Cation / proton interactions and acid strengths in salts of 12-tungstophosphoric acid prepared from 1A, 1B and 3B monovalent cations

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The substitution of the protons in 12-tungstophosphoric acid by 1A, 1B and 3B monovalent cations leads to increases in surface area, the introduction of micropore structures and alterations in the interactions experienced by the protons, as well as the expected decreases in the concentration of protons. The resultant changes in the distribution of acidic strengths and the effect of changes in the preparative stoichiometry and the nature of the cation have been assessed from proton MAS NMR and NH_3 TPD measurements and correlated with the catalytic activities in the dehydration of 1-, 2- and tert-butanol on stoichiometric and nonstoichiometric compositions of the aforementioned solids.

Keywords: cation / proton interactions, acidity, butanols, NH_3 TPD, ^1H NMR, heteropoly oxometalates

1. Introduction

Metal–oxygen cluster compounds (also known as heteropoly oxometalates) have been synthesized with a variety of compositions and structures [1,2] and have been investigated as heterogeneous catalysts for both acid-catalyzed and oxidation processes. Although a wide variety of these metal–oxygen cluster compounds is extant, those with anions of Keggin structure $(XM_{12}O_{40})^{-n}$, often referred to as 12-heteropoly oxometalates, have been most frequently studied for their catalytic properties. The anion contains a central atom (X) bonded to four oxygen atoms arranged tetrahedrally. This tetrahedron is surrounded by twelve interconnecting octahedra, each consisting of a peripheral metal atom (M) at their approximate centres and oxygen atoms at their vertices. The resulting charge on the Keggin anion, $(XM_{12}O_{40})^{-n}$, is dictated by the oxidation states of the central and peripheral metal atoms. The Keggin anion retains its structure on substitution of different elements for the central and peripheral metal atoms. A solid acid is formed when protons balance the charge of the Keggin anion, forming a neutral species, $H_nXM_{12}O_{40}$.

X-ray and neutron diffraction studies have shown that 12-tungstophosphoric acid hexahydrate ($H_3PW_{12}O_{40}{\cdot}6H_2O$) [3] has a cubic structure with hydrated protons, $(H_5O_2)^+$, linking four Keggin anions by the formation of hydrogen bonds with the terminal oxygen atoms of the anions. Although interstitial voids are created by the terminal oxygen atoms linking the hydrated protons, since these are not interconnected the resulting solid acids have low BET (N_2) surface areas [4]. In contrast, salts containing the group 1A monovalent cations have been shown, from the analysis of nitrogen adsorption–desorption isotherms, to possess microporous structures and relatively high surface areas [4], apparently resulting from the translation and rotation of the Keggin anions when accommodating the larger cations so as to remove, at least partially, the barriers separating the interstitial voids from each other [4]. Both X-ray diffraction [3,5] and ^{17}O MAS NMR [6] data have confirmed the assumption that the monovalent cations occupy the positions previously held by the protons in the lattice structure with the Keggin anions. ^{129}Xe NMR studies have provided additional evidence for the existence of the microporous structure with the group 1A monovalent cations [7]. The creation of a microporous structure is believed to be responsible, at least in part, for the increased catalytic activity of these salts.

Earlier photoacoustic FTIR studies have shown that both the nonstoichiometric as well as the prepared as stoichiometric microporous salts contain residual quantities of protons which are apparently responsible for the catalytic activities of these solids in processes requiring the presence of Brønsted acidic sites [8]. Such studies employing pyridine as sorbate have also demonstrated that little or no Lewis acidity is present in either the heteropoly acids or their salts, with the exception of those prepared with aluminum cations.

More recently, stoichiometric and nonstoichiometric salts of 12-tungstophosphoric acid prepared from the monovalent cations of silver and thallium, representatives of the 1B and 3B groups in the periodic table, have

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been synthesized with high surface areas and microporous structures [9]. Both temperature-programmed desorption and ^1H MAS NMR spectroscopy revealed that residual protons remain in the salts and the relative number of these appear to decrease with the increase of the cation to acid ratio.

Earlier work from this laboratory has provided results indicative of changes in the distribution of the Brønsted acidic strengths as the protons in the heteropoly acids are substituted by larger cations. Such effects appear to be dependent not only on the nature of the substituting cations but also on the number of these relative to the protons remaining. The present work borrows on the techniques, results and interpretations of a number of workers which have been applied to a variety of catalysts in studies of the butanols [10–18]. Together with ancillary measurements of proton NMR and NH_3 TPD, further information on the dependence of the catalytic properties of the cesium, silver and thallium stoichiometric and nonstoichiometric derivatives of 12-tungstophosphoric acid on the nature of the cation, and the stoichiometry and morphology of the salts will be obtained and thus provide further insight into the perturbations of acidic strength resulting from the introduction of nonprotonic cations.

2. Experimental

12-tungstophosphoric acid ($H_3PW_{12}O_{40}$, abbreviated as HPW, BDH AnalaR Grade) was recrystallized prior to use. Silver nitrate (BDH), thallous nitrate (BDH) and cesium nitrate (Aldrich) were used as received. Ammonia and 1-butene were obtained from Praxair (CP Grade), 1-butanol from Fisher (Reagent A.C.S.), 2-butanol from BDH (AnalaR Grade) and tert-butanol from MCB Reagents. All three alcohols were used as received.

The silver(I), thallium(I) and cesium(I) salts (abbreviated as AgPW, TlPW and CsPW, respectively) were prepared from molar ratios 0.50, 0.85, 1.00, 1.15 and 1.50 of the cation to the protons of the acid by a method reported previously [9]. It is important to emphasize that the aforementioned molar ratios refer to the relative amounts of the preparative reagents employed in the syntheses such that, for example, three molar equivalents of the cation were added per mole of HPW for a preparative cation : proton ratio of 1.00. The salts were dried overnight under a low vacuum at room temperature and stored in a desiccator.

^1H MAS NMR spectra were obtained with a Bruker AMX-500, with an external reference of benzene, at room temperature and spinning rate of 7 kHz. Prior to the ^1H MAS NMR measurements the salts were heated to 120°C for 1.5 h, allowed to cool to room temperature for 1.5 h, under vacuum, and stored in a desiccator. The mass of the sample placed in the zirconia holder was recorded prior to each measurement.

The measurement of nitrogen adsorption–desorption isotherms has been described earlier [9]. For temperature-programmed desorption of ammonia the sample was heated to 150°C over a 20 min period with a 20 ml/min flow of helium, after which an aliquot of gaseous ammonia (20 ml) was injected. After 1 min, the system was cooled to 30°C over 30 min. The ammonia was desorbed with a temperature ramp of 10°C/min from 30°C to 650°C, under a flow of helium (20 ml/min), and monitored by a HP5890 gas chromatograph equipped with a HP5970 series mass selective detector.

The catalytic reactions for the dehydration of the butyl alcohols were carried out in a flow system with a glass tube reactor filled with catalyst sample blocked at two ends by quartz wool. The sample (100 mg) was pretreated in situ at the reaction temperature for 15 min for tert-butanol and 20 min for the 1- and 2-butanols under a flow of helium (9 ml/min). To introduce the reactant, helium was passed through a saturator containing the alcohol at 25°C, at 9 ml/min, and then passed through the glass reactor tube containing the catalyst. Initial activity was measured at 5 min after the catalyst was in contact with the reactant mixture. The reactant and products were analyzed with a HP5890 gas chromatograph equipped with a TCD. The selectivity was calculated on the product basis. The dehydration of tert-butanol was carried out at 46°C and the dehydration of 1- and 2-butanol at 108°C.

3. Results

The characterization of the micropore structure present in the AgPW and TlPW salts has been reported previously [9]. Infrared spectra and powder X-ray diffraction patterns confirmed that the structure of the Keggin anion is maintained with the substitution of protons by the silver(I) and thallium(I) cations, and that the orientation of the cations and Keggin anions is consistent with the lattice structure present for the 12-tungstophosphoric acid. The three cation to proton ratios (0.85, 1.00 and 1.15) of the CsPW salt were investigated for comparative purposes since the microporous structures of stoichiometric salts containing group 1A monovalent cations are well characterized and established [4]. Characterization of the present stoichiometric CsPW salt is in agreement with previous measurements [4a].

The surface areas of the salts were determined by the Brunauer/Emmett/Teller (BET) method from nitrogen adsorption–desorption isotherms [19] and are summarized in table 1. For all of the salts examined, a ten-fold increase in surface area is apparent when compared to the parent acid, HPW ($S_{BET} = 8\ m^2/g$) [4e]. With the exception of the 0.50 cation : proton compositions, the surface areas of both the stoichiometric and nonstoi-

Table 1
Surface areas [a] of stoichiometric and nonstoichiometric salts

Salt	Preparative stoichiometry [b]				
	0.50	0.85	1.00	1.15	1.50
$Ag_3PW_{12}O_{40}$	77.6	86.2	100.9	101.4	100.5
$Tl_3PW_{12}O_{40}$	62.0	126.9	131.6	128.6	103.6
$Cs_3PW_{12}O_{40}$	–	137.3	147.9	148.5	–

[a] m^2/g.
[b] Preparative cation/proton ratio.

chiometric salts increase as the diameters of the substituted cations increase from silver(I) to cesium(I). For a given salt, the surface area increases as the relative amount of the cation is increased to a preparative cation : proton ratio of 1.00. Similar surface areas of two of the CsPW salts have been reported [20].

The MP method [21] was employed to generate the micropore distribution from the data in the *t*-plots. *t*-plots were constructed using the method of Lecloux and Pirard [22] for calibration purposes. The mean micropore radius (r_{MP}) (table 2) increases as the diameter of the cation forming the salt increases. However, the r_{MP} remains virtually unchanged with the amount of cation employed to synthesize the salt, consistent with the hypothesis advanced earlier for the source of the microporous structures in the salts of monovalent cations [4].

The volumes of the micropores (V_{MP}) were estimated from *t*-plots by extrapolating the linear pressure region of $0.4 < P/P_0 < 0.6$ to obtain the *y*-intercept. These micropore volumes are summarized in table 2 and follow the trend previously discussed with the surface areas, the largest V_{MP} being associated with the stoichiometric salts, again consistent with the earlier hypothesis [4].

^1H MAS NMR spectra were obtained for the CsPW, AgPW and TlPW salts. The spectrum for TlPW salts consists of a single resonance and as the cation ratio increases, the relative peak area attributed to the residual protons decreases [9]. The chemical shift for protons in HPW has been reported at $\delta = 9.6$ ppm [23]. As summarized in table 3, with an increase in the relative amounts of cation used in the synthesis of the salt, the resonance for the residual protons in the TlPW shifts upfield, reflecting a change in the chemical environment of the residual protons. In contrast to the TlPW salts, two resonances are present for the residual protons in the AgPW salts. The larger, more intense peak mimics the TlPW salts and shifts upfield with the increase in the cation ratio while a smaller weak resonance only moves slightly downfield (table 3). The ^1H MAS NMR spectra for the CsPW salts are similar to those observed for the TlPW salts, with one resonance moving upfield as the cation ratio is increased. The exception to this is found with the 0.85 salt which exhibits a shoulder on the downfield side of its peak, indicating a portion of the residual protons reside in a second, slightly different environment. This shoulder disappears with those preparations which employ a stoichiometric or excess amount of the cation to synthesize the salt. It should be noted that all the peaks observed were overlapped with a very broad peak attributed to the presence of water.

The absolute integrals were measured for each of the ^1H MAS NMR spectra. The value obtained for HPW, accounting for the amount of the sample measured, was set to be equivalent to 3 moles of protons per mole of Keggin anion. The absolute integrals of the salts were then normalized with this value, taking into account the mass of each sample measured. The resulting values are summarized in table 4 and confirm previous indications that the relative amounts of residual protons decrease with the increase in the relative amounts of cation used in the synthesis. It is important to emphasize that the number of protons calculated from the NMR data should be considered as valid only for comparative purposes. The silver salts contain a larger portion of protons in comparison to the salts containing either thallium or cesium, which are similar. These differences may be attributed to the solubility limits characteristic of each salt.

Temperature-programmed desorption (TPD) of ammonia was carried out on the three cation to proton ratios (0.85, 1.00 and 1.15) for each cation examined. (For illustrative purposes that for 0.85 AgPW is shown in figure 1.) Three distinct temperature ranges at which ammonia desorbed were present in the patterns observed

Table 2
Micropore volumes (V_{MP}) [a] and mean micropore radii (r_{MP}) [b] of stoichiometric and nonstoichiometric salts

Salt	Preparative stoichiometry									
	0.50		0.85		1.00		1.15		1.50	
	V_{MP}	r_{MP}	V_{MP}	r_{MP}	V_{MP}	r_{MP}	V_{MP}	r_{MP}	V_{MP}	r_{MP}
$Ag_3PW_{12}O_{40}$	0.027	8.0	0.031	7.8	0.037	7.9	0.037	7.8	0.035	7.7
$Tl_3PW_{12}O_{40}$	0.021	7.6	0.043	8.2	0.045	8.2	0.043	8.0	0.030	7.9
$Cs_3PW_{12}O_{40}$	–	–	0.043	8.2	0.045	8.3	0.043	8.3	–	–

[a] ml/g.
[b] Å.
[c] Preparative cation/proton ratio.

Table 3
Chemical shifts (ppm) of residual protons of stoichiometric and non-stoichiometric salts

Salt	Preparative stoichiometry		
	0.85	1.00	1.15
$Ag_3PW_{12}O_{40}$	6.4 [a]	6.0 [a]	5.7 [a]
$Tl_3PW_{12}O_{40}$	7.3	6.2	5.2
$Cs_3PW_{12}O_{40}$	7.2 [b]	6.5	5.4

[a] A peak of weak intensity was also observed at 4.3 ppm.
[b] A shoulder was also observed at 8.1 ppm.

for the salts and are classified as weak (100–300°C), intermediate (300–500°C) and strong (> 500°C) acid sites (table 5).

Dehydration of tert-butanol at 46°C produced only isobutene and was a facile reaction for all of the salts investigated. Figure 2 shows the conversion measured at 5 min for the salts examined while the conversion for the pure acid, HPW, was calculated to be 36.7% at 5 min. All three stoichiometries of the AgPW salts displayed a higher activity than the pure acid. Both the thallium and cesium salts synthesized with a deficit of the cation as well as the stoichiometric TlPW salt produced higher conversions than the pure acid at 5 min. A decrease in activity occurred for these salts when left on-stream with the tert-butanol, but the stoichiometric and deficit salts maintained higher conversions than found with HPW. For the initial and subsequent measurements, similar activities were noted for the various stoichiometries of the cesium and thallium salts.

A decrease in conversion of tert-butanol to isobutene is observed with all of the salts as the cation ratio is increased, both with the fresh catalyst and after remaining on-stream. The exception to this is the slight increase in activity observed for the 0.50 TlPW and AgPW salts relative to the respective 0.85 salts (not shown).

Table 4
Composition of salts containing residual protons

Salt	Cations : protons [a]	H^+/Keggin anion [b]
$H_3PW_{12}O_{40}$		3.0 [c]
$Ag_3PW_{12}O_{40}$	0.50	0.94
	0.85	1.78
	1.00	1.27
	1.15	1.26
	1.50	1.14
$Tl_3PW_{12}O_{40}$	0.50	0.46
	0.85	0.41
	1.00	0.26
	1.15	0.15
	1.50	0.16
$Cs_3PW_{12}O_{40}$	0.85	0.36
	1.00	0.20
	1.15	0.07

[a] Preparative ratio.
[b] Calculated from absolute integrals in ^1H MAS NMR data (mol/mol).
[c] Assumed for calibration purposes.

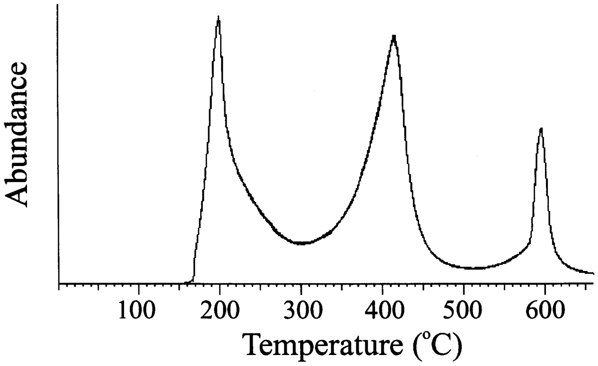

Figure 1. TPD of ammonia with 0.85 $Ag_3PW_{12}O_{40}$.

The dehydration of 1- and 2-butanols was carried out at 108°C, under otherwise identical conditions. Figures 3 and 4 summarize the conversion for both alcohols with the salts investigated (figure 3 for 2-butanol and figure 4 for 1-butanol). For the dehydration of 2-butanol with the fresh catalysts, all three salts synthesized with a deficit or stoichiometric amount of the cation have a conversion similar to that with HPW, which was observed to be 95.2%. Except for the salt containing silver, a significant decrease occurs for the salts made with an excess of the cation. At this high reaction temperature, little deactivation of HPW is observed. A similar trend is evident for the silver salts. However, the stoichiometric thallium and cesium salts show a significant decrease in conversion with time-on-stream, with only a trace of activity observed with the 1.15 salts (not shown).

In comparison, for the dehydration of 1-butanol only the 0.85 AgPW salt had a greater activity than that (77.6%) for the parent acid. Both the silver and cesium salts show a decline in the activity as the cation to proton ratio is increased. Of the three cation : proton ratios examined for the thallium salts, only the salt made with a deficit of the cation shows activity for the dehydration of 1-butanol. With increasing time-on-stream, the conversion with the pure acid decreases by half, while the three stoichiometries of the silver salts show little deactivation (not shown). The 0.85 TlPW salt maintains a similar level of conversion with increasing time-on-stream. However, the analogous cesium salt displays a decrease in activity, to a level slightly lower than the 0.85 TlPW salt. No activity was present for the stoichiometric and 1.15 CsPW salts at higher times-on-stream.

The products produced by the dehydration of 1- and 2-butanol were primarily the cis and trans isomers of 2-butene, together with 1-butene. In some instances, particularly with a fresh surface and a shortage of the cation, trace amounts of butane were present. Despite the dependence of the activity on the nature of the cation or

Table 5
Distribution of acid strengths and total acidity [a]

Salt	Preparative cation : protons ratio	Acid strength distribution [b,c]			Total specific acidity [d]
		weak	intermediate	strong	
$Ag_3PW_{12}O_{40}$	0.85	37	48	15	51.9
	1.00	37	48	15	34.6
	1.15	42	46	12	51.7
$Tl_3PW_{12}O_{40}$	0.85	33	29	38	6.0
	1.00	15	43	42	1.2
	1.15	58	31	11	4.7
$Cs_3PW_{12}O_{40}$	0.85	16	26	58	2.1
	1.00	20	37	43	1.2
	1.15	30	42	27	0.8

[a] Calculated from temperature-programmed desorption of ammonia.
[b] % of total area.
[c] Temperature ranges used for acid strength: weak (100–300°C); intermediate (300–500°C); strong (> 500°C).
[d] Total specific acidity = total area count / (S_{BET} × mass of sample).

the amount of cation used to synthesize the salt, the product distribution remains similar for the AgPW and TlPW salts, regardless of their stoichiometries, with average selectivities of 64, 28 and 8% found for trans-2-butene, cis-2-butene and 1-butene, respectively. This pattern is maintained at the higher time-on-stream (not shown). The product distribution for the dehydration of the 1- and 2-butyl alcohols is more variable with the cation ratio of the CsPW salts. It is of interest to note that the selectivity to 1-butene increases with the increase of the cation to proton ratio with the fresh catalyst for both alcohols, although it is more pronounced with 1-butanol (not shown).

4. Discussion

Increasing the cation size used to form salts of 12-tungstophosphoric acid permits the Keggin anions to rotate and translate to a larger extent in the lattice framework, removing barriers between the interstitial voids and creating more channels throughout the structure. This is reflected in the larger surface areas, micropore volumes and mean micropore radii present in the series of cesium salts. When altering the cation to proton ratio, isolation of salts by filtration shows less variation in surface areas than salts previously isolated by evaporation [24]. The maximum micropore volume occurs when stoichiometric quantities of the preparative reagents are employed. However, the mean micropore radii show little dependence on the relative quantities used. Filtration may minimize the concentration of peripheral impurities on the solid, but when a deficit of the cation is employed in the synthesis, residual protons may block the channels. Use of an excess of the cation can produce a similar effect with the cations.

^1H MAS NMR has provided evidence that residual protons remain in the isolated salts. As noted in the introduction PAS FTIR studies showed that the precipi-

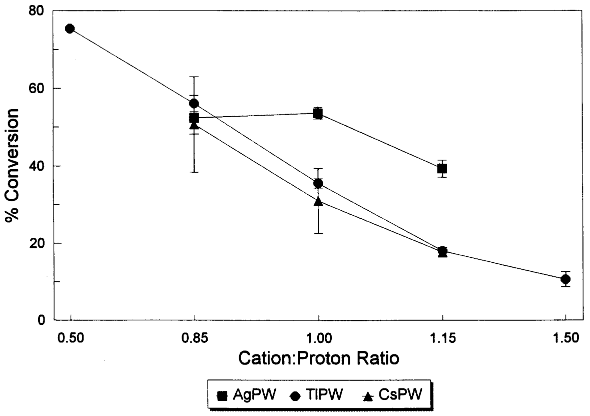

Figure 2. Conversion of tert-butanol at 46°C.

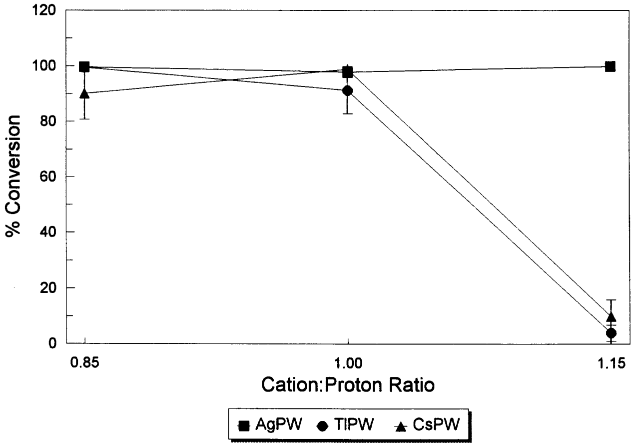

Figure 3. Conversion of 2-butanol at 108°C.

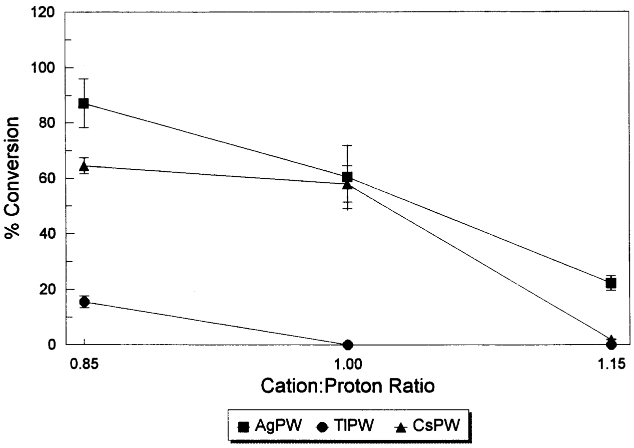

Figure 4. Conversion of 1-butanol at 108°C.

tation of salts, prepared as stoichiometric, was incomplete and protons remained in the isolated solid [8]. For the series of TlPW salts, the protons apparently reside in a single chemical environment with the peak area decreasing as the cation to acid ratio is increased.

As discussed previously [9], the two chemical shifts present for the AgPW salts could result from two different stoichiometries of the salt coprecipitating, due to similar solubility limits in water. However, the powder X-ray diffraction patterns are not amorphous, as would be expected if two different stoichiometries were present in the isolated solid. Alternatively, only one stoichiometry of the salt is formed but the residual protons may be able to reside in more than one site, differing in the chemical environment as the number of cations substituted into the neighbouring sites varied. This would explain the gradual shift upfield of the resonance as the amount of cation is increased and would account for the second resonance disappearing for the CsPW salts as the cation ratio is increased.

The smaller chemical shift, as compared to the parent acid, and the upfield shift with the increase in the cation to acid ratio indicates that both the nature and numbers of cations are affecting the chemical environment of the residual protons and, thus, their Brønsted acidity. A number of arguments has been presented in support of the suggestion that the chemical shift can serve as a measure of acid strength [25] and an increase in the protium chemical shift reflects an increase in the Brønsted acid strength [26,27]. The intensity of the resolved line in the ^{1}H MAS NMR spectrum is directly proportional to the concentration of Brønsted acid sites [27]. From these results it is apparent that the decrease in peak area and chemical shift as the cation to proton ratio increases is indicative of a decrease in both the number and acid strength of the residual protons as compared to 12-tungstophosphoric acid, in agreement with previous work with a series of zeolites [28]. The acid strength of the zeolites decreased on exchange of the protons with metallic cations with the stronger acid sites exchanging first.

The temperature-programmed desorption of ammonia from the silver salts, synthesized with a 15% deficit or excess of the cation, revealed that these two salts have similar numbers of acid sites and distributions of acid strengths (table 5). This correlated with the chemical shift in the ^{1}H MAS NMR spectra differing for the two salts by 0.7 ppm (table 3). In contrast to this, the TlPW and CsPW salts have a 2.0 ppm difference in chemical shift between the salts with a shortage and an excess of the cation. This change in the protium environment is reflected in the ammonia TPD spectra with a decrease in the number of strong acid sites as the cation to acid ratio for the TlPW salts is increased (table 5). A similar trend occurs in the ammonia TPD of the CsPW salts. It is also of interest to note that the quantity of ammonia adsorbed by the TlPW and CsPW salts is approximately an order of magnitude less than that adsorbed by the AgPW salts, consistent with the higher concentration of residual protons in the silver salts (table 5). Evidently the distribution of acid strength is shifting with the numbers of sites of higher acidity decreasing as the relative amounts of the cations are increased. Although temperature-programmed desorption experiments with ammonia cannot differentiate between Lewis and Brønsted acid sites, previous photoacoustic FTIR studies have shown that the acidity of 12-tungstophosphoric acid can be attributed to Brønsted acid sites with little or no evidence of Lewis acid sites [8a]. It is expected that the derivatives prepared in the present work are similar in this respect.

The dehydration of tert-butanol, 2-butanol and 1-butanol is expected to form the tertiary, secondary and primary butyl carbenium ions, respectively. Since the stability of these carbocations decreases in the order tertiary > secondary > primary, the strength of the acid sites required to dehydrate the alcohols should increase for the same series. The dehydration of butyl alcohols can occur through monomolecular and/or bimolecular mechanisms. However, for a bimolecular process, the formation of dibutyl ether is expected [18]. Studies by Shi and Davis with alumina catalysts revealed that the formation of ethers from secondary alcohols is dependent on the reaction conditions [10]. In the dehydration of the three alcohols only C_4 products were formed with no evidence for the formation of dibutyl ether or a variation on the chain length of the hydrocarbons was found. This suggests that the process is monomolecular at least under the conditions employed in the present work.

Dehydration of tert-butanol was a facile process for all of the salts investigated. The only product formed was isobutene, with the conversion decreasing as the cation to acid ratio increased (figure 2). This correlates well with the ^{1}H MAS NMR data which shows that the total number of acid sites available for the reaction is decreasing with the increased substitution by the cation.

The dehydration of 1- and 2-butanol required a higher temperature than that used for the dehydration of tert-butanol. The formation of the products is believed to follow a mechanism similar to that postulated for the isomerization of 1-butene [29]. However, the dehydration of 1-butanol would be expected to form the primary butyl carbenium ion, which would readily convert to the more stable secondary butyl carbenium ion, the latter also forming from 2-butanol. As a result, the dehydration of 1-butanol would require stronger acid sites to form the primary carbocation, and thus a decrease in the conversion is expected when compared to the dehydration of 2-butanol carried out at an identical reaction temperature (figures 3 and 4). The stoichiometric and 1.15 TlPW salts lack sites strong enough to facilitate the dehydration of 1-butanol and the analogous cesium salts are deactivated after the initial sampling at 5 min. In contrast, all three AgPW salts are capable of this reaction, indicating the change in the distribution of acid strengths when the amount of silver(I) is increased is not as significant as with the thallium and cesium series of salts. The observation that the stoichiometric TlPW salt had little or no activity in the dehydration of 1-butanol at 108°C but was capable of the dehydration of 2-butanol under the same conditions is consistent with the expectation that stronger acid sites are required to form the primary butyl carbenium ion.

For all of the catalysts investigated, none possessed sites of sufficient strength to facilitate the skeletal isomerization required to form isobutene during the dehydration of the primary and secondary butyl alcohols. This is not surprising since both the ^{1}H MAS NMR and TPD experiments with ammonia revealed that there is a decrease in the Brønsted acidity with the increased substitution of cations in comparison to the pure acid.

Generally, the dehydration of an alcohol requires weaker acidic sites than those required for double bond isomerization of an olefin [17]. On deactivation of relatively strong acid centres in an alumina membrane the overall conversion of 1-butanol was partially reduced but the selectivity to 1-butene was significantly increased. Examining the selectivities for the various stoichiometries of the salts used in the dehydration of 1- and 2-butanol found in the present work (64, 28 and 8% for the trans-2-butene, cis-2-butene and 1-butene, respectively), it is evident that the selectivity to 1-butene is larger for the salts than that (< 8%) with the pure acid, HPW. Although this increase is relatively small for the AgPW salts, the difference becomes more significant for the TlPW (56, 29 and 15%, respectively) and CsPW salts in the dehydration of 1-butanol (not shown). Also of note is the increase of the initial selectivity to 1-butene in the dehydration of 1-butanol observed with the CsPW salts as the cation to acid ratio increases.

Formation of the cis and trans isomers of 2-butene occurs through the secondary butyl carbocation which is considered to be a metastable species, not equivalent to a transition state [30]. A ratio of 1 is expected for the cis : trans isomers from this carbocation since the activation energy to form either is identical, although the trans isomer is slightly more thermodynamically stable. For 1-butene isomerization, this ratio is expected when the reaction is kinetically limited and the intermediate secondary butyl carbenium ion is considered to be "free" [31]. However, the equilibrium distribution of 1-butene : cis-2-butene : trans-2-butene is 9.3 : 29.8 : 60.9 at 150°C, [18i,18j] giving a cis/trans ratio of 0.49. The silver salts and HPW exhibit a similar product distribution for the dehydration of the primary and secondary butyl alcohols to that which is observed for the isomerization of 1-butene at 100°C [32]. The stoichiometric and excess salts of CsPW tend to approach a cis/trans ratio of 1 for the 2-butanol reactions. The distribution of products for the 1-butanol reactions differed from equilibrium values with the tendency to increase the selectivity to 1-butene at a cost of that to trans-2-butene with the CsPW salts.

For the dehydration of the butyl alcohols, there is a noticeable decrease in the catalytic activity, although not necessarily the selectivity to the products, from the initial sample of the fresh catalytic surface to the deactivated catalyst in as little as 15 min after exposure of the catalyst to the reactant mixture. It is believed that this decrease in conversion results from the relatively slower rate of regeneration of the Brønsted acid sites in comparison with the rate of formation of the olefinic products on a release of a proton. It should also be noted that mass balances of less than 100% are common in the present work, due to the retention of the alcohols and/or their decomposition products on the catalyst [18].

As evident from the nitrogen adsorption–desorption isotherms, ^{1}H MAS NMR and ammonia TPD, partial substitution of the protons by monovalent cations of cesium, silver and thallium affects three characteristics of the salts: a microporous structure is created, the number of Brønsted acid sites is decreased and the distribution of acid strengths is shifted. As noted earlier in this report, variations in the cation : proton ratios have significant effects on the pore volumes but little or no influence on the mean micropore radius, as would be expected from the hypothesis of the source of the pore structure advanced earlier [4]. Not surprisingly, however, the number of residual protons and the chemical environment in which they reside are altered by changes in this ratio. In examining the catalytic properties of the salt synthesized, it is important to determine which of these variables has the most significant effect in the dehydration of butyl alcohols.

It is evident that four factors play significant roles in influencing the conversions of the butanols: (1) the nature of the cation, (2) the morphological properties of the catalysts, (3) the number of protons, and (4) the distribution of acid strengths. For a given cation, the latter three factors are determined by the preparative stoichiometry of the catalyst. To elucidate the effect of the cations on the protons the conversions were divided by

Table 6
Conversions of the 1-, 2- and tert-butanols

Salt	Preparative stoichiometry	Conversion [a,b,c] /[(m^2)(H$^+$)]		
		1-butanol [d]	2-butanol [d]	tert-butanol [e]
$Ag_3PW_{12}O_{40}$	0.85	2.1	8.7	10.8
	1.00	2.1	8.4	12.6
	1.15	0.9	11.6	10.0
$Tl_3PW_{12}O_{40}$	0.85	1.4	21.1	25.8
	1.00	0	42.2	28.1
	1.15	0	1.4	31.9
$Cs_3PW_{12}O_{40}$	0.85	4.2	28.9	33.2
	1.00	0.8	38.2	35.5
	1.15	0.6	11.6	51.9

[a] For measurements taken at 5 min.
[b] Moles converted multiplied by (1×10^{28}).
[c] Relative number of protons from ^{1}H MAS NMR data.
[d] Reaction temperature of 108°C.
[e] Reaction temperature of 46°C.

the appropriate surface areas and numbers of protons (table 6). The resulting quantities should substantially reduce or eliminate the effect of the numbers of protons and morphological differences among the catalysts on the observed conversions.

As would be expected, assuming a carbocation mechanism, the conversions of tert-butanol are generally higher than those for 2-butanol and, in turn, those for the latter are higher than for 1-butanol for each cation and stoichiometry, although the reaction temperature for tert-butanol is lower than that employed with the remaining alcohols. Further, the conversions of a given alcohol increase, in general, with the cation in the order Ag < Tl < Cs. Finally, significant changes are observed, for a given cation, as the preparative stoichiometry is altered. Since the acidic strengths required to generate the carbocations increase in the order, tert-, 2-, 1-butanol it would be expected that the most significant differences in the conversions/[(m^2)(H$^+$)] would be found with 1-butanol as can be seen in table 6. However, in general the conversion decreases, for a given cation and alcohol, as the preparative stoichiometry increases.

Since the separation between the ^{1}H chemical shift in AgPW and that in HPW is larger than those with the remaining cations and the concentration of strong acid sites is the smallest in the former it would be anticipated that the conversions would generally be the smallest with AgPW regardless of the alcohol. Further, in view of the relatively large number of residual protons in the silver salts, regardless of the stoichiometry, the perturbational effect of the cations on the protons would be expected to be diminished.

It is clear that the nature of the cation as well as the preparative stoichiometry have a profound effect on the resulting salts, in particular both the morphological and the acid-based catalytic properties, the latter as evidenced from the results of ^{1}H MAS NMR, NH_3 TPD and butanol conversion measurements. For a given cation, changes in the preparative stoichiometry alter the relative numbers of cations and protons with consequent perturbations of the distribution of acidic strengths and catalytic activities in the reactions of butanols while similar effects also result from changes in the nature of the cations.

The acidic strengths of the heteropoly acids are related to the mobility of the protons which is dependent, at least in part, upon the magnitude of the negative charge of the adjacent terminal oxygen atoms of the heteropoly anion. Earlier calculations have suggested that the coulombic binding of the proton will increase with the charge on these oxygen atoms and concomitantly the protonic mobility and the acidity will decrease. The introduction of cations larger than the proton apparently reduces the mobility of the remaining protons. This effect may result from a number of factors. The larger cations may perturb the electron densities of the anions and in doing so alter the magnitude of the charge on the terminal oxygen atoms. It also may be speculated that the large cations actually impede the movement of the protons as a result of their size and repulsive interactions. In this regard it is noteworthy that the charge densities increase in the order $Cs^+ < Tl^+ < Ag^+$ which is in approximate agreement with the trends seen for the NH_3 TPD, ^{1}H MAS NMR and butanol conversion results. While such comments are evidently speculative direct evidence of the influence of the larger cations on the acidic properties of the heteropoly acids has been provided and hence direct and/or indirect interactions between the protons and larger cations have been shown to exist. Further work to provide additional information is required and is in progress.

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