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# The Catalysis of Methanol and Ethanol Conversions on Molybdenum and Tungsten Heteropoly Compounds

J. B. McMONAGLE AND J. B. MOFFAT[1]

*Department of Chemistry and Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1*

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The alkylammonium and ammonium 12-heteropolyates of general formula $A_3XM_{12}O_{40}$, where A is the monovalent ammonium cation, X is the central or heteropoly ion ($P^{5+}$ or $As^{5+}$), and M is the metal cation ($Mo^{6+}$ or $W^{6+}$), have been studied in this work. Catalytic activities and selectivities for the conversion of methanol and ethanol, thermal stability, and bulk and surface structures were examined. The size and/or shape of the alkylammonium cation appeared to be the major criteria determining crystal secondary structure, although no major modifications in catalytic behavior were evident on altering the latter or on increasing the surface area. The salts studied herein showed only transient methanol to hydrocarbon selectivity and results are discussed in terms of the main factors which control hydrocarbon selectivity. The alkylammonium and ammonium 12-molybdophosphate salts all showed prolonged activity for ethanol conversion (between 498 and 623 K), the major products being ethylene (from dehydration), acetaldehyde (from dehydrogenation), and ethane. Evidence is presented to suggest the secondary hydrogenation of ethylene as a source of the latter product. Although the formation of ethane by such a mechanism is thermodynamically favorable, results indicated the reaction to be kinetically limited by the availability both of ethylene (at low reaction temperatures) and of hydrogen (at high reaction temperatures).

## INTRODUCTION

The catalytic and ion exchange properties of the 12-heteropoly compounds, attributable to their unique structure and chemistry, have attracted increasing research interest in recent years. Their bifunctional nature, with both acidic and redox properties, has resulted in the use of these heteropoly compounds for a wide variety of reactions including partial oxidation (*1, 2*), dehydration (*1, 3*), oxidative dehydrogenation (*4*), and methanol to hydrocarbon conversion (*5–8*).

Investigations of the catalytic behavior of the heteropoly acids $H_3PW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$ (hereafter abbreviated as HPW and HPMo) have revealed that the main factor controlling activity for oxidation of methacrolein to methacrylic acid is the oxidizing power (or reducibility) of the catalyst (*9*), whereas the primary influence on activity for methanol to hydrocarbon conversion is the concentration and strength of Brønsted acid centres present (*5–7, 10, 11*). The results of recent theoretical calculations (*12*) suggest that the activity of the heteropoly compounds in reactions requiring acidic sites may be correlated with the net charge on the peripheral or outer oxygen atoms of the anion, while in the case of oxidation processes the strength of the outer metal–oxygen bond of the anion is of particular importance. The participation of both the surface and bulk heteropoly acid molecules in "heterogeneous" catalytic processes involving oxygenated organic compounds has been proposed by several workers (*1–3*).

The situation is more complex in the case of the heteropoly salts due to the additional effects of the cation on both the chemical and physical properties of the solid (*1, 4, 6, 7, 13*). The electronegativity of 12-mo-

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[1] To whom correspondence should be addressed.

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lybdophosphates containing alkali-metal and alkali-earth cations has been correlated with catalytic activity and selectivity for oxidation-type reactions (*4*). This parameter was thought to be an important factor in affecting the chemical properties of the Keggin unit anion via the electrostatic effects of the counterion on both the molybdenum–oxygen bond strength and the acid–base properties of the molybdenum ions. Cation redox properties, on the other hand, have been proposed (*14*) as being a major influence on the catalytic behavior (for oxidation-type reactions) of 12-molybdophosphates containing transition metal cations. Activity patterns of the 12-heteropoly salts in acid-catalyzed reactions (such as methanol to hydrocarbon conversion) have been correlated with the estimated charge on the outer oxygen atoms of the anion, which presumably is inversely related to the acidic strength of either residual or generated protons (*6*, *11*). The production of protons in systems catalyzed by salts of the heteropoly acids has been attributed to a redox process involving the metal cations and molecular or atomic hydrogen (*8*, *15*) or to the dissociation of water by the cations or metallic elements of the anion (*4*, *15*). It should be noted, however, that such correlations of activity with acidic property do not take into account potentially complicating factors such as bulk or surface structure effects, and are thus of limited use in explaining differences in methanol to hydrocarbon activity.

The effects of the heteropoly cation on the surface and bulk physical structure have been examined in a recent study done at this laboratory (*16*). Cation valency and size were found to affect critically the bulk secondary structure. Salts with monovalent cations of diameter less than about 4 Å generally displayed a cubic (*Pn*3*m*) crystal structure detailed by Brown *et al.* (*17*). Within this group of salts minor modifications in bulk secondary structure brought about by the influence of the cation (primarily its size) were thought to be responsible for the observed presence of structural microporosity in some of these compounds (*16*).

The degree of involvement of both the bulk and surface of the heteropoly salts in catalyzing various reactions, and the effect of surface structure (in the highly porous salts) on reaction efficiency and selectivity are subjects in this field which currently require investigation.

The present work, in an attempt to gain more insight into some of these problems, is concerned with an investigation of the structure, thermal stability, and catalytic properties of the 12-tungsto- and 12-molybdophosphates containing monovalent cations. In particular, the ammonium [$(NH_4)_3PMo_{12}O_{40}$ abbreviated as $NH_4PM$] and alkylammonium salts, which show a variety of bulk and surface structures, have been examined. Some chemically and structurally related compounds have also been studied in an attempt to assess the effects of physical and chemical structure on the catalysis of methanol to hydrocarbon reactions by the tungsten-containing heteropolys. The reaction of ethanol over the ammonium and alkylammonium 12-molybdophosphates has been investigated, and a novel secondary hydrogenation reaction of the dehydration product (ethylene) is reported.

## EXPERIMENTAL

Alkylammonium 12-heteropoly salt preparation, X-ray powder diffraction (XRD), nitrogen adsorption, and pulse reactor techniques have been described elsewhere (*7*, *16*). Ammonium 12-tungstoarsenate was prepared in a similar fashion to the procedure used by Malik *et al.* (*18*) for pyridinium 12-tungstoarsenate except that ammonium nitrate was used in this case to precipitate out the desired salt. Differential thermal analysis (DTA) was done on a Dupont model 900 instrument.

Continuous flow reactor studies were performed using a glass reactor with the catalyst sample (typically 0.2 g) held in place between two glass wool plugs. Helium was used as a diluent and the reactant vapor was added by passing a proportion of the helium flow through a saturator containing the liquid reactant. Reactor effluent was sampled and analyzed by GLC using the following columns and conditions: (a) Porapak Q (50–80 mesh, 0.63 × 50 cm and 80–100 mesh, 0.63 × 250 cm in series) at 343 K for C1–C4 alkanes and alkenes, methanol, and dimethyl ether; (b) as (a) at 373 K for C1–C4 alkanes and alkenes, acetaldehyde, and ethanol; and (c) 15% squalane on Chromosorb W (0.63 × 300 cm) and Carbowax 400 on Poracil C (0.63 × 50 cm) in series at 323 K for C1–C6 hydrocarbons, methanol, ethanol, acetaldehyde, and diethyl and dimethyl ethers. Carrier (He) flow was 30 cm$^3$ min$^{-1}$ in all cases. No significant homogeneous reactions were observed in the empty reactor under normal operating conditions.

## RESULTS

### *Bulk and Surface Structures*

The physical structures of the methyl-, dimethyl-, trimethyl-, tetramethyl-, and *n*-propylammonium salts of 12-tungsto- and 12-molybdophosphoric acids were investigated in the present work. The unsubstituted ammonium salts were also included for comparison purposes.

The following structural features were apparent from the XRD powder pattern analyses:

(i) The presence of cations of size greater than $MeNH_3^+$ (where Me = methyl) resulted in crystal structures other than the cubic (*Pn*3*m*) type commonly associated (*17*) with the 12-heteropoly compounds. The situation is illustrated in Fig. 1, which shows the XRDs obtained from a series of alkylammonium 12-molybdophosphates. While it is possible that some cubic component may be present in the $Me_2NH_2PMo$ case, no such observation can be made for salts which contain larger cations; (ii) XRD powder patterns were almost identical for both the tungsten and molybdenum analogues which contained the same alkylammonium cation, further emphasizing the predominant influence of the cation on the bulk structure of the salts studied in the present work.

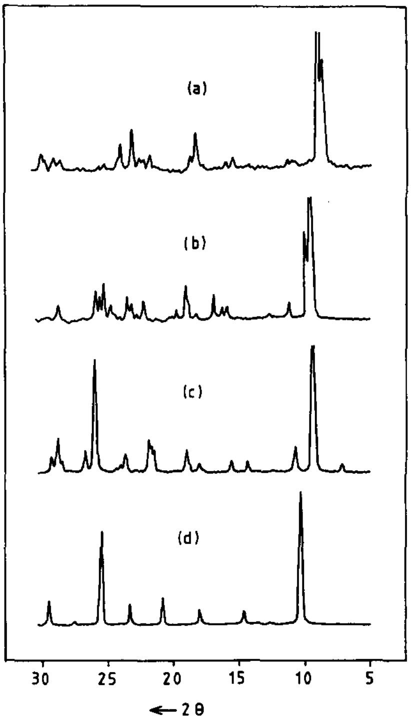

FIG. 1. XRD powder patterns of the alkylammonium 12-molybdophosphates: (a) tetramethyl-, (b) trimethyl-, (c) dimethyl-, and (d) methylammonium 12-molybdophosphate.

The BET surface areas were low (<10 m$^2$ g$^{-1}$ for all of the alkylammonium salts examined in this work. Nitrogen adsorption isotherms were predominantly Brunauer type II and hysteresis above p/p = 0.4 was absent, indicating the lack of significant micro- or mesoporosity. This behavior is in marked contrast to that of the high surface area $NH_4PW$ and $NH_4PMo$ salts which are known (*19*) to possess both micro- and mesopores, and have been discussed in detail elsewhere (*16*).

### *Thermal Stability*

Unlike the parent acids and water soluble

TABLE 1

DTAs of Alkylammonium 12-Heteropoly Salts

| RPW salts *R* | DTA peaks (K)[a] | |
|---|---|---|
| | Exo | Endo |
| $Pr_4N$ | 765m, br | 511w, br; 698w, br |
| $Me_4N$ | 808m, br | [b] |
| $Me_3NH$ | 763m, br; 788m, br | 485w; 549w |
| $Me_2NH_2$ | 738m, br; 790m, br | [b] |
| $MeNH_3$ | 728w, br; 788m, br | [b] |
| $NH_4$[c] | Stable to at least 823 K | |
| RPMo salts | | |
| $Pr_4N$ | 511w | 496w; 504w; 539w; 556w; 663s |
| $Me_4N$ | [b] | 523w, br; 661m; 691s |
| $Me_3NH$ | [b] | 583w; 595w; 668m |
| $Me_2NH_2$ | 578w; 596m | 606m; 663m, br |
| $MeNH_3$ | 598m; 615m, br | 631m |
| $NH_4$[d] | 773s | [b] |

[a] w, Weak; m, medium; s, strong; br, broad.

[b] No peak observed below 873 K.

[c] See ref. (*7*).

[d] From literature ref. (*20*).

12-heteropoly salts, the secondary crystal structures of the water insoluble alkylammonium salts are stable irrespective of the amount of residual water in the compound. DTA results for the alkylammonium 12-heteropoly salts are summarized in Table 1. The tungsten-containing salts appeared to be the more thermally stable of the two types, and the unsubstituted ammonium compounds were always the most stable in each series. The general order of thermal stability of the secondary structure (as characterized by XRD) in both series was $NH_4PM > R_4NPM > R_xNH_{4-x}PM$. Decomposition of $NH_4PW$ is known to proceed via elimination of ammonia, water, and nitrogen beginning around 823 K (*21*). Likewise in the present work the $R_4NPW$ salts have been observed to decompose in each case by elimination of a gaseous base, accompanied by destruction of the secondary structure. The mono-, di-, and tri-substituted alkylammonium compounds on the other hand gave no detectable evidence of the production of gaseous base on thermal decomposition. Comparing the DTA results for the $R_4NPW$ salts with those from the $R_xNH_{4-x}PW$ compounds, it can be seen that an additional exothermic peak is present (usually as a shoulder on the higher temperature peak) in the latter, and moreover that the position of this peak shifts toward lower temperatures in the order $Me_3NH > Me_2NH_2 > MeNH_3$. Thus it is clear that an additional decomposition event occurs which is facilitated by a lower degree of substitution in the cation. It is apparent from the data in Table 1 that the tungsten-containing salts thermally dissociate by predominantly exothermic processes whereas the alkylammonium molybdophosphates tend to follow endothermic decomposition pathways. The situation is illustrated in Fig. 2 which shows the DTAs for $Me_4NPW$ and $Me_4NPMo$.

### *Catalytic Reactions*

The activities of the ammonium and alkylammonium 12-heteropolyates as catalysts for the conversion of methanol to hydrocarbons and for the dehydration–dehydrogenation of ethanol have been examined in the present work.

*Methanol to hydrocarbon conversion.* The activity and selectivity of $NH_4PW$ in this reaction have been examined previously by pulse reactor techniques (*7*). The aim of this study is twofold: to investigate the catalytic behavior of this salt under more demanding continuous flow reactor conditions, and to assess the activities of the other tungsten-containing alkylammonium salts for this reaction. (The molybdenum heteropoly compounds are known (*5*)

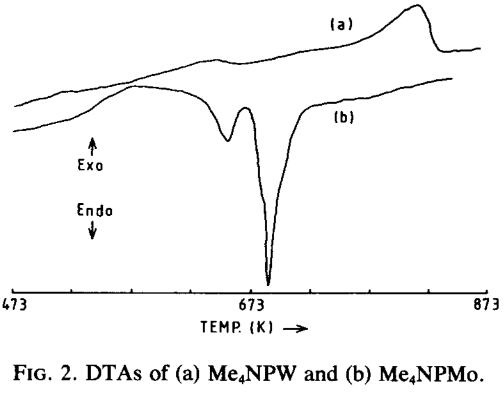

FIG. 2. DTAs of (a) $Me_4NPW$ and (b) $Me_4NPMo$.

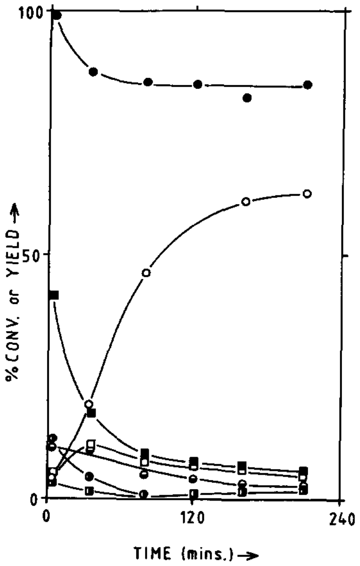

FIG. 3. Methanol conversion over $NH_4PW$: continuous flow reactor, 573 K, 0.249 g cat · min $ml^{-1}$ MeOH, pretreated in helium at 673 K; (●) conversion, (○) dimethyl ether, (◨) $C_1$, (⊖) $C_2$, (□) $C_3$, (■) $C_4$, and (◑) $C_5$.

to give poor selectivity toward hydrocarbon formation.)

Figure 3 shows the hydrocarbon yields and conversion as a function of time on stream at 573 K for $NH_4PW$, pretreated in helium at 673 K. While the overall activity decreases only by about 15% between initial and steady-state conditions, it is apparent that a profound dropoff in selectivity for hydrocarbon production and a large increase in dimethyl ether (DME) formation occur with increasing exposure time.

Activity and hydrocarbon yields for $Me_4NPW$, obtained under pulse reactor conditions, are given in Table 2. This salt compares well with HPW in terms of overall activity and selectivity toward C1–C3 but gives substantially smaller yields of C4 and C5 than either HPW or $NH_4PW$. The other alkylammonium 12-tungstophosphates behaved in a similar fashion to the tetramethylammonium salt, usually with slightly lower hydrocarbon yields.

*Ethanol dehydration/dehydrogenation.* The catalytic activities of $NH_4PMo$ and $Me_4NPMo$ for these reactions were examined under various pretreatment and reaction conditions. These two salts were chosen since they appeared to be the most thermally stable of the molybdenum containing compounds.

The main products from ethanol were ethylene (C2′), ethane (C2), and acetaldehyde. Only trace amounts of diethyl ether (DEE) were detected under the conditions used. This is in marked contrast to the results of Okuhara *et al.* (*3a*), who have reported DEE as a major product from ethanol over HPW.

The effects of various pretreatment environments on the catalytic activity of $NH_4PMo$ are illustrated in Fig. 4. Pretreatment in hydrogen at <623 K or in helium resulted initially in low product yields (expressed as %C2) and a long initiation period. The latter could be eliminated either by pretreatment in hydrogen at 623 K or by seasoning the catalyst at elevated temperatures in the reactant stream. In general, activation in hydrogen at 623 K or higher was the preferred method, since catalyst seasoning in the reactant flow at temperatures

TABLE 2

Catalytic Data[a] for Methanol Conversion over Tetramethylammonium 12-Tungstophosphate

| Product | Yield (as %Cl) | | |
|---|---|---|---|
| | $Me_4NPW$ | HPW[b] | $NH_4PW$[c] |
| Cl | 4.9 | 4.0 | 2.5 |
| C2 | 5.9[d] | 5.8[d] | 3.1[d] |
| C3 | 5.9[d] | 6.2[d] | 18.0[e] |
| C4 | 5.0[f] | 12.0[f] | 45.2[f] |
| C5 | 0.8[f] | 1.8 | 6.7 |
| DME | 3.8 | 12.0 | 0 |
| Conversion (%)[g] | 95.7 | 95.0 | 100 |

[a] Pulse reactor, reaction temp. = 623 K.
[b] From ref. (5), W/F = 400 g cat · min $ml^{-1}$.
[c] From ref. (7), W/F = 246 g cat · min $ml^{-1}$.
[d] Olefin predominates.
[e] Alkane predominates.
[f] Iso-alkane predominates.
[g] Including carbonization.

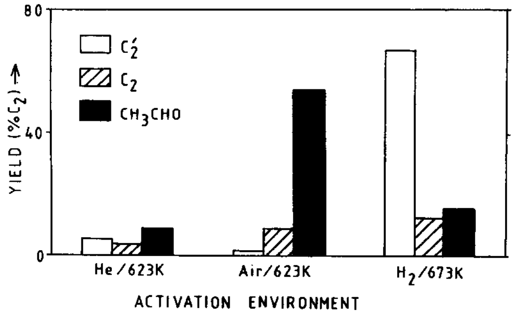

FIG. 4. Activation environment effects on ethanol conversion over $NH_4PMo$: continuous flow reactor, 523 K, 0.46 g cat · min ml$^{-1}$ EtOH.

TABLE 3

Comparison[a] of Activities and Selectivities of $NH_4PMo$ and $Me_4NPMo$ for Ethanol Conversion

| | $NH_4PMo$ (623K, $H_2$) | $Me_4NPMo$ (623K, $H_2$) | $NH_4PMo$ (693K, $H_2$) | $Me_4NPMo$ (693K, $H_2$) |
|---|---|---|---|---|
| Conv.[b] | 38.3 | 9.7 | 68.2 | 35.9 |
| C2'[c] | 15.3 | 27.6 | 56.6 | 47.0 |
| C2[c] | 32.9 | 30.6 | 13.0 | 15.4 |
| $CH_3CHO$[c] | 51.8 | 41.8 | 30.0 | 37.6 |

[a] Continuous flow reactor, reaction temp = 498K, W/F = 1.61 g cat · min ml$^{-1}$ EtOH.

[b] Excluding carbonization products.

[c] Selectivities (%).

>573 K was found to lead to excessive carbonization and a resultant lowering in activity. Catalyst samples, activated in hydrogen at 623 K, showed little or no change in activity with ethanol reaction time, and were usually blue in color indicating significant reduction to have taken place. Catalyst pretreatment in air resulted in a predominance of the dehydrogenation product, a large decrease in the yield of C2', and a slight reduction in that of C2.

Figure 5 illustrates the effect of activation temperature (in hydrogen) on the catalytic behavior of $NH_4PMo$. Selectivities toward C2 and acetaldehyde dropped off quite markedly at activation temperatures about 653 K, whereas that towards C2' increased significantly. The overall activity of the $Me_4NPMo$ salt was approximately 25–50% of that of the $NH_4PMo$ compound, although the effects of activation temperature on product distributions were remarkably similar in both cases (see Table 3). It is apparent from both Fig. 5 and Table 3 that conversion increases with activation temperature irrespective of the degree of decomposition of catalyst secondary structure (samples of $Me_4NPMo$ activated above 653 K were found to be amorphous).

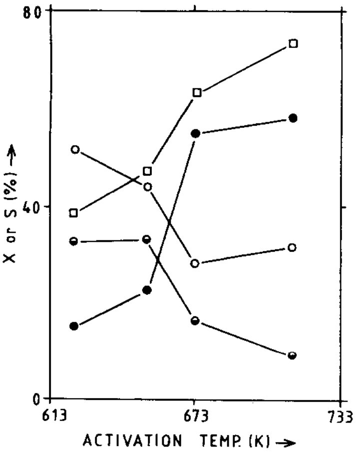

FIG. 5. Activation temperature effects (in hydrogen) on ethanol conversion over $NH_4PMo$: continuous flow reactor, 498 K, 1.61 g cat · min ml$^{-1}$ EtOH; (□) conversion (omitting carbonization), (●) $C_2'$, (◒) $C_2$, and (○) acetaldehyde.

Variations in activity and selectivity as a function of residence time (W/F = 0.23–1.44 g cat · min ml$^{-1}$ EtOH), and ethanol concentration (0.7–3.06%) were examined for $NH_4PMo$. Although no major changes in selectivity were evident over the range of conditions studied, some consistent trends were found. In particular, the selectivity toward C2 was observed to increase with increasing reactant concentration and with decreasing residence time.

The presence of ethane in the reaction products is not normally a feature of the dehydration/dehydrogenation of ethanol and one or more of several possible mechanisms may be involved. The secondary hydrogenation of primarily formed ethylene was thought to be a likely pathway for this

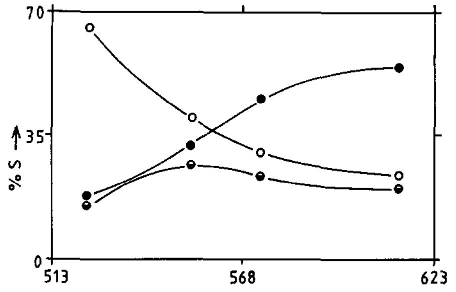

FIG. 6. Effect of reaction temperature on selectivity for ethanol conversion over $NH_4PMo$: continuous flow reactor, 0.49 g cat · min $ml^{-1}$. EtOH, pretreated at 673 K in hydrogen; (●) $C_2'$, (◒) $C_2$, and (○) acetaldehyde.

process, since both ethylene (from dehydration) and hydrogen (from dehydrogenation to the aldehyde) were available from the primary reactions (it should be noted however that hydrogen was not detected among the reaction products). Figure 6 shows the effects of reaction temperature on selectivity in the case of $NH_4PMo$. The selectivity for ethane production seems to be dependent on both ethylene and acetaldehyde selectivity, as might be expected if the alkane is produced by secondary hydrogenation of the alkene with the dehydrogenation reaction as a hydrogen source. In order to assess the importance of this mechanism for the production of ethane, a series of continuous flow reactor experiments were carried out in which the carrier gas was a 1 : 1 helium to hydrogen mixture. Using HPMo which had been activated in $H_2$ at 623 K (in a helium carrier stream this showed slightly better selectivity toward ethylene than either $NH_4PMo$ or $Me_4NPMo$), it was found that the yield of C2′ decreased by 69.7% whereas that of C2 increased by 55.2% on the introduction of hydrogen into the reactant gas stream (reaction temperature = 498 K, W/F = 1.61 g cat · min $ml^{-1}$ EtOH). Similar decreases and increases in ethylene and ethane yields respectively were obtained for the ammonium salts.

## DISCUSSION

The inherently different thermal decomposition pathways of the molybdenum and tungsten-containing alkylammonium salts (endo- and exothermic, respectively), evident from Table 1 and Fig. 2, indicate the critical influence of the Keggin unit peripheral metal atom on thermal stability. This is in contrast with the observed minimal effects of the peripheral metal atom on either crystal secondary structure (see above) or micropore surface area, both of which seem to be dominated by cation size and/or shape effects (*16*). The mode of thermal decomposition of $Me_4NPMo$ must involve the participation of both the Keggin unit and the tetramethylammonium cation since neither $NH_4PMo$ nor the alkylammonium 12-tungstophosphates appear to decompose endothermically. Inspection of the data in Table 1 for the partially substituted alkylammonium molybdophosphates reveals even more complex behavior with, in some cases, the presence of both endo-and exothermic DTA peaks within a narrow temperature range.

From Table 4, it is possible to summarize our present understanding of the effects of 12-heteropoly chemical and physical structure on their catalytic properties for the

TABLE 4

Summary of Catalytic Selectivities of 12-Heteropoly and Related Compounds for Methanol Conversion[a]

| Compound | Major product | | | References |
|---|---|---|---|---|
| | Hydrocarbons (C1–C6) | | Oxidation (CO, $CO_2$) | |
| | Initial | Prolonged | | |
| $NH_4PW$[b] | + | – | – | This work and (*7*) |
| $NH_4AsW$[b] | – | – | + | This work |
| AgPW[b] | – | + | – | (*8, 15*) |
| AgPW[c] | + | + | – | (*8, 15*) |
| HPW[b] | + | + | – | (*5, 10*) |
| HPMo[b] | – | – | + | (*5*) |
| $H_6P_2W_{18}O_{62}$[b] | – | – | + | (*5*) |

[a] Excluding dehydration or esterification products.
[b] Pretreated in helium.
[c] Pretreated in hydrogen.

conversion of methanol to hydrocarbons in the following way:

(i) Brønsted acid sites must be present in or on the compound in order to facilitate this reaction. In the case of the reaction of methanol over $NH_4PW$ (Fig. 3), it appears that although such sites may have been present at the onset of reaction, the selectivity toward hydrocarbon formation rapidly decreases with reaction time. Two possible explanations can be put forward for this effect: blocking of the Brønsted acid active sites by carbonization as the reaction proceeds, and/or irreversible consumption of the latter sites as part of the overall methanol to hydrocarbon surface reaction mechanism. Although it is well known that substantial carbonization occurs during this type of reaction, one might expect such a process to affect adversely the yields of all of the products formed and to cause a gradual decrease in overall conversion with time. It is evident from Fig. 3, however, that the yield of DME increases and that the conversion stabilizes after an initial drop to steady-state conditions. Furthermore, when the sample of $NH_4PW$ was calcined in air at 673 K in order to remove the carbonaceous deposit (pretreating this salt in such a fashion is known (*7*) to have little affect on selectivity towards hydrocarbon formation in this reaction and XRD analysis showed the secondary structure to be intact), it was found that the yields of hydrocarbons higher than C1 were not restored to their original high values. It must be concluded therefore that Brønsted acid sites active for hydrocarbon production are being irreversibly consumed during the course of the reaction. Thus an effective catalyst must possess some means of Brønsted acid regeneration as the reaction proceeds, in order to prolong the catalytic activity.

(ii) The presence of the Keggin unit primary structure is essential in maintaining the selectivity toward hydrocarbon formation. The dimeric 9-tungstophosphoric acid (*5*), which possessed both Brønsted acidity and non-Keggin unit primary structure showed little or no selectivity toward hydrocarbon formation on normal activation in helium.

(iii) The chemical constitution of the Keggin unit is a critical factor in determining catalyst selectivity. Both theoretical (extended Hückel) (*12*) and IR (*22, 23*) studies of bonding within the Keggin unit anion show the terminal oxygens to be more strongly bound to the metal in the case of HPW than in HPMo, hence explaining the greater selectivity toward oxidation reactions observed in the latter. The nature of the central (heteropoly) atom can affect selectivity in a similar manner. Consider the order of central atom–oxygen bond strengths (*22*) found in the tungsten heteropolys: PW > SiW > AsW. Compounds of the former two are known (*5*) to give selective formation of hydrocarbons whereas those of the latter have been found in the present work to initially produce mainly oxidation products. Thus it appears that oxidation selectivity decreases with increasing central atom–oxygen bond strength.

(iv) Changes in 12-heteropoly bulk secondary structure, whether brought about by cation size (see above) or valency (*6*), do not drastically affect the catalytic behavior in this reaction.

(v) Increased catalyst surface area is found to improve at least the initial activity for this reaction. Compare for example the reported (*7*) activity data for HPW (low surface area) and $NH_4PW$ (high surface area). This effect can be complicated however by reactions occurring as a result of absorption of methanol into the catalyst bulk (*3b*).

Both the hydrogen activation and reactant initiation effects observed in the reaction of ethanol over the 12-molybdophosphates appear to be a result of the catalyst reduction ($Mo^{6+} \rightarrow Mo^{5+}$). In the latter case, ethanol is converted to acetaldehyde and water with concomitant removal of oxygen from the Keggin unit anion. Thus, for most of the ethanol conversion data reported herein, the catalysts are in a reduced or partially reduced state after activation and during reaction (the exception being the data reported in Fig. 4 for the sample of pretreated in air).

The selectivity toward acetaldehyde initially falls off with increasing activation temperature (Fig. 5) although the yield remains fairly constant. This can be ascribed to the increased conversion and ethylene yields after hydrogen activation at temperatures above 653 K rather than a loss of active sites for dehydrogenation.

Although the formation of ethane from ethanol over dehydration/dehydrogenation catalysts is not a common reaction, other examples of alkane formation under such circumstances are known (*24, 25*). In both these cases, butane was observed as a major product from butanols and the predominant mechanism was thought to be nucleophilic substitution (SN2) of $OH^-$ in the alcohol by $H^-$ originating from water (dehydration by-product) or heterolytically adsorbed hydrogen (dehydrogenation by-product). In the present work, the observed increases in ethane yield and selectivity with added hydrogen and the fact that the yield of acetaldehyde was always larger than that of ethane, except when hydrogen was added, indicate the formation of ethane over the 12-molybdophosphates to arise mainly from the secondary hydrogenation of ethylene. The possibility of the ammonium or alkylammonium cation being a source of hydrogen for ethane production was thought unlikely since the latter product was also obtained using KPMo as the catalyst. The selectivity trend in ethane with respect to increasing activation temperature of $NH_4$PMo (Fig. 5) is somewhat similar to that of acetaldehyde mentioned above, except that it continues to decrease at higher temperatures. The yield of ethane was also found to decrease after such pretreatment. Since formation of this product is proposed to be indirectly related to acetaldehyde production, some similarity in selectivity trend is to be expected. The continued decrease in both yield and selectivity at higher activation temperatures, however, indicates removal of the appropriate active sites for ethane formation.

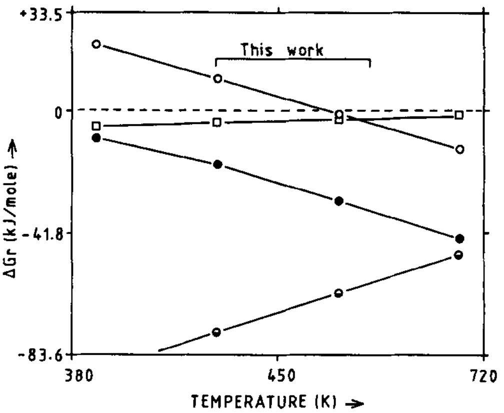

FIG. 7. Effects of reaction temperature on calculated reaction free energy change ($\Delta$Gr): (□)2EtOH $\rightleftharpoons$ $Et_2O$ + $H_2O$, (●) EtOH $\rightleftharpoons$ $C_2H_4$ $H_2O$, (O) EtOH $\rightleftharpoons$ $CH_3CHO + H_2$, and (◒) $C_2H_4 + H_2 \rightleftharpoons C_2H_6$.

The effects of reaction temperature on calculated free energy changes ($\Delta$Gr) for some of the ethanol conversion reactions observed in this study are illustrated in Fig. 7. Standard free energies of formation for the various reactants and products were obtained from the literature (*26*). The absence of significant amounts of diethyl ether as a reaction product in the present work may be explained by the fact that, at the reaction temperatures used (498–623 K), $\Delta$Gr for this reaction has a smaller negative value than that for dehydration to ethylene. Okuhara *et al.* (*3a*), studying ethanol dehydration over HPW at a lower (and more thermodynamically favorable) reaction temperature (373 K), observed the ether as a major product. The relatively high yields of acetaldehyde found at temperatures 590 K in the present work might seem somewhat surprising in view of the positive $\Delta$Gr's for the dehydrogenation reaction at such temperatures. A possible explanation (aside from kinetic factors) might lie in the fact that acetaldehyde can also be formed by reaction of ethanol with heteropoly oxygen resulting in further reduction of the catalyst. Observed production of ethylene increases with increasing reaction temperature in parallel with the corresponding change in ΔGr (Figs. 6 and 7). The large negative values of ΔGr for ethane formation might, at first sight, imply this product to predominate. It is obvious from Fig. 6, however, that this secondary reaction is kinetically limited to a large extent by the availability of both precursors (ethylene at low temperatures and hydrogen at higher temperatures).

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