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Isomerization of 1-butene on silver and thallium 12-tungstophosphate: the effect of the cation on acid strength distributions

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Substitution of the protons in 12-tungstophosphoric acid by monovalent cations of the Groups 1B and 3B, in particular Ag^+ and Tl^+, respectively, produces high surface area microporous solids whose morphological properties and numbers of residual protons are dependent upon the relative amounts of the preparative reactants. Temperature-programmed desorption of NH_3, ^1H MAS NMR and the isomerization of 1-butene have been employed to demonstrate that both the numbers of protons and the distribution of the acidic strengths are dependent upon the nature of the cation and the preparative proton/cation ratios.

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

1. Introduction

Heteropoly oxometalates of Keggin structure with protons as cations are solid acids with large, approximately spherical anions [1]. The acids containing molybdenum are less acidic than those containing tungsten [2] and the latter, for example, 12-tungstophosphoric and 12-tungstosilicic acids have been shown from microcalorimetric measurements with ammonia to have heats of adsorption in the range expected for superacids [3]. Measurements have also shown that the proton conductivities of the aforementioned two acids are the highest observed to this date [4].

Although the surface areas of these solid acids are small (<10 m^2/g) salts with certain of the monovalent cations of Group 1 of the periodic table can be synthesized with relatively high surface areas and microporous structures [5]. Thus, for example, the potassium salt of 12-tungstophosphoric acid has been prepared with a surface area of 90.0 m^2/g [5(a)]. The existence of the micropores has been attributed to the rotation and translation of the Keggin anions so that the interstitial voids separated by terminal oxygen atoms in the acids are converted into interconnected channels [5]. Photoacoustic FTIR experiments showed that residual protons remained in the monovalent salts prepared from stoichiometric quantities of the preparative reagents [6] and further work showed that the morphological properties of the salts varied with the relative amounts of the reactants used in their preparation [7]. Recent work has shown that the high area microporous salts are not restricted to Group 1 elements but can be prepared from monovalent cations from Groups 11 and 13 [8].

The effect of the use of nonstoichiometric quantities of the preparative reagents appears to be two-fold. While altering the surface area and micropore volume, the presence of both protons and monovalent cations appears to influence the distribution of acidic strengths. Although little or no studies of this effect have been reported in the literature, experiments with the conversion of methanol to hydrocarbons have provided some indirect evidence for the latter effect [9]. While 12-tungstophosphoric acid was found to be active for this process, the ammonium salt of the acid was more active and additionally the products from the latter were primarily saturated as opposed to the olefinic species found from the acid itself. More recently, studies of the dehydration of 1-, 2- and *t*-butanol and the effect of changes in the composition of the anion have provided additional information [10,11].

The present work utilizes the temperature-programmed desorption of NH_3, ^1H MAS NMR and the isomerization of 1-butene to examine the changes in the acidic strength of 12-tungstophosphoric acid as silver and thallium cations are introduced into the acid. This isomerization process has been studied on a wide variety of heterogeneous catalysts for the last three decades [12], but more recently has taken on renewed importance as a consequence of its use in the synthesis of methyl *tert*-butyl ether and rekindled interest in the mechanism of the isomerization process [13–18].

2. Experimental

Helium and 1-butene were purchased from Praxair.

The silver and thallium salts of 12-tungstophosphoric acid were prepared as previously described [8]. The cation : proton ratios of 0.50, 1.00 and 1.50 were examined for

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the silver and thallium salts of 12-tungstophosphoric acid (denoted as AgPW and TlPW, respectively, hereafter). Particle sizes <75 μm were employed except for AgPW for which sizes 106–150 μm were used.

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

The measurements of nitrogen adsorption–desorption isotherms have been described earlier [8]. 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 to 650 °C, under a flow of helium (20 ml/min), and monitored by a HP5890 gas chromatograph equipped with a HP5970 mass selective detector.

The catalytic reaction for the isomerization of 1-butene was carried out in a flow system with a glass tube reactor (6 mm o.d., 4 mm i.d.) of 21 cm in length with a small bubble (15 mm in length, 10 mm o.d.) placed in its centre, in which the sample of catalyst (150 mg) was supported between two plugs of quartz wool.

The catalyst was pretreated *in situ* in a flow of helium (20 ml/min) at the reaction temperature for 1 h prior to exposure to a mixture of 17% 1-butene : 83% helium, at the same flow rate. The reactant and products were analyzed with a HP5880A gas chromatograph equipped with a TCD and a Carbopack C column (2 m $\times$ $1/8''$ o.d.) with the oven temperature set at 50 °C. No conversion of 1-butene was observed with an empty reactor in the range of temperatures employed in the present work. The measurements reported with the catalysts were obtained after 10 min on-stream in order to minimize any catalyst deactivation.

3. Results

3.1. Characterization of micropore structure

The characterization of the micropore structure present in the AgPW and TlPW salts has been reported previously [8]. 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 surface areas of the salts were determined by the Brunauer/Emmett/Teller (BET) method from nitrogen adsorption–desorption isotherms 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 ($S_{\mathrm{BET}} = 8$ m^2/g) [5(d)]. With the exception of the 0.50 cation : proton compositions, the surface areas of both the stoichiometric and nonstoichiometric 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 cation : proton ratio of 1.00.

Table 1
Surface areas (S_{BET}), micropore volumes (V_{MP}) and mean micropore radii (r_{MP}) of stoichiometric and nonstoichiometric salts.

Preparative	AgPW			TlPW		
stoichiometry[a]	S_{BET} (m^2/g)	V_{MP} (ml/g)	r_{MP} (Å)	S_{BET} (m^2/g)	V_{MP} (ml/g)	r_{MP} (Å)
0.50	77.6	0.027	8.0	62.0	0.021	7.6
0.85	86.2	0.031	7.8	126.9	0.043	8.2
1.00	100.9	0.037	7.9	131.6	0.045	8.2
1.15	101.4	0.037	7.8	128.6	0.043	8.0
1.50	100.5	0.035	7.7	103.6	0.030	7.9

[a] Preparative cation : proton ratio.

The MP method [19] 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 [20] for calibration purposes. The mean micropore radius (r_{MP}) (table 1) 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 [5].

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 1 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 [5].

3.2. Distribution of acid sites and strengths

^{1}H MAS NMR spectra have been obtained for the silver and thallium salts of 12-tungstophosphoric acid. The spectrum for TlPW consists of a single resonance and as the cation to proton ratio increases, the relative peak area attributed to the residual protons decreases. The chemical shift for protons in HPW has been reported as $\delta =$ 9.6 ppm [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 (table 2). 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 : proton ratio, while a smaller weak resonance moves slightly downfield (table 2). The exception to this is found with the 0.85 salt, which

Table 2
Chemical shifts (ppm) of residual protons for the stoichiometric and nonstoichiometric salts.

Salt	Stoichiometry		
	0.85	1.00	1.15
AgPW	6.4[a]	6.0[a]	5.7[a]
TlPW	7.3	6.2	5.2

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

Table 3
Composition of 12-tungstophosphate salts containing residual protons.

Salt	Cation : proton ratio[a]	H^+/Keggin anion[b] (mol/mol)
$H_3PW_{12}O_{40}$		3.0[c]
AgPW	0.50	0.94
	0.85	1.78
	1.00	1.27
	1.15	1.26
	1.50	1.14
TlPW	0.50	0.46
	0.85	0.41
	1.00	0.26
	1.15	0.15
	1.50	0.16

[a] Preparative ratio.
[b] Calculated from absolute integrals in ^{1}H MAS NMR data.
[c] Assumed for calibration purposes.

Table 4
Distribution of acid strengths and total acidity[a] of 12-tungstophosphate salts.

Salt	Cation : proton ratio	Acid strength distribution[b] (% of total area)			Total specific acidity[c]
		Weak	Intermediate	Strong	
AgPW	0.85	37	48	15	51.9
	1.00	37	48	15	34.6
	1.15	42	46	12	51.7
TlPW	0.85	33	29	38	6.0
	1.00	15	43	42	1.2
	1.15	58	31	11	4.7

[a] Calculated from temperature-programmed desorption of ammonia.
[b] Temperature ranges used for acid strength: weak (100–300 °C); intermediate (300–500 °C); strong (>500 °C).
[c] Total specific acidity $=$ total area count$/(S_{\mathrm{BET}} \times$ mass of sample). Values multiplied by 10^8.

exhibits a shoulder on the downfield side of its peak, indicating a portion of the residual protons resides 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 (table 2).

The absolute integrals were measured for each of the ^{1}H MAS NMR spectra. The values obtained for HPW, accounting for the amount of the sample measured, were set to be equivalent to three moles of protons per mole of Keggin anion. The absolute integrals of the salts were then normalized with the value of the parent acid, taking into account the mass of each sample measured. The resulting values show that the relative amounts of residual protons decrease with the increase in the relative amounts of cation used in the synthesis (table 3). The silver salt contains a larger portion of protons, in comparison to that containing thallium. This difference may be attributed, at least in part, to the solubility limits characteristic of each salt. The significantly larger number of protons present in the silver salt, in comparison to that containing thallium, may explain the anisotropic nature of the resonances present in the ^{1}H MAS NMR spectra of the former. Although expected to have the largest number of protons per mole of Keggin anion present in the series, the 0.50 AgPW salt contains the smallest number of these. This anomaly may be related to the anisotropic resonance. The portion of the absolute integral for the anisotropic peak in the ^{1}H MAS NMR spectra, including the area contributed by the spinning sidebands, recorded for the 0.85, 1.00 and 1.15 silver salts is approximately 52–55%. In contrast to these three salts, the 0.50 AgPW salt has the upfield peak as the most intense in the spectrum and accounts for a significantly larger portion of the total area. The presence of spinning sidebands, resulting from anisotropy, contributes to the error associated with the absolute integral measured.

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 salt examined. Three distinct temperature ranges at which ammonia desorbed were present in the patterns observed for the AgPW salts and are labelled as weak (100–300 °C), intermediate (300–500 °C) and strong (>500 °C) acid sites. The three stoichiometries of the silver salts appear almost identical, with three peak maxima appearing at similar temperatures and similar distributions between the three ranges of acid strengths (table 4). The total specific acidity for each salt was determined by normalizing the total area recorded for the TPD pattern by the surface area (S_{BET}) and mass of the sample.

In contrast, the amount of ammonia adsorbed by the TlPW salts is at least an order of magnitude less than observed with the silver salts, which is consistent with the decreased number of residual protons calculated from the ^{1}H MAS NMR spectra. Three peaks are present in the TPD pattern for the 0.85 TlPW salt, with the largest peak appearing at approximately 580 °C. The pattern for the stoichiometric TlPW salt shows a very weak peak at approximately the same temperature, but significantly less ammonia is present on this salt than that made with a deficit of the cation. With the TlPW salt having an excess of thallium, a significant difference occurs with the most intense peak at the lowest temperature, as reflected in the distribution in table 4, and a gradual decline in intensity as the temperature increases. Two shoulders are present on the higher temperature side of the peak, but a peak at greater than 500 °C is now absent.

3.3. Isomerization of 1-butene

Isomerization of 1-butene with the silver and thallium salts of 12-tungstophosphoric acid was carried out at 100,

Table 5
Isomerization of 1-butene at 10 min with salts of $H_3PW_{12}O_{40}$.

Salt	Preparative ratio	Conversion (%)			*Cis*/*trans* ratio of 2-butene		
		100 °C	200 °C	300 °C	100 °C	200 °C	300 °C
AgPW	0.50	93	87	81	0.426	0.513	0.620
	1.00	91	87	82	0.425	0.527	0.634
	1.50	88	87	82	0.458	0.544	0.648
TlPW	0.50	88	87	82	0.366	0.545	0.654
	1.00	25	87	83	1.312	0.575	0.655
	1.50	0	0	0	–	–	–

200 and 300 °C, with the cation : proton ratios of 0.50, 1.00 and 1.50. The only products formed were the *cis* and *trans* isomers of 2-butene.

The conversions at 100, 200 and 300 °C are summarized in table 5. A slight decrease in the conversion occurs as the cation to proton ratio is increased in the silver salts. The decrease in activity is more apparent for the TlPW salt series, particularly the salt with an excess of cation having no activity. Both the AgPW and TlPW salts have *cis/trans* ratios which increase with the cation : proton ratio at each temperature, although changes are generally small for the AgPW series. However, the stoichiometric TlPW salt has a marked increase in the amount of *cis*-2-butene isomer in comparison to the salt made with a deficit of the cation.

Increasing the reaction temperature to 200 °C eliminated any decline in activity as the cation : proton ratio was increased. With the increased temperature, the deficit and stoichiometric TlPW salts attain activities similar to those of the silver salts. The 1.50 TlPW salt does not display any activity. At 300 °C there appears to be little variation in the conversion between the various stoichiometries of silver and thallium salts with the exception of the thallium salt with a 50% excess of cation.

4. Discussion

^{1}H MAS NMR has provided evidence that residual protons are still present in the isolated salts. Previous photoacoustic (PAS) FTIR studies have shown that the substitution of protons by larger monovalent cations in precipitated salts, prepared as stoichiometric, was incomplete and protons still remained in the isolated solid [6]. 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. The chemical shift of the pure acid, $H_3PW_{12}O_{40}$, is $\delta = 9.6$ ppm [3]. With the increase of the cation : proton ratio in the TlPW salts, the resonance moves upfield to a smaller chemical shift. Two resonances are present in the ^{1}H MAS NMR spectra for the AgPW series of salts. The larger of the two peaks moves upfield with the increase in the cation : proton ratio, while the smaller resonance is displaced slightly downfield, to a larger chemical shift.

The two chemical shifts present for the AgPW salts could result from two different stoichiometries of the salt coprecipitating, due to similar solubilities 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 may be 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 varies. This would explain the gradual shift upfield of the resonance as the amount of cation is increased. The anisotropic nature of only one of the two resonances observed for the AgPW salts supports this assumption.

The smaller chemical shift, as compared to the parent acid, and the upfield shift with the increase in the cation to acid ratio indicate that both the nature and amount 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 for acid strength [21] and an increase in the protium chemical shift has been taken as an indication of an increase in the Brønsted acid strength [22–24]. The intensity of the resolved line in the ^{1}H MAS NMR spectrum is directly proportional to the concentration of Brønsted acid sites [23]. From these results it is apparent that the decrease in chemical shift (table 2) and peak area (table 3) as the cation : proton ratio increases is indicative of a decrease in both the number and acid strength of the residual protons as compared to 12-heteropoly acids. This is in agreement with previous work with zeolites [25]. 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 of HPW, synthesized with a 15% deficit or excess of the cation, revealed that the two stoichiometries of the salt have similar numbers of acid sites and distributions of acid strengths (table 4). This correlated with the chemical shift in the ^{1}H MAS NMR spectra, differing for the two cation : proton ratios by 0.7 ppm for AgPW (table 2). In contrast to this, the TlPW salt has a 2.0 ppm difference in chemical shift between the salts with a deficit 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.

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 [6(a)]. It is expected that the derivatives prepared in the present work are similar in this respect.

Isomerization of 1-butene by the salts was carried out to gain an understanding of the number and nature of acid sites available in the catalyst by analysis of the conversion levels and product distribution, in comparison to that of the parent acid. The monomolecular mechanism appears to be followed with the formation of the secondary butyl carbenium ion as the initial step. From this carbenium ion double-bond isomerization will form the *cis* and *trans* isomers of 2-butene while skeletal isomerization will form isobutene provided that sites of sufficient acidic strength are present and other conditions are suitable. Recent experiments in this laboratory [12] with 12-tungstophosphoric acid supported on silica have suggested that an equilibrium is established between the secondary carbenium ion, 1-butene, *cis*- and *trans*-2-butenes with the 2-butenes as precursors to isobutene, indicating that the former species are the primary products while isobutene is a secondary product. Stronger Brønsted acid sites and an increase in temperature are required to facilitate the skeletal rearrangement of the secondary butyl carbenium ion to a primary carbenium ion required for this product. It has been shown that skeletal isomerization can be suppressed while maintaining activity for the linear isomers, indicating that skeletal isomerization requires a site of higher acid strength than that involved in linear isomerization [26], although the acidity need not be very strong and, in fact, is not desirable since this induces excessive by-product formation [27]. A decrease in isobutene also correlated with a decrease in the by-product formation, indicating the latter is formed by a consecutive reaction [26]. Parenthetically it should be noted that mechanisms other than those involving carbocations are possible although the weight of current information strongly favours the latter [27].

The decrease in activity for the salts of HPW at 100 °C as the cation : proton ratio increases indicates the number of acid sites strong enough to facilitate the reaction is decreasing. With the increase of the reaction temperature to 200 °C, all of the AgPW salts now maintain similar conversion levels, while the stoichiometric TlPW salt decreases in activity as the reaction progresses. At 300 °C all of the salts, with the exception of 1.50 TlPW (which is inactive), have similar activities.

In all of the reactions carried out with the silver and thallium salts of HPW only the *cis* and *trans* isomers of 2-butene were formed. No evidence of $C_3, C_4, C_5, \ldots, C_8$ species was found to give an indication of a bimolecular process. None of the catalysts investigated possessed sites of sufficient strength to facilitate the skeletal isomerization required to form isobutene during the isomerization of 1-butene at the reaction temperatures investigated. 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. Although isomerization of 1-butene at 300 °C by 12-tungstophosphoric acid failed to produce isobutene, supported HPW was capable of forming isobutene during the isomerization of 1-butene at these temperatures [12]. ^{1}H MAS NMR studies of the supported acid revealed a downfield shift of the protium resonance, to a larger chemical shift, from that reported for the unsupported HPW, indicating an increase in acid strength when the acid is supported [12]. With the supported HPW, there was also evidence of a bimolecular process under the reaction conditions employed, but this may apply only to the formation of the by-products [26].

Formation of the *cis* and *trans* isomers of 2-butene occurs through the secondary butyl carbenium ion, which is considered to be a metastable species, not equivalent to a transition state [28]. The equilibrium distribution of 1-butene : *cis*-2-butene : *trans*-2-butene is 9.3 : 29.8 : 60.9 at 150 °C [29], giving a *cis/trans* ratio of 0.49, and 18.0 : 32.5 : 49.5 with a *cis/trans* ratio of 0.656 at 300 °C [30]. Isomerization of 1-butene with HPW results in *cis/trans* ratios similar to the equilibrium distribution values (table 5) with reaction at 100 °C slightly lower than the distribution reported for 150 °C.

AgPW produced the *cis* and *trans* isomers of 2-butene in ratios not too dissimilar from equilibrium values. Relatively small variations occurred with the increase in the cation : proton ratio used to prepare the salt. This is consistent with the ammonia TPD spectra in which little change in the distribution of acid strengths occurred with the stoichiometry of the salt.

TlPW prepared with a 15% deficit of the cation produced the two isomers of 2-butene in ratios similar to those expected at equilibrium. However, when the cation content was increased, the proportion of *cis*-2-butene increased to produce a *cis*/*trans* ratio higher than the equilibrium value.

It has been concluded that the formation of the *cis* isomer is favourable for catalysts which are weakly acidic [14,31], although numerical values reported for the *cis/trans* ratio are largely dependent upon the nature of the acid sites (Lewis or Brønsted) and the resulting mechanism for isomerization [14,31]. This is consistent with the observations for the ammonia TPD, in which a greater portion of acid sites are classified as weak with the increase in the cation : proton ratio for all the three series of thallium salts examined. At reaction temperatures of 300 °C the *cis/trans* ratio remains unaltered on changes in the preparative ratio of the salt.

As evident from the nitrogen adsorption–desorption isotherms, ^{1}H MAS NMR and ammonia TPD, partial substitution of the protons by monovalent cations of silver and thallium affects three characteristics of the salts: a micro-

Table 6
Conversion of 1-butene at 10 min with salts of $H_3PW_{12}O_{40}$.

Salt	Preparative ratio	Conversion[a] (m^2 H^+) 100 °C	200 °C	300 °C
AgPW	0.50	3.4	3.7	3.2
	1.00	1.8	2.9	2.0
	1.50	1.9	0.2	1.6
TlPW	0.50	8.9	7.4	5.9
	1.00	9.0	3.6	1.4
	1.50	0.0	0.0	0.0

[a] Moles of products multiplied by 10^{26}; relative number of protons from ^1H MAS NMR data.

porous structure is created, the number of Brønsted acid sites is decreased and the distribution of acid sites is shifted. As noted earlier, 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 [5]. Not surprisingly, however, the number of residual protons and the chemical environment in which they reside are altered by changes in this ratio. With respect to the isomerization of 1-butene, the change in the distribution of acid sites for the thallium salts is reflected in the product distribution of the two isomers of 2-butene formed. A significantly larger number of protons present in the silver salts in combination with a consistent distribution of acid strengths, despite variations in the cation : proton ratio, contributes to conversions and selectivities which change relatively little with the stoichiometry of the salt.

It is evident that four factors play significant roles in influencing the isomerization of 1-butene: (1) the nature of the cation, (2) the morphological properties of the catalyst, (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 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.

For the salts displaying activity, the thallium-containing salts generally had higher conversions in the isomerization of 1-butene than the analogous silver salts, at each of the three reaction temperatures. These findings are consistent with the larger separations between the ^1H chemical shift for the silver(I) salts and that observed for the parent acid in comparison with the analogous thallium salts and the smaller number of strong acid sites present in the former.

The results of semiempirical quantum mechanical calculations have suggested that the negative charge on the terminal oxygen atoms in the Keggin anions has an effect on the mobility of the protons, and thus the acidity of the heteropoly acid [2]. Changing the peripheral metal atoms from tungsten to molybdenum would increase the coulombic binding of the proton as the charge on the terminal oxygen atoms is increased, while protonic mobility and acidity will decrease. It appears that the introduction of larger cations into the lattice structure with the Keggin anions also reduces the mobility of the protons. The larger size and repulsive interactions of the cations could restrict the physical movement of the protons. In addition, the nonprotonic cations may perturb the electron densities of the anions, altering the magnitude of the charge on the terminal oxygen atoms. The charge density of Ag^+ is greater than Tl^+, which is in approximate agreement with the trends observed in the NH_3 TPD, ^1H MAS NMR and butene conversion results.

It should be noted that while these interpretations are speculative, the influence of the larger nonprotonic cations on the acidic properties of the heteropoly acids as a result of direct and/or indirect interactions of the protons and the cations is evident.

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