid and presumably in hydrogen-bonded form, desorbs in the range from 373 to 523 K, while protons can be lost as water from 12-tungstophosphoric acid (HPW), 12-tungstosilicic acid (HSiW), and 12-molybdophosphoric acid (HPMo) by their reaction with anionic oxygen atoms at sufficiently high temperatures (623–773 K). However, X-ray diffraction and PAS data suggest that the Keggin structure is largely retained even after loss of such oxygen atoms.

The calcination temperature and environment (air, helium, and hydrogen) have been shown to have considerable effect on the catalytic activity of 12-tungstophosphoric acid and its ammonium salt in the conversion of methanol to hydrocarbons (*7–10*). Calcination in air considerably reduces the activity of the catalyst, possibly due to extraction of acidic sites by oxygen, while that in hydrogen or helium produces an enhanced yield of hydrocarbons. The latter effect may result from a shift in the distribu-

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tion of acid sites due to a loss of the more highly acidic protons.

The catalytic activity and selectivity of heteropoly compounds is dependent on both the cation and the anion (*7–10, 17*). Although the central or heteroatom of the anion cannot be completely ignored, the influence of the peripheral atoms is particularly important. It has been shown that both HPW and HSiW are effective catalysts in the conversion of methanol to hydrocarbons, while HPMo produces primarily undesirable oxidation products. This appears to be consistent not only with TPD data (*13, 15, 16*) which shows that protons may be extracted from HPMo more easily than from either HPW or HSiW, possibly due to both less strongly bound protons and/or anionic oxygen atoms, but also the results of extended Hückel calculations (*18–21*) which predict that the magnitude of the charge on the terminal oxygen atoms in HPMo is higher than that in either HPW or HSiW, while the bond-partitioned energy of the same oxygen atoms to the peripheral metal atoms of the anion is smaller for the former than the latter two. The former parameter inversely reflects the Brønsted acidity, while the latter provides a measure of the lability of the anionic terminal oxygen atom.

The present work involves 12-tungstophosphoric acid and its salts of Na^+, Ca^{2+}, Mg^{2+}, Zn^{2+}, Al^{3+}, and Zr^{4+} and 12-tungstosilicic acid and its salts of NH_4^+ and Cs^+. The study reports the determination of acidity by using an indicator method. The effect of pretreatment temperature and environments (nitrogen, air, and hydrogen) on the acidity have also been examined.

EXPERIMENTAL

Materials

12-Tungstophosphoric acid and its Na, Ca, Zn, Mg, Al, and Zr salts were used. HPW (BDH AnalaR grade) was used without further purification. The preparation of the salts has been described elsewhere (*8*). The salts of Na, Ca, Mg, and Zn were previously prepared from an aqueous solution of HPW by addition of stoichiometric quantities of the carbonates or basic carbonates. Salts of Al and Zr were prepared by the reaction of the alkoxides with the acid. 12-tungstosilicic acid as obtained from Baker Chemicals Company (Baker Analyzed Reagent) was used. The NH_4 and Cs salts of HSiW were prepared earlier and the procedure has been described elsewhere (*22*).

Catalyst Pretreatment

The salts of heteropoly acids were pretreated at 593 K for 2 h under nitrogen flow and the heteropoly acids, HPW and HSiW were pretreated at different temperatures for 2 h under the flow of three different environments: nitrogen, air, and hydrogen. The flow rate was held at ca. 70 ml/min.

HPW which had been pretreated at 723 and 773 K under nitrogen flow for 2 h was maintained under N_2 flow containing ca. 2% water at room temperature for 2 h and finally pretreated at 593 K under nitrogen flow for 2 h. This part of the experiment was performed to examine whether the acidity lost at or above 723 K pretreatment can be regained by hydrothermal treatment.

Acid Strength Distribution

Acid strength distribution of the catalysts pretreated under different conditions was determined following the procedure described by Benesi (*23*) using the following visible Hammett indicators (H_0): neutral red (6.8), bromothymol blue (6.8), *p*-ethoxycrysoidin (5.0), butter yellow (3.3), benzeneazodiphenylamine (1.5), dicinnamalacetone (−3.0), and benzalacetophenone (−5.8). About 2.0 g of the pretreated catalyst was transferred to each of 15 preweighed screwcap vials of ca. 25 cm^3 volume. The catalyst was covered with ca. 10 cm^3 of dry benzene and then increasing aliquots of 0.2 mol dm^{-3} *n*-butylamine in benzene were added to the vials from a microburette. The samples were equilibrated by using an ultrasonic mixing tank for at

TABLE 1

Acid Strength Distribution of HPW and Its Salts, after Pretreatment at 593 K in Nitrogen for 2 h

Catalysts	Acidity ($\mathrm{mmol\ g^{-1}}$)					
at H_0 =	6.8	5.0	3.3	1.5	−3.0	−5.6
$Ca_{3/2}PW_{12}O_{40}$	1.49	0.41	0.20	0.10	—	—
$Mg_{3/2}PW_{12}O_{40}$	1.58	0.54	0.30	0.10	—	—
$Zn_{3/2}PW_{12}O_{40}$	1.60	1.02	0.30	0.15	0.08	0.03
$AlPW_{12}O_{40}$	1.84	1.37	0.69	0.31	0.10	0.05
$Zr_{3/4}PW_{12}O_{40}$	3.04	1.60	1.13	0.90	0.25	0.15
$H_3PW_{12}O_{40}$	3.09	1.84	1.65	1.46	1.18	0.90
$Na_3PW_{12}O_{40}$	0.25	0.20	0.14	0.04	—	—

least 1 h and then small amounts of each suspension transferred to small vials and tested with a few drops of a ca. 0.1% solution of each indicator in benzene. The vials in which the appropriate color change occurred were noted, and the acidity was determined from the number of millimoles of *n*-butylamine which had to be added before the appropriate color change occurred.

XRD Analysis

X-Ray powder diffraction patterns of HPW and HSiW were recorded with the aid of a Philips Model PW-1011/60 diffractometer using Cu$K\alpha$ radiation filtered through nickel. X-Ray patterns were recorded immediately after various heat treatments for 2 h in nitrogen at 393, 493, 673, 773, 823, and 873 K.

RESULTS

Acidity of HPW and Selected Salts

The salts of HPW, after pretreatment at 593 K in flowing nitrogen for 2 h, show broad distributions in acidic strengths (Table 1, Fig. 1). While the salts of Zr, Al, and Zn are shown to be strongly acidic with H_0 values as low as −5.6, the remaining salts possess no acidic sites at H_0 values of −3.0 or −5.6. A comparison of the data obtained for the salts with that obtained for the parent acid (Table 1) shows that the effect of salt formation is most strongly felt on the most acidic sites, while the numbers of weakly acidic sites are decreased relatively little.

A strong Brønsted site may be generated from the strong interaction between the lattice oxygen atom to which the hydrogen atom is attached and a cation of high polarizing power. Thus it is of interest to correlate the acid strength of the metallic salts with a physical parameter such as the polarizing power of the cation (*8*, *10*). As noted earlier, the Brønsted acidic strength can be considered as inversely proportional to the magnitude of the negative charge on the oxygen atoms of the anion in the heteropoly compounds. A semiempirical estimate of the effect of the cation on such a quantity can be obtained from the equalization method (*24*). The method of calculation and the results obtained for the salts of HPW have been reported earlier (*8*). The number of acidic sites is found to decrease exponentially with increasing magnitude of the charge on the anionic oxygen atoms, for various ranges of acidity (Fig. 2). However, for the more acidic ranges of H_0, the number of acidic sites decreases more sharply with increase of the oxygen charge, reflecting the relative paucity of strongly acidic sites on the salts of magnesium, calcium,

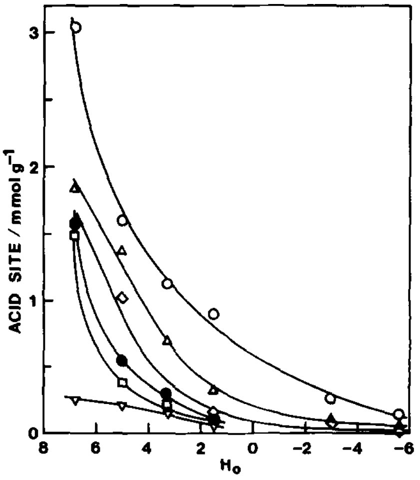

FIG. 1. Acid strength distribution of salts of 12-tungstophosphoric acid. (○) Zr, (△) Al, (◇) Zn, (●) Mg, (□) Ca, (▽) Na, after pretreatment at 593 K in nitrogen for 2 h.

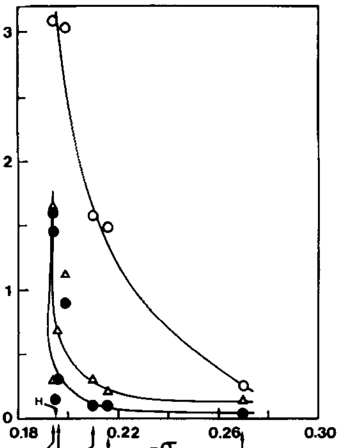

FIG. 2. A correlation between the acidity (after pretreatment at 593 K in nitrogen for 2 h) and the partial charge on the oxygen atom (σ_0) of the metallic salts of 12-tungstophosphoric acid. (○) $H_0 \leq 6.8$, (△) $H_0 \leq 3.3$, (●) $H_0 \leq 1.5$.

and sodium. It may also be recalled that similar correspondences with oxygen charges were earlier obtained for methanol conversion on the salts of HPW (*8, 10*).

The total number of acid sites determined by using the indicator with $H_0 = 6.8$ is 1.5–1.8 mmol/g for the Al, Zn, Mg, and Ca salts and 3.0 mmol/g for the Zr salt, considerably larger than that of 1.0 mmol/g expected for the parent acid, while the corresponding value 0.25 mmol/g for the Na salt is significantly lower. However, the number of acid sites found with an indicator with an H_0 of 3.3. is less than 1.0 mmol/g for all the salts except that of Zr for which a value of approximately 1.0 mmol/g was obtained.

Acidity of HSiW and Salts of Cs and NH$_4$

HSiW, like HPW, possesses a significant number of the most acidic H_0 (≤ -5.6) sites (Fig. 3), although the concentrations found with HSiW, for all acidic strengths, are considerably lower than those found with HPW, all after pretreatments at 593 K under nitrogen. However, both the Cs and NH_4 salts of HSiW possess relatively small numbers of acidic sites over the whole range of acid strengths.

Effect of Pretreatment Temperatures and Environments on the Acidity of HPW and HSiW

With HPW, the most significant effect of pretreatment temperatures can be observed with the most strongly acidic sites ($H_0 \leq 5.6$) (Fig. 4A), which increase in number with the pretreatment temperature to approximately 673 K, and then decrease abruptly with further increases in temperature. The number of acidic sites over the entire range of strength follows a somewhat similar pattern with a decrease in number, although less precipitous than the aforementioned, at approximately 673 K.

Similar trends, although less pronounced, can be observed in the data for HSiW (Fig. 4B). Although certain irregularities can be observed in the data for both heteropoly acids, increase in pretreatment temperature appears to increase the number of more strongly acidic sites with relatively little change in the number of weakly acidic sites up to approximately 673 K, followed by decreases in both the former and the latter as pretreatment temperature is increased still further.

A change in the pretreatment environment may alter both the number and

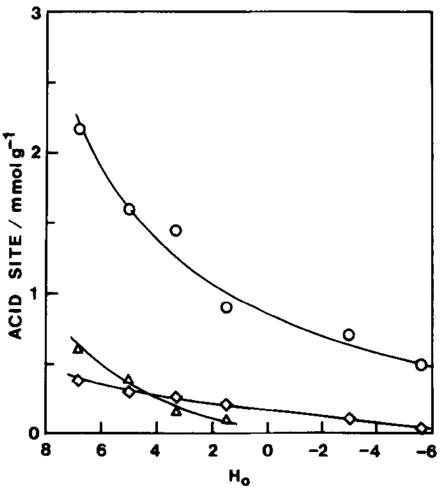

FIG. 3. Acid strength distribution (after pretreatment at 593 K in nitrogen for 2 h) of 12-tungstosilicic acid (HSiW) and its salts. (○) HSiW, (△) NH_4, (◇) Cs.

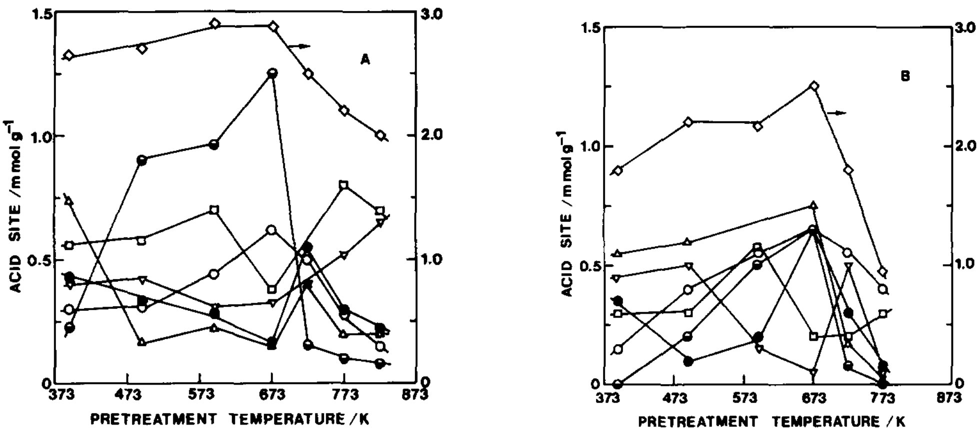

FIG. 4. Effect of pretreatment temperatures on the acid strength distribution of 12-tungstophosphoric acid (A) and 12-tungstosilicic acid (B): (◒) $H_0 \leq -5.6$, (△) $-5.6 < H_0 < -3.0$, (●) $-3.0 < H_0 < 1.5$, (○) $1.5 < H_0 < 3.3$, (▽) $3.3 < H_0 < 5.0$, (□) $5.0 < H_0 < 6.8$, (◇) $H_0 \leq 6.8$.

strength of the acidic sites. Although no remarkable effects are evident with either HPW or HSiW (Figs. 5a–d) the number of strongly acidic sites appears to be higher in both cases when the pretreatment occurs in nitrogen than that found with hydrogen or air, although the latter environments were not employed in the whole temperature range.

XRD Analysis

The XRD patterns for HPW and HSiW after various pretreatments show a decrease of intensity with widening of the peaks when the pretreatment temperature is in the 673–773 K range (not shown). Heating at or above 823 K significantly reduced or eliminated virtually all of the XRD

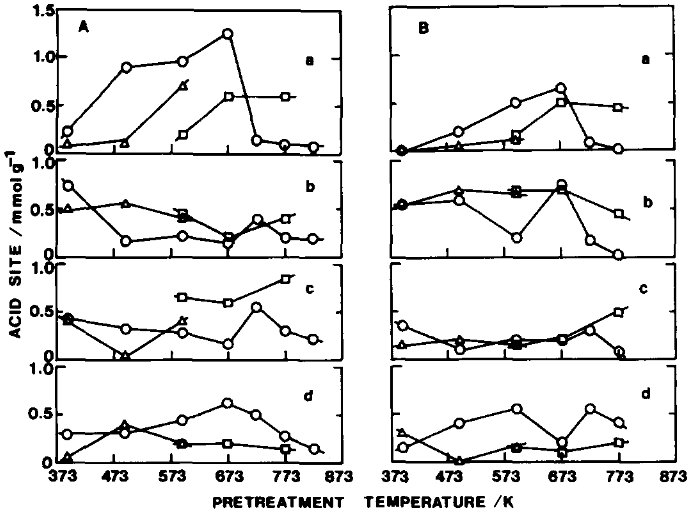

FIG. 5. Effect of environment at 593 K on the acid strength distribution of 12-tungstophosphoric acid (A) and 12-tungstosilicic acid (B): (○) N_2, (△) H_2, (□) air; (a) $H_0 \leq -5.6$, (b) $-5.6 < H_0 < -3.0$, (c) $-3.0 < H_0 < 1.5$, (d) $1.5 < H_0 < 3.3$.

peaks. Concomitant with the temperature increases, the peaks with 2θ values of 25.7 shifted to 24.2, while an additional peak was observed at a 2θ value of 23.4.

DISCUSSION

While the structure and composition of the anion of heteropoly compounds play an important role in their catalytic properties, the effect of the cation cannot be disregarded. In the salts of HPW, as examined in the present work, the acid strength of the salts increases with the polarizing power of the cations. Apparently similar effects have been earlier observed and reported for metallic-cation-exchanged zeolites (*25*) and ascribed to the electric field strength of the cation. Specifically, in the case of divalent cation-exchanged X and Y zeolites, it has been argued that the associated electrostatic field of the divalent cation is sufficiently strong to induce dissociation of coordinatively bound water molecules. In those cases the proton generated by the dissociation of water is

$$\mathrm{Me}^{n+}(\mathrm{OH}_2)_{n-1} \rightleftarrows \mathrm{Me(OH)}^{+}_{n-1} + (n-1)\mathrm{H}^+$$

believed, supported by data from infrared spectroscopy, to associate with the lattice oxygen to give structural hydroxyl groups which are the same as those in the hydrogen zeolite. Various workers have related the numbers and strengths of acidic sites in zeolites to the electric field strength generated, at least in part, by the cations. Although, by nature of the difference in structure of the zeolites and heteropoly compounds, the correspondence between the cationic effects cannot be quantitative, nevertheless the qualitative similarities are apparent.

Echigoya *et al.* (*26*) showed that the catalytic activities of the metal salts of 12-molydophosphoric acid in the dehydration of 2-propanol could be related to the electronegativities of the metal cations, with the exception of the alkaline-metal salts, and have proposed a process for generation of protons from water similar to that suggested earlier for zeolites (*25*). More recently Ono *et al.* (*27*) have also attributed the generation of protons in the aluminum salt of HPW to a stoichiometry similar to that employed for the zeolites. The activity and selectivity of a number of salts (Na, Zr, Zn, B, Mg, and Al) of HPW in the conversion of methanol to hydrocarbons has been studied in this laboratory (*8, 10*). It was found that the yield of C_4 hydrocarbons decreases exponentially with the charge on the anionic oxygen, beginning with aluminum and ending with sodium. A comparison of the relevant figures from that work and the present shows that the formation of C_4 hydrocarbons in the conversion of methanol correlates with the acidic sites of strength $H_0 \leq 3.3$ or ≤ 1.5.

Recent experimental and theoretical work from this laboratory has shown the similarity in properties of HSiW and HPW (*7, 13, 15, 18–21*). Relatively little work has been reported on the salts of HSiW. Ono *et al.* (*28*) reported that the silver and copper salts of HSiW are more active in the methanol conversion process than the corresponding acid. The present work suggests that the apparent acidity of HSiW is lower than that of HPW over all acid strengths examined, while the NH_4 and Cs salts of HSiW are still further reduced in acidity from that of the parent acid.

The measurements of the acidity of the heteropoly acids obtained after different pretreatment temperatures indicate that the degree of dehydration plays an important role in the number and strength of the acidic sites. The number of weakly or moderately strong acidic sites remains relatively unchanged with pretreatment temperatures to a maximum value at approximately 673 K and then decreases. In contrast, the number of strongly acidic sites (e.g., $H_0 - 5.6$) increases significantly with pretreatment temperature up to approximately 673 K. Brown *et al.* (*29*), from their X-ray and neutron diffraction studies of HPW, have shown that each proton in the acid is surrounded by four water mole-

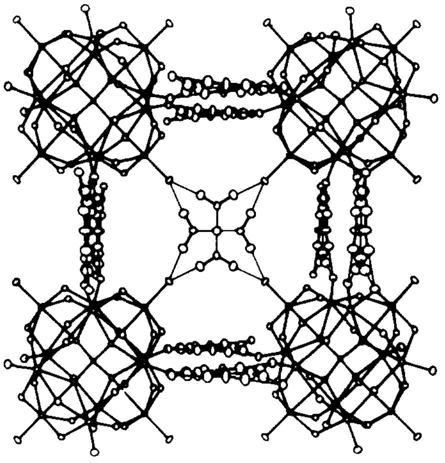

FIG. 6. Arrangement of cations, water, and anions in $H_3PW_{12}O_{40} \cdot 6H_2O$ (*29*).

cules, arranged with their oxygen atoms adjacent to the acidic proton (Fig. 6). A twofold thermal disorder exists such that only two of the water molecules are hydrogen-bonded to the acidic proton at a given time. The protons of the water molecules are, in turn, hydrogen-bonded to the terminal oxygen atoms of the anions. Thus the acidic protons are effectively guarded by the hydrogen-bonded water. Recent TPD work from this laboratory has shown that, while the low-temperature water peak in the spectra of HPW and of HSiW is essentially complete by 573 K, the high-temperature peak, also shown to be due to water, does not begin to emerge until approximately 650 K (*13, 15, 16, 18–21*). From an examination of desorption energies, and the numbers of water molecules responsible for the high-temperature peak it is apparent that this water is formed from the acidic protons, three per anion in the case of HPW, and four per anion for HSiW, apparently as a result of the extraction of the appropriate number of oxygen atoms from the anion. Evidently the downturn in number of highly acidic sites which is seen to occur at 673 K corresponds to the emergence of the high-temperature peak in the TPD spectra. Photoacoustic FT-IR spectra of HPW evacuated at room temperature contained a broad band at approximately 3200 cm^{-1} due to water, and one at about 1710 cm^{-1} assigned to the oxonium ion, H_3O^+ (*11, 13, 14, 19–21*). After heating *in vacuo* at 473 K the band at 1710 cm^{-1} disappears, and one at 2240 cm^{-1}, probably originating from crystal water, sharpens. On heating to 623 K the band at 2240 cm^{-1} appears to intensify and at 723 K disappears, indicating complete loss of lattice water. These observations also appear reasonably consistent with the present data which shows an increase in the number of most strongly acidic sites up to approximately 673 K. Both PAS and XRD data show that the subsequent loss of protons is able to occur without destruction of the anionic structure (*11, 13–15, 19–21*).

The present study shows that the total number of acidic sites of HPW at any positive value of H_0 is significantly higher than 1.0 mmol/g, the value anticipated for HPW considered as a strong acid. However, the total number of strongly acidic sites ($H_0 \leq 5.6$) approximates the expected value after pretreatment between 473 and 673 K. In contrast, with HSiW, the total number of acidic sites of all strengths ($H_0 \leq 6.8$) appears to be more nearly equivalent to the stoichiometric value of 1.4 mmol/g. Both PAS and TPD studies have shown that, while the small NH_3 molecule readily penetrates the bulk structure of the heteropoly compounds and quantitatively converts any protons to NH_4^+, the sorption of the larger pyridine molecule into the bulk structure is a more complex process (*12–16*). After pretreatment in vacuo at 523 K, exposure of HPW to excess pyridine at 25°C resulted in the sorption of up to 6 pyridine molecules per anion. However, evacuation at 463 K reduces the quantity of irreversibly sorbed pyridine to that expected from the stoichiometry of HPW. While no definitive evidence exists at this time, the substantial number of weakly acidic sites measured with HPW and HSiW in the present work, may at higher pretreatment temperatures be related to a similar phenomena, and at lower pretreatment temperatures be associated with the induced dissociation of entrapped water molecules.

ACKNOWLEDGMENT

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