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INFLUENCE OF COUNTER CATION ON THE THERMAL STABILITY, THE ACIDITY AND THE CATALYTIC PROPERTIES IN THE DEHYDRATION OF TERT-BUTANOL OVER 12-MOLYBDOPHOSPHATES

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The silver, ammonium, copper, and aluminum acidic salts of 12-molybdophosphoric acid have been prepared, mono-substitution, and their catalytic behavior measured for dehydration of tert-butanol. The reaction has been carried out in a flow system at the temperature range of 323-423 K and the reaction product was analyzed chromato-graphically. The effects of pretreatment temperature, time, partial pressure of alcohol, and non-steady-state regimes have been studied. The samples were characterized by TG, DSC, and BET surface areas. These studies have confirmed a correlation between structural stability and the salt cation, with the silver salt of $H_3PMo_{12}O_{40}$ being the most thermally stable. However, the ammonium molybdophosphate is the less stable catalyst due to the catalyst reduction. Mono-substitution of protons in $H_3PMo_{12}O_{40}$ with silver and ammonium form high surface area solids, as compared to copper and aluminum salts. The number of weakly or moderately strong acidic sites remains relatively unchanged with pretreatment temperature to 673 K. All catalysts are highly selective to produce isobutene which is predominate product. Isobutene formation is zero order reaction independent of the partial pressure of tert-butanol. This revealed that the dehydration reaction proceeded on the surface of solid catalysts (a surface-type reaction). In this case, the catalytic activities were determined by the concentration of protons on the catalyst surface and hence on the surface acidity.

Keywords: thermal stability, acidity, tert-butanol, heteropoly compounds.

Introduction

Isobutene is an alkene precursor in the synthesis of methyl tert-butyl ether. MTBE is widely used as an oxygenate for gasoline(1) not only to enhance the octane number but also to make motor vehicle fuel burn more cleanly, replacing toxic additives like lead, thereby significantly reducing toxic tailpipe pollution(2).

Heteropoly acids and related compounds have attracted considerable attention owing to their highly promising potential in industrial applications for acidic catalysis and selective oxidation(3-20). These types of compounds display a great potential of specific synthesis reactions for replacing sulfuric acid to satisfy the requirements of environmental protection(21).

Heteropoly acids are composed of primary, secondary, and tertiary structures. The primary structure is the structure of the heteropoly anions, and the secondary structure is the three dimensional arrangement of the polyanion and counter cation(6d,15,22,23). It was very important to realize that the primary structure is stable, whereas the secondary structure is flexible. The tertiary structure is very influential on the catalytic function of solid heteropoly acids (6d, 15). The tertiary structure is the structure of solid heteropoly acids as assembled. The size of the particles, pore structure, distribution of protons in the particle, surface area, mode of aggregation, etc., are the elements of the tertiary structures(15). Counter cations greatly influence the tertiary structure of HPAs.

For anhydrous sample, each polyanion interacts with three isolated acidic protons. When the water content increases, the water molecules protonated in the pseudo liquid phase to form H_3O^+ and $H_5O_2^+$ accompanied by the decrease in the amount of isolated acidic protons(24). One of the remarkable characteristics is that some solid HPAs (group A, hydrogen forms included) absorb easily a large quantity of polar or basic molecules such as alcohol and nitrogen bases in the solid bulk(25). The absorption depends on basicity and the size of the molecule to be absorbed and the rigidness of the secondary structure. The rigidness of HPAs depends on the counter cation (size, charge, etc) and apparently on the water content(26). Group B salts like $Cs_xH_{3-x}PW_{12}O_{40}(x>2)$ adsorbed even polar molecules only on the surface(27).

It is generally accepted that dehydration of alcohols takes place on either Bronsted or Lewis acid sites. The reactivity of alcohols is in the order: MeOH < EtOH < PrOH, BuOH, and EtOH < iso-PrOH < tert-BuOH(28,29), which can be interpreted in view of the relative stability of corresponding carbenium ions or affinity of each alcohol to protons.

The aim of this study is to examine the influence of mono, di- and trivalent cations on the activity, selectivity and stability of the molybdophosphoric acid towards the dehydration of tert-butanol to produce isobutene as a predominate product.

Experimental

Catalyst preparation

The acidic salts of multivalent cations ($M_x^{n+}H_{3-nx}P Mo_{12}O_{40}$, abbreviated as M_x, where M = Ag, NH_4, Cu, and Al) were prepared by the titration of an aqueous solution of $H_3PMo_{12}O_{40}$ (0.025 mol dm^{-3}) at 323 K with aqueous solutions of the corresponding nitrates (0.025 mol dm^{-3}). The aqueous solution of nitrate was added dropwise at a rate of about 1 ml min^{-1} with constant stirring for 2h. For $Cu_{0.5}$ and $Al_{0.33}$, precipitates were not obtained by the titration, so that the solution was evaporated at 343 K to give a solid. In cases of NH_4 and Ag, solutions containing precipitates were obtained. These were also evaporated to dryness in a similar way. All the solid samples were dried at 393 K for 4 hours.

Catalysts characterization

Several techniques were employed for the characterization of solids such as:

The surface area was determined by nitrogen adsorption-desorption at 77 K. Thermal and differential scanning calorimetry analyses were carried out on a thermogravimeter (Shimadzu TGA-50) at a heating rate of 20 and 10 K min^{-1}, respectively.

The Ag^+, Cu^{2+}, and Al^{3+} contents of the salts were determined by atomic absorption spectrophotometry (AAS). For the ammonium salt, the cation composition was calculated from the nitrogen content determined by elemental analysis.

Catalytic reactions

Synthesis of isobutene from tert-butanol was performed in a flow system at an atmospheric pressure in the temperature range from 323 to 423 K. Tert-butanol was fed by bubbling argon through an isothermal saturator kept at a constant temperature. Prior to the reaction, the samples were pretreated in situ at 623 K in the argon flow for 3 hours. The pressure of tert-butanol was changed from 13.5 to 300 Torr by changing the saturator temperature. Gases at the outlet of the reactor were analyzed with a gas chromatograph (Perkin Elmer AutoSystem XL having an FID) equipped with a capillary column of 15 m length packed with Carbowx 20M).

Blank runs have been performed without catalyst under the same experimental conditions similar to those measurements. No conversion of tert-butanol was observed in the temperature range investigated.

Results

Characterization of catalysts

Table 1 shows the chemical composition, surface areas and the surface acidity calculated for the investigated catalysts. It can be seen that the acidic salts of silver, copper, and aluminum, the degree of exchange of protons in the parent acid was in good agreement with the expected theoretical value, whereas it was higher for the NH_4^+ salt. The deviation of the ammonium salt with respect to the expected degree of exchange has also been observed by others**(30-32)**. Moffat *et al.* found that a deficit of ammonium carbonate employed in the preparation produces a substantial change**(31)**. However, an excess of cation was used during the precipitation step in order to obtain the stoichiometric ammonium compounds**(30,32)**.

Table 1: Chemical composition, surface area and surface acidity calculated for acidic salts of molybdophosphoric acid.

Sample	Cation/K.U.[a]	S_{BET}[b] (m^2g^{-1})	Surface[c] acidity (μ mol g^{-1})	Chemical formulae
$H_3PMo_{12}O_{40}$	-	8.0	20.7	$H_3PMo_{12}O_{40}$
$AgH_2PMo_{12}O_{40}$	0.93	60.9	106.5	$AgH_2PMo_{12}O_{40}$
$NH_4H_2PMo_{12}O_{40}$	1.40	47.5	66.5	$(NH_4)_{1.4}H_{1.6}PMo_{12}O_{40}$
$Cu_{0.5}H_2PMo_{12}O_{40}$	0.54	21.2	36.9	$Cu_{0.5}H_2PMo_{12}O_{40}$
$Al_{0.33}H_2PMo_{12}O_{40}$	0.31	19.1	33.6	$Al_{0.33}H_2PMo_{12}O_{40}$

a : Cation content per Keggin unit as calculated from chemical analysis

b: Measured from the nitrogen adsorption measurements.

c: Calculated from chemical formulae and surface areas

BET surface area of HPMo was 8 m^2 g^{-1}. For all the salt examined, the surface area is increased when compared to the parent acid. On the other hand, the surface areas increase as the diameters of the substituted cations are increased from group A (Cu^{2+}, Al^{3+}) to group B(NH_4^+, Ag^+). The surface area is large for silver and ammonium molybdophosphates because very fine particles are formed during titration due to the very low solubility in water(33,34). However, the low surface areas of copper and aluminum salts, as compared to the silver and ammonium salts, can be explained by their high solubility in water and the fine particles did not precipitate(33,35). Also, Moffat *et al.* have been explained the larger surface areas for the salts of large monovalent cations by the rotation and translation of the Keggin anions, so that the barriers between the interstitial voids presents in the parent acid are partially removed allowing the formation of channels between the anions and the counter cations(36-39).

The surface acidity is estimated from BET surface area and the content of H^+ in the chemical formulae(15,40,41) (Table 1). The surface acidity of the present acid increases with the partial substitution of proton by the cations. This can be attributed to their high surface area (19-61 $m^2 g^{-1}$) compared with 8 $m^2 g^{-1}$ for the parent acid.

The number of the crystallization water and the thermal stability of the parent acid and its acidic salts were performed by TG and DSC analyses *(Figs 1* and *2).*

During thermal gravimetric analysis, water of hydration evolved first, leaving anhydrous Keggin units with associated protons at temperatures up to 573 K. As the temperature continued to increase, above 673 K "protonic water" usually called "constitutional H_2O" evolved. This water is formed by extraction of an oxygen atom from the Keggin anion by two protons, thus decomposing the hetropoly anion structure. The decomposition of HPMo is observed at 697 K with $\Delta H = -61\ Jg^{-1}$ *(Table 2).* In agreement with previous findings, the complete dehydration of free and constitutional water from HPMo is mostly achieved by > 673 K. Above 703 K the Keggin structure of HPMo is completely destroyed(42-44). It is found that the introduction of copper and aluminum cations lead to decrease in the thermal stability of the parent acid. This is consistent with results of previous findings(45). They concluded that bi- and trivalent metal salts are not stable.

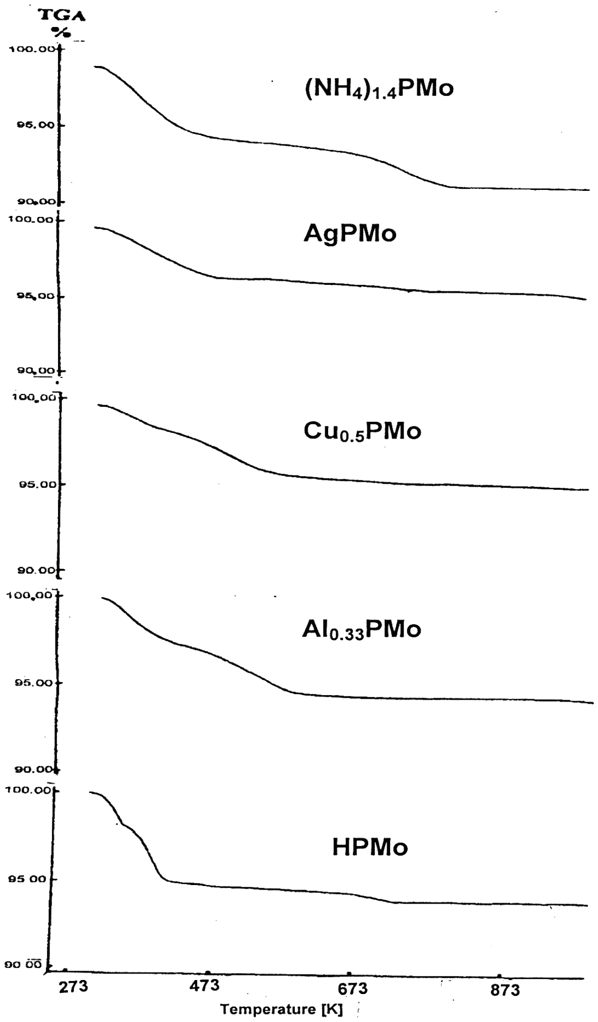

Fig. 1: TGA curves of molybdophosphoric acid and its acidic salts

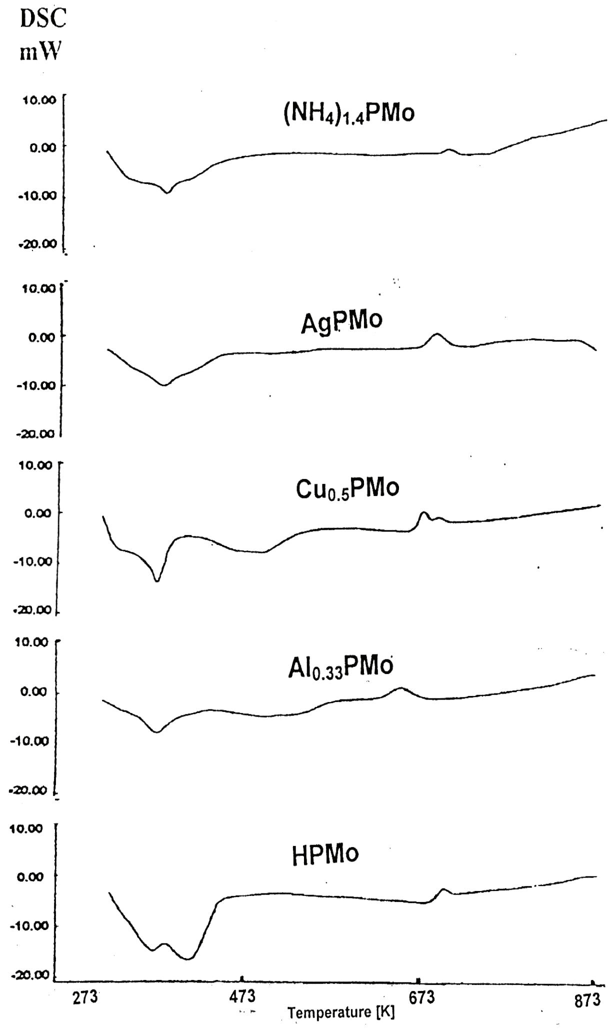

Fig. 2: DSC curves of molybdophosphoric acid and its acidic salts

Table 2: TG-DSC data for acidic salts of molybdophosphoric acid.

Sample	Abbreviation	Physisorbed hydration/KU[a]	Protonic water/KU[b]	DSC	
				Exo [K]	ΔH $J\ g^{-1}$
$H_3PMo_{12}O_{40}$	HPMo	12	1.5	697	-61
$AgH_2PMo_{12}O_{40}$	AgPMo	8	1.0	694	-82
$(NH_4)_{1.4}H_{1.6}PMo_{12}O_{40}$	$(NH_4)_{1.4}PMo$	6	…..c	695	-29
$Cu_{0.5}H_2PMo_{12}O_{40}$	$Cu_{0.5}PMo$	10	0.95	675	-41
$Al_{0.33}H_2PMo_{12}O_{40}$	$Al_{0.33}PMo$	12	1.0	652	-60

a : Water evolved at low temperature (less than 573 K).

b: Water loss from decomposition of Keggin unit.

c: Decomposition of ammonium molybdophosphate to ammonia, water and nitrogen(52).

The higher thermal stability of AgPMo is ascribed to the partial substitution of protons by large monovalent cation$^{(16, 46-48)}$. The reason could be that the larger cations are coordinated to more oxygen atoms on the periphery of Keggin structure and consequently cause atoms in anions to have small mobility, which means the crystal is more stable$^{(49)}$. However, in case of ammonium molybdophosphate the exothermic peak do not seem to suffer temperature shift, although the enthalpy values is decreased from - 61 to - 29 Jg^{-1} for the parent acid and ammonium salt, respectively (Table 2). This can be explained by the reduction of catalyst leading to formation of the reduced heteropoly anions, due to the possibility of NH_4^+ cation being a source of hydrogen$^{(50,51)}$. It is known that decomposition of ammonium molybdophosphate is proceed via elimination of ammonia, water, and nitrogen beginning around 673 K$^{(52)}$.

Catalytic reaction

Effect of pretreatment temperature for molybdophosphoric acid

The effect of pretreatment temperature on tert-butanol dehydra-tion and selectivity towards isobutene formation is shown in *Fig. 3*. As the pretreatment temperature increases from 373 to 673 K, the conversion is relatively increased and then decrease with further increase in temperature up to 723 K, while the selectivity is nearly constant. This can be attributed to slightly increasing the number of acid sites of sufficient strength required to facilitate the reaction as the pretreatment temperature increase to 673 K beyond which it decreases. This is consistent with the results of Moffat *et al.*$^{(53a)}$ who reported that the number of weakly or moderately strong acidic sites relatively little changed with pretreatment temperatures to a maximum value at approximately 673 K and then decreases as pretreatment temperature increased. This result shows that the strongly acidic sites is not necessary for this reaction.

The significant decrease in the catalytic activity at 723 K is ascribed to the decomposition of the acid into the corresponding single oxides. This is evident from TG-DSC data (Table 2).

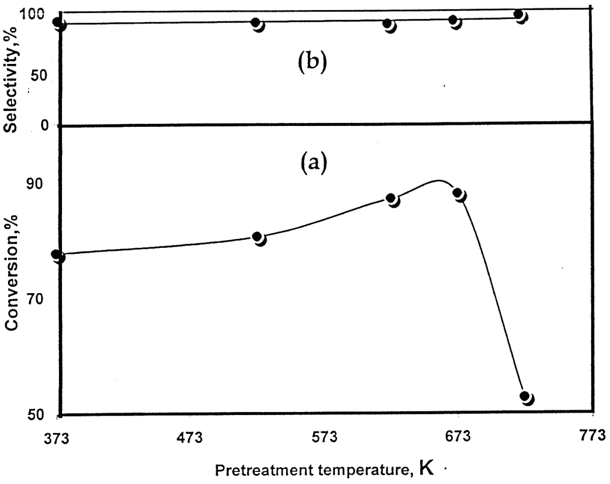

Fig. 3: Effect of pretreatment temperature on conversion of tert-butanol (a) and selectivity for isobutene formation (b) over molybdophosphoric acid

Effect of reaction temperature

Fig. 4 shows the changes in the conversion for the acidic salts of HPMo upon the variation of the reaction temperature. In these experiments the data were collected after the reaction reached approximately the stationary state at each temperature. The results obtained indicate that the activity increases with reaction temperature up to 373 K, beyond which the activity changes little. The predominate product is isobutene with small amount of isooctene. The isooctene is formed as a result of the dimerization of isobutene$^{(30,53b)}$. The maximum conversion to isooctene, 7%, was obtained over $Al_{0.33}PMo$ at 373 K (not shown) which may be attributed to presence of both Bronsted and Lewis acid sites on aluminum molybdophosphate catalyst$^{(54a\&b)}$. This agrees with the results of Connor *et al.*$^{(54c)}$, who found that the aluminum substituted of HPW is a good catalyst for propene oligomerization. The dehydration activity is in the following order:

AgPMo > $Cu_{0.5}PMo$ > $Al_{0.33}PMo$ > HPMo > $(NH_4)_{1.4}PMo$

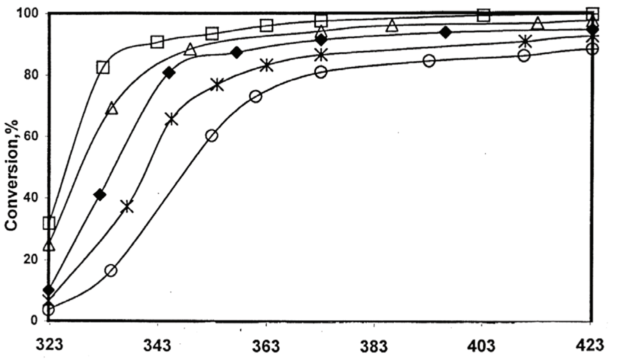

Fig . 4 . Conversion as a function of reaction temperature over heteropoly compounds .

The significant enhancement of AgPMo can be attributed to: (i) its high surface acidity which arise from its high surface area (Table 1). And/or (ii) the rapid migration of protons which participate in the reaction. This is evident from the conductance value obtained in this study, the value is increased from 200.3 to 240.4 ohm^{-1} cm^2 mol^{-1} for HPMo and AgPMo, respectively. This is consistent with results of BaBa *et al.*(55,56). They found that the mobility of protons was enhanced by the presence of silver.

The partial substitution of protons by copper and aluminum cations enhances the catalytic activity of parent acid. This can be explained by (i) these salts do not form precipitate by the titration, the solution was evaporated to dryness to obtain the solid salts. During this procedure, pH of the solution increased and in consequence the hydrolysis of the polyanion possibly took place to certain extent. The hydrolysis would form weakly acidic H^+(33). (ii) the dissociation of coordinated water(6d,14,57) and/or water produced during the reaction(29,58,59) as a function of the electronegativity of the metal cations, which form protons by a following reaction.

$$M^{n+} + mH_2O \rightarrow [M(H_2O)_m]^{n+} \rightarrow [M(H_2O)_{m-1}(OH)]^{(n-1)+} + H^+$$

and/or (iii) their high surface acidity (Table 1).

However, the ammonium molybdophosphate although having a high surface acidity is less active as compared to the HPMo. Due to the possibility of NH_4^+ cation being a source of hydrogen, resulting of the catalyst reduction. The catalyst reduced or partially reduced after pretreatment(50,51).

The selectivity towards isobutene formation over all investigated samples remains nearly constant with the reaction temperatures in the range 94-98%. This can be attributed to the dimerization activity being little changed with the reaction temperature (not shown).

Effect of reaction time

Fig. 5 shows the time courses of tert-butanol dehydration at 373 K catalyzed by molybdophosphates. The conversion decreases with time and reaches a stationary state value at different time-on-stream. It is believed that this decrease in conversion results from the relatively slower rate of regeneration of the Bronsted acid sites in comparison with the rate of formation of the olefinic products on a release of protons(37). Previous studies(28a,60-62) showed that the decrease in conversion due to the retention of the alcohols and/or their decomposition products on the catalysts.

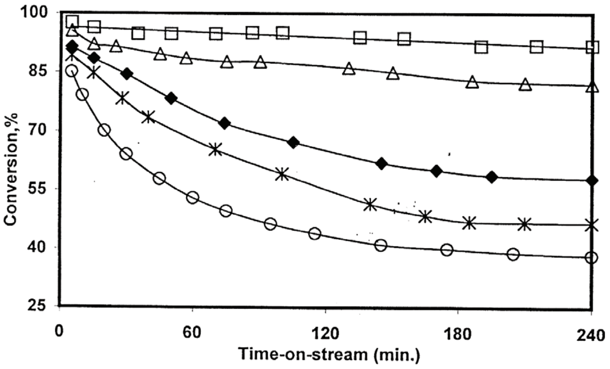

Fig .5 . Conversion of tert-butanol as a function of time -on- stream over heteropoly compounds at 373 K .

The stability of the catalyst during the reaction was estimated from the value of the activity retained (A_r) by the catalyst at the end of the experiment. This value is the ratio of the conversion at 4h to that at initial stage. The results obtained are summarized in *Table 3.* The highest stability of silver molybdophosphate among these salts may be attributable to its highest mobility of protons(55,56). On the other hand, the stability increased from 0.52 for HPMo to about 0.63, and 0.86 for $Al_{0.33}PMo$ and $Cu_{0.5}PMo$, respectively. This indicates that the formation of H^+ species, as mentioned before, over these catalysts improve also the stability of catalysts(6d, 14, 29,57-59).

The selectivity to isobutene was nearly 100% for all investigated catalysts. This indicates that all of the catalysts possess sites of sufficient acidic strength to facilitate the dehydration reaction and are inactive for isobutene dimerization under these conditions.

Table 3: Initial activity (A_i), final activity (A_f), activity retained (A_r), and apparent activation energy for tert-butanol dehydration over acidic salts of molybdophosphoric acid.

Sample (abbreviated)	A_i. 10^{-3} mol h^{-1} g^{-1}	A_f. 10^{-3} mol h^{-1} g^{-1}	A_r	E_a kJ mol^{-1}
HPMo	44.6	23.3	0.52	32.8
AgPMo	48.8	46.0	0.94	18.1
$(NH_4)_{1.4}PMo$	42.5	19.2	0.45	42.8
$Cu_{0.5}PMo$	47.8	41.0	0.86	23.2
$Al_{0.33}PMo$	45.7	29.0	0.63	18.3

Effect of alcohol partial pressure

The pressure dependence for isobutene formation over investigated catalysts is shown in *Fig. 6.* The conversion is independent of the partial pressure of alcohol, whatever the catalyst examined. The zeroth-order dependence for tret-butanol dehydration indicates that the surface is fully covered by alcohol because an adsorbed species of strong tertiary carbenium ion is mostly likely to form on the surface. This data agrees with the results obtained by several authors**(28a,61,63)**.

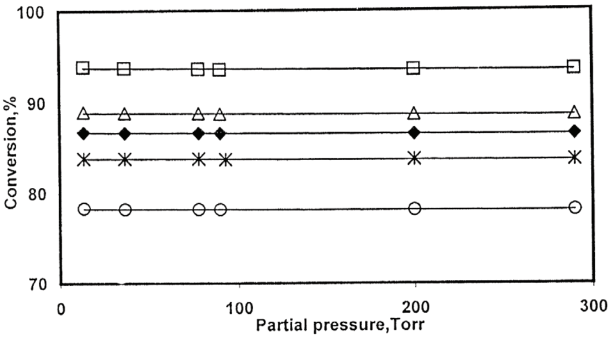

Fig. 6 . Effect of tert-butanol partial pressure on isobutene formation over acidic salts of HPMo at 373 K.

On cessation of the flow of alcohol to the sample after steady state is reached, the rate of isobutene formation gradually decreases and not falls sharply at the onset of purging for 45 minutes *(Fig. 7).* This behavior can be explained by the existence of strongly adsorbed species on the acid sites of catalyst surface**(63)**.

For AgPMo catalyst, the interaction of tert-butanol on acid sites is stronger than other investigated samples (Fig.7).

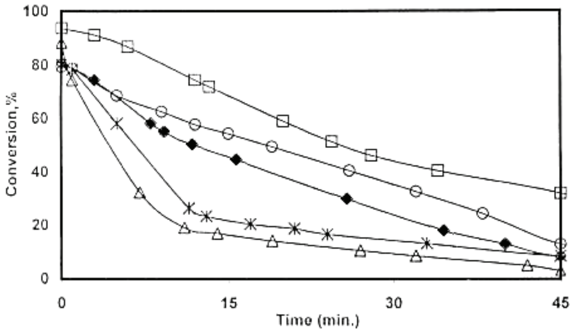

Fig . 7 . Desorption of isobutene from preadsorbed tert-butanol over acidic salts of HPMo at 373 K

Apparent activation energy

The apparent activation energy, E_a, cab be calculated from the slope of a plot log k versus 1/T by application of Arrhenius equation. The values of E_a thus obtained are listed in Table 3. It is evident that the partial substitution of the protons in HPMo by Ag^+, Cu^{2+}, and Al^{3+} cations decreases the Ea value from 32.8 to 18.1, 23.3 and 18.3 kJ mol^{-1}, respectively. The decrease in the value of Ea is due to enhancement of their catalytic activity, which is the normal case for catalytic promotion. However, the catalyst containing ammonium cation produces an increase in Ea than the parent acid. Such behavior can be attributed to a decrease of its catalytic activity.

Mechanism of isobutene formation

The dehydration of alcohols over heteropoly compounds proceeds via a carbenium ion mechanism**(28,64)**. The following conclusion can be drawn from the data obtained in this study:

1- The activity correlates well with the surface acidity, indicating that the dehydration of tert-butanol over heteropoly compounds belongs to the surface-type reactions. However, the effect of acidity on the selectivity towards isobutene formation is not significant.

2- The predominate product was isobutene with small amounts of isooctene.

3- Isobutene formation took place via a unimolecular mechanism, whereas isooctene via a biomolecular mechanism.

4- The dehydration of tert-butanol is a zeroth-order reaction. This indicates that the surface is fully covered by tert-butanol, due to the strong interaction of the alcohol on the acid sites (Bronsted sites).

From the previous data, the following reaction mechanism is proposed:

$$(CH_3)_3COH + H^+ \ldots O^{2-}_{Ku} \underset{298\ K}{\overset{fast}{\longrightarrow}} (CH_3)_3COH_2^+ \ldots O^{2-}_{Ku} \quad (1)$$

$$(CH_3)_3COH_2^+ \ldots O^{2-}_{Ku} \underset{\Delta < 323\ K}{\overset{slow}{\longrightarrow}} (CH_3)_3C^+ + H_2O + O^{2-}_{Ku} \quad (2a)$$

$$(CH_3)_3C^+ + O^{2-}_{Ku} \overset{fast}{\rightarrow} (CH_3)_3C\text{-}\ O^-_{Ku} \quad (2b)$$

$$(CH_3)_3C\text{-}O^-_{Ku} \rightarrow (CH_3)_2\text{-}C{=}CH_2 + H^+ \ldots O^{2-}_{Ku} \quad (3)$$

The process is clearly analogous to that already described for the dehydration of methanol and ethanol**(28,29)**. They suggest that the alkylation of the catalyst may be vital intermediate step in the dehydration of alcohol in general.

In step (1), tert-butanol is rapidly bound to the catalyst via a strong H-bonding interaction with the proton, forming the molecular ion $(CH_3)_3CO\ H_2^+$. The dissociation of this molecular ion (step 2) is identified as the rate determining step in the dehydration reaction. The role of the proton is evidently to weaken the C-O bond sufficiently, via a complex formation, to induce cleavage by mild thermal activation.

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