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Advances in Catalysis by Heteropolyacids

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The advances in acid catalysis by heteropolyacids are examined and data on the acidity of heteropolyacids are surveyed. The characteristics of homogeneous and heterogeneous acid catalysis by heteropolyacids are discussed and its applied aspects are noted.
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I. INTRODUCTION

Heteropolycompounds (HPC) have come to be widely used as homogeneous and heterogeneous acid and oxidative catalysts by virtue of their unique physicochemical properties.[1-8] They are also of great interest as model systems for the study of fundamental problems of catalysis.[1,4,5] This is due to the available of reliable data on the structure of the HPC, the possibility of the specific variation of their acidity and oxidation potentials, and the similarity of their catalytic action in solution and in the solid state ("pseudo-liquid phase"[1,5]). As a results of studies carried out in the last decade in the USSR and abroad, the scientific principles of the selection of effective HPC catalysts have been formulated. The high Brønsted acidity of heteropolyacids (HPA), greatly surpassing in this respect the usual inorganic acids[4] and traditional acid catalysts,[5] is of fundamental importance for catalysis. The use of HPC as catalysts of oxidation processes is based on the reversibility of their redox reactions and their ability to enter into many-electron oxidation-reduction reactions.[4] Many new catalytic processes in which they participate have been developed, including amongst others a wide variety of processes involving fundamental and fine organic synthesis,[3,4,8] the preparation of hydrocarbons from methanol,[2,7] the photochemical liberation of hydrogen from water.[6] Some of them have already begun to be used in industry abroad, for example, the liquid-phase hydration of propene in the presence of tungsten HPA[9] and the vapour-phase oxidation of methacrolein to methacrylic acid on molybendum HPC.[5] In the future the number of such processes will undoubtedly increase. Catalysts based on HPC are characterised by a higher activity compared with their existing traditional analogues. With their aid, it is frequently possible to achieve a higher selectivity and also to solve successfully environmental problems.

This communication is devoted to the consideration of the present state of one of the most important aspects of catalysis by HPC—acid catalysis by HPA. Attention is concentrated on the discussion of the acid properties of HPA in solutions and in the solid state, their proton structure, and the characteristic features of the homogeneous and heterogeneous acid

catalysis. The use of HPC as oxidation catalysts has been considered in a number of reviews.[3-6]

II. STRUCTURAL CHARACTERISTICS OF HETEROPOLY-ACIDS IN THE SOLID STATE AND IN SOLUTION

HPA and their salts are polyoxo-compounds incorporating anions (heteropolyanions) having metal–oxygen ocathedra MO_6 as the basic structural units. They contain one or several heteroatoms X, which are usually located at the centre of the anion (central atoms). The MO_6 octahedra are linked together and form an extremely stable and compact skeleton of the heteropolyanion (HPAN). The cations may be hydrogen, alkali metal, and other metal ions.[10-12] More than twenty types of structures, incorporating from 4 to 40 metal atoms and from 1 to 9 heteroatoms, are now known for molybdenum, tungsten, vanadium, and niobium HPAN.[12] The commonest compounds, belonging to the saturated 12th series (M : X = 12) are of greatest importance for catalysis. They contain HPAN having Keggin's structure

$$XM_{12}O_{40}^{x-8},$$

where X is the central atom (Si^{IV}, Ge^{IV}, P^{V}, As^{V}, etc.), x the degree of its oxidation, and M is molybdenum or tungsten, which can be partly replaced by other metals. HPA and their acid salts are mainly used in acid catalysis and the neutral salts capable of generating strong acid centres on interaction with the reaction medium are more rarely employed.[7]

The compounds considered are usually obtained by acidifying an aqueous solution containing the salt of the heteroelement and the alkali metal molybdate or tungstate with subsequent isolation of the HPA salt as the hydrate. The acids can be obtained by extracting with ether acidified solutions of the salts and also by ion exchange.[10]

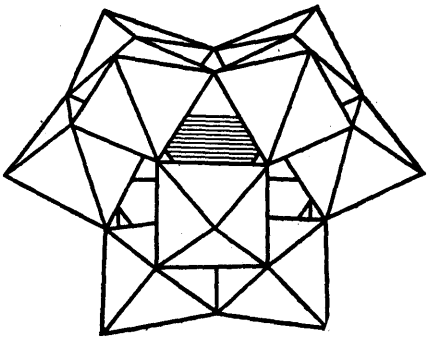


Figure 1. The structure of the heteropolyanion $XM_{12}O^{x-8}$ (α-isomer).[13]

The molecular structure of the 12th series HPC was established by Keggin as early as 1934 by the X-ray diffraction analysis of the hydrates of 12-tungstophosphoric acid.[13] This study played the most important role in the understanding of the laws governing the formation of the HPC structure.[10-12] Keggin's structure for the $XM_{12}O_{40}^{x-8}$ anion (α-isomer) is illustrated in Fig.1. It incorporates the central XO_4 tetrahedron surrounded by 12 MO_6 octahedra having common vertices and edges. The MO_6 octahedra are grouped in four M_3O_{13} triads, which are connected by common vertices. The radius of the HPAN is ~0.6 nm. The anion contains 12 quasi-linear M–O–M linkages between the octahedra forming part of different M_3O_{13} triads, 12 angular $M\overset{O}{\diagup\diagdown}M$ bonds between the octahedra within a single triad, 4 X–O–M bonds whereby the triads are joined to the central atom, and 12 terminal M=O bonds. These bonds exhibit characteristic vibration frequencies in the IR spectrum in the range 600–1100 cm^{-1}.[10-12,14]

Keggin's structure is fairly stable. It is preserved in HPC hydration–dehydration and dissolution processes and also on substitution of the metal in the HPAN, on replacement of the outer-sphere cations, and in not too extensive oxidation-reduction reactions.[4,5,10-12]

A less common type of 12th series HPC consists of compounds containing the anions $XM_{12}O_{42}^{x-12}$, where M is molybdenum and X is cerium(IV), uranium(IV), or thorium(IV). They have the Dexter–Silverton structure (Fig.2).[10] The central atom in these compounds is surrounded by 12 oxygen atoms and is located at the centre of the eicosahedron. The MO_6 octahedra are located in pairs on the common face.

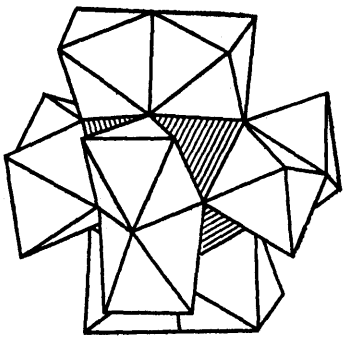


Figure 2. The structure of the hetropolyanion $XM_{12}O_{42}^{x-12}$.[10]

Together with the saturated 12th series HPC, a wide variety of derivatives of unsaturated series are known; the 11th series HPC XM_{11} have a defective Keggin's structure, in which one metal atom is missing, while the 9th series compounds XM_9 are obtained from the 12th series compounds by removing the M_3O_{13} fragment. They dimerise with formation of dinuclear derivatives $X_2M_{18}O_{62}^{x-16}$, having the Dawson structure (Fig.3).[10] The X_2Mo_{18} structure is chiral as a consequence of the slight shift of the Mo atoms relative to one another in two XMo_9 fragments (D_3 symmetry). As a result of this, the X_2Mo_{18} compounds can be used as catalysts in asymmetric synthesis (see below). In contrast to X_2Mo_{18}, the compounds X_2W_{18} possess no chirality and their symmetry is higher, close to the D_{3h} symmetry.[10]

The crystal structure of HPC consists of a three-dimensional lattice made up of HPAN, the cations, and the molecules of the water of crystallisation. In contrast to the rigid molecular structure of the 12-heteropolyanions, it varies within wide limits when their chemical composition and also the conditions of their synthesis and heat treatment are varied.[5,14]

Water-soluble HPC (the acids and salts of many metals) crystallise as hydrates containing a variable number of water molecules (up to 30 and above). Most of the water of crystallisation is readily removed on heating to 100–150 °C.[14]

This process is reversible. It is usually assumed that the main bulk of the water of crystallisation is within the pores of the HPC, as happens in zeolites.[12] The HPAN in the hydrates are not linked to one another and their packing is achieved as a result of the formation of hydrogen bonds with the molecules of the water of crystallisation.[10–12] As a result of this, the HPAN exhibits an appreciable mobility in the crystal matrix.[15] The water molecules in the crystal unit cell form clusters, because the hydrogen bonds between them are stronger than those between the water molecules and the oxygen atoms of the HPAN.[12]

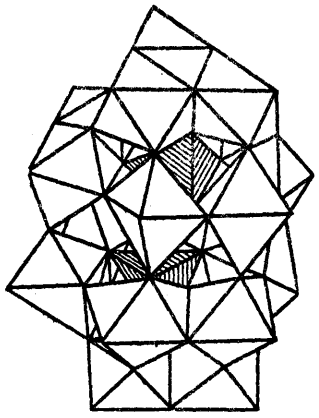


Figure 3. The structure of the heteropolyanion $X_2M_{18}O_{62}^{2x-16}$.[10]

In the dehydration process Keggin's structure of the 12-heteropolyanions is retained, as has been confirmed by the invariance of the IR spectra, but the cell parameters change significantly. Thus, according to X-ray diffraction data, the lattice constant of $H_3[PW_{12}O_{40}].29H_2O$ is 2.33 nm, while $H_3[PW_{12}O_{40}].6H_2O$ has a constant of 1.25 nm.[14] Thus, on dehydration, the unit cell contracts and the distance between neighbouring HPAN diminishes. Consequently, in this case one cannot assume that the water of crystallisation is "zeolitic" in nature. However, the removal of water from the insoluble salts of the acid $H_3[PW_{12}O_{40}]$ hardly alters their crystal structure and in this case the water of crystallisation can be assumed to be "zeolitic".[14]

Like hydrates, HPC form crystalline solvates with molecules of polar organic substances such as alcohols, ethers, ketones, amines, etc. This property plays an important role in heterogeneous catalysis and is manifested in the behaviour of HPA as the "pseudo-liquid phase"[5,7] (see below). The nature of the solvates and the products of their thermal decomposition have been investigated.[16]

The thermal stability of HPC is fairly high. For acids with Keggin's structure, it increases in the sequence $H_4[SiMo_{12}O_{40}] < H_3[PMo_{12}O_{40}] < H_4[SiW_{12}O_{40}] < H_3[PW_{12}O_{40}]$, so that the last acid decomposes at a temperature in excess of 400 °C.[17] The salts are usually more stable than the acids. The thermal stability of the HPC increases in the presence of water vapour.[18]

HPA are as a rule readily soluble in water and water-containing solvents. For example, the solubility of the acid $H_4[SiMo_{12}O_{40}].8H_2O$ at 25 °C is 88 wt.% in water, 86 wt.% in ethyl acetate, and 85 wt.% in diethyl ether.[11] The solubility falls sharply when dehydrated HPA and thoroughly dried non-aqueous solvents are used.[19] HPA do not dissolve in solvents such as benzene, petroleum ether, and chloroform.

The state of the HPC in solution depends on the acidity of the medium, the composition and concentration of the compound, and the nature of the solvent.[4,10,11] Keggin's structure is retained in fairly concentrated solutions but in dilute solutions account must be taken of the possibility of the destruction of the HPAN. The HPAN exist in moderately acid solutions, while in a stronger acid medium they undergo acid hydrolysis with formation of metal oxo-cations. In an alkaline medium hydrolysis with formation of the anions of simple acids of the corresponding heteroatoms and metals takes place. The resistance of the HPAN to hydrolysis in aqueous solutions decreases in the series of metals W>Mo>V [11] and increases in organic media.[4] Recently, significant progress has been achieved in the study of the state of HPC in solutions as a result of the application of ^{31}P, ^{51}V, ^{17}O, ^{183}W, ^{95}Mo, etc. NMR.[10] The NMR method makes it possible to identify HPAN of different structural types and also to detect geometrical isomers without disturbing the equilibrium in the system.

By virtue of their large size, HPAN have a low surface charge density. For this reason, HPA and their salts are almost fully dissociated in aqueous solution and the HPAN are weakly solvated. Nevertheless, saturated HPAN can function as ligands and can give rise to extremely stable complexes with transition and lanthanide metal ions. Several conveniently disposed peripheral M=O groups participate simultaneously in the formation of such complexes. For example, the stability constants of the complexes of anions having the Dexter–Silverton structure, namely $CeMo_{12}O_{42}^{8-}$ and $UMo_{12}O_{42}^{8-}$, with the cations Cu^{2+} and Er^{3+} are 10^5–10^6 litre mol^{-1}.[20,21] The metal cations in these complexes are linked to three oxygen atoms of the HPAN at once, and the HPAN is thus a tridentate macroligand. Heteropolytungstates having Keggin's structure form complexes with the cations Fe^{2+}, Fe^{3+}, MoO_2^{2+}, VO^{2+}, and VO_2^+, characterised by a stability constant of ~10^2 litre mol^{-1}.[22] The complexes of heteropolytungstates with hydrogen peroxide have been discovered and characterised.[23] The complexes of metal cations with defective anions of the type XM_{11} and X_2M_{17},[10] which have a vacancy in Keggin's or Dawson's structure and exhibit a high coordinating capacity, are well known.

The individual metal–oxygen fragments of the compact structure of the HPAN are appreciably mobile and therefore each can be regarded as a discrete ligand. The mobility of the ligands in the HPAN has been established by studying the ^{99}Mo, ^{185}W, and ^{17}O isotope exchange.[24–27] It has been demonstrated with the aid of the ^{32}P isotope that there is no exchange of the central atom in $PMo_{12}O_{40}^{3-}$.[24] The kinetics and mechanism of the substitution of W(VI) in the $SiW_{12}O_{40}^{4-}$ and $PW_{12}O_{40}^{3-}$ anions by the VO^{2+}, VO_2^+, MoO_2^{2+}, Fe^{2+}, and Fe^{3+} cations have been investigated.[22]

III. ACID PROPERTIES OF HETEROPOLYACIDS

Heteropolyacids are strong polybasic acids, greatly surpassing in strength the usual inorganic acids.[4] The basicity of the heteropolyacids $H_{8-x}[X^xM_{12}^{VI}O_{40}]$, where M = Mo of W, follows from Keggin's structure and has been demonstrated by numerous direct measurements.[4,11,12]

1. The Acidity of Solid Heteropolyacids

Two types of protons have been found in crystalline HPA:[12,28–30] (1) non-localised hydrated protons bound to one HPAN as a whole and rapidly exchanging with the protons

of the water molecules in the hydration shell of the acid; (2) non-hydrated protons localised at the peripheral oxygen atoms of the polyanion. When the water of crystallisation is removed, dehydration takes place and all the protons become localised. Thus water plays an important role in the formation of the proton structure of crystalline HPA.[12] It has been suggested[31] that the oxygen atoms of the angular groups M–O–M serve as the proton localisation centres because the greatest electron density is concentrated on these particular groups as a consequence of the weaker reversed d_π–p_π interaction. The majority of the spectroscopic (broad band ^{1}H NMR and IR) and structural methods do not allow an unambiguous solution of the problem of the site where the protons are localised in polyanions.[12] The ^{17}O NMR method is promising in this respect. Data[26,32] obtained by this method confirm that the O atoms of the angular bridges are protonated in solution. However, one should note that different centres may protonated in crystalline and dissolved HPA.

The hydrated protons in HPA hydrates with a high water content exist in the form of dioxonium ions $H_5O_2^+$ and more complex hydrates $H^+(H_2O)_n$.[12,33,34] This has been established by ^{1}H NMR and neutron diffraction methods in relation to the hexahydrates of the acids PMo_{12} and PW_{12}. The ion $H_5O_2^+$ appears as a result of the formation of the strong quasi-symmetrical hydrogen bond $H_2O...H^+...OH_2$. In the acid $H_3[PW_{12}O_{40}].6H_2O$, it has an almost planar structure. The O–O distance in the dioxonium ion is significantly reduced owing to the formation of a strong hydrogen bond and amounts to 0.237 nm. The dioxonium ion is linked by hydrogen bonds via the protons of the water molecules to the terminal oxygen atoms of the M=O groups in the HPAN.[34] We may note that, according to the available data,[35] in aqueous solutions of strong acids the simplest stable hydrate is also the dioxonium ion and not H_3O^+. The difference between the H_3O^+ and $H_5O_2^+$ ions is very small and is determined solely by the degree of asymmetry of the $H_2O...H^+...OH_2$ hydrogen bond. If this bond is symmetrical, then the $H_5O_2^+$ complex must be regarded as the dixonium ion and if it is assymetric it should be regarded as the hydroxonium hydrate $(H_3O)^+H_2O$. Apparently such fine differences are not very significant for acid catalysis.

The nature of the acid centres in solid HPA has been established by the method involving the adsorption of bases, mainly pyridine.[1,14,18] Pyridine is adsorbed on strong Brønsted acid centres in the form of the pyridinium ion $C_5H_5NH^+$, while on the Lewis centres it is adsorbed in the form of a complex with a donor–acceptor bond. The difference between the IR spectra of these forms made it possible to establish that the entire pyridine adsorbed on the HPA exists in the form of the pyridinium ion, i.e. the acidity of the HPA is of the Brønsted type.[1,14,18]

The following sequence of crystalline HPA in terms of acid strength has been established by ^{1}H NMR [30] and pyridine and ammonia thermal desorption[1,14,18,36] methods (the ammonia desorption temperatures in degrees C are indicated under the formulae):

$$\underset{592}{H_3[PW_{12}O_{40}]} > \underset{532}{H_4[SiW_{12}O_{40}]} > \underset{463}{H_3[PMo_{12}O_{40}]} > \underset{423}{H_4[SiMo_{12}O_{40}]}.$$

The acidity of phosphoric acids is greater than that of silicic acids and that of tungstic acids is greater than the acidity of molybdic acids. This agrees with the higher negative charge on the oxygen atoms in molybdic acids compared with tungstic acids. The effective charges on the oxygen atoms of the HPA have been determined by X-ray photoelectron spectroscopy.[12] Quantum-chemical calculations have also shown that the charge on the peripheral oxygen atoms increases when W is replaced by Mo.[37]

Crystalline HPA have a stronger acidity than traditional solid acids such as aluminosilicates, H_3PO_4/SiO_2, etc. Thus pyridine adsorbed on SiO_2–Al_2O_3 is fully desorbed at 300 °C, while on $H_3[PW_{12}O_{40}]$ it is strongly retained even at a higher temperature in the form of the pyridinium ion.[14] At the same time the number of Brønsted acid centres per unit area of the $H_3[PW_{12}O_{40}]$ and SiO_2–Al_2O_3 surfaces is approximately the same.[14]

In many respects, crystalline HPA behave like solutions. This is manifested primarily by the mobility of the elements of their structure. As already mentioned, the HPAN exhibits an appreciable mobility.[15] The HPA protons exchange rapidly with the protons of the molecules of the water of crystallisation.[28,29] Anhydrous HPA exhibit proton conductivity and water vapour accelerates the diffusion of H^+.[30] As in solution, the oxygen atoms of crystalline HPA exchange with the oxygen of water.[1] The rate of such exchange in HPA is much higher than in metal oxides. Crystalline HPA also exchange ^{18}O oxygen with CO_2 and O_2, the rate of exchange diminishing in the sequence $H_2O \gg CO_2 \gg O_2$.[14] The similarity between the molecular structures and the types of behaviour in the crystalline state and in solution makes it possible to treat the mechanisms of homogeneous and heterogeneous catalytic reactions involving them from a single standpoint.

2. The Acidity of Heteropolyacids in Solution

In aqueous solutions there is no adequate justification for subdividing the HPA protons into localised and non-localised. It is more correct to treat HPA as the usual polybasic Brønsted acids in which all the protons are hydrated and equivalent and are linked to the anion as a whole and not to individual basic centres. In solutions all the acid protons are capable of being substituted by other cations, provided that the HPAN is sufficiently stable with respect to alkaline hydrolysis.

Table 1. The dissociation constants of heteropolyacids in water at 25 °C.

pK	$H_5[PMo_{10}V_2O_{40}]$ (Ref.39)	$H_6[PMo_9V_3O_{40}]$ (Ref.39)	$H_7[PV_{12}O_{36}]$ (Ref.38)	$H_8[NpMo_{12}O_{42}]$* (Ref.40)	$H_8[CeMo_{12}O_{42}]$* (Ref.40)	$H_8[UMo_{12}O_{42}]$* (Ref.40)
pK_1	1.16	1.25	3.4	3.24	—	—
pK_2	2.14	1.62	4.9	3.43	2.12	—
pK_3	—	2.00	6.4	3.64	1.98	2.13
pK_4	—	—	7.9	4.28	2.99	3.02
pK_5	—	—	—	5.73	4.16	4.31

*At 20 °C.

In aqueous solution, HPA are strong acids in which the first three protons are fully dissociated. The stepwise character of the dissociation is not observable as a consequence of the levelling influence of the solvent. The subsequent dissociation proceeds stepwise as the pH of the solution is raised. The dissociation constants, starting with K_4, have been measured for certain acids with the Keggin and Dexter–Silverton structures in aqueous solution[38–40] (Table 1).

Non-aqueous solvents have a differentiating effect on the dissociation of the acids. They are more suitable for the investigation of the stepwise dissociation of polybasic acids. It is also significant that in non-aqueous media the HPA are much more stable towards degradation than in aqueous solutions.[4] In ethanol and acetone the first proton and to a large extent also the second proton are fully dissociated in Keggin's structures, while the first and second protons in acids such as $H_3[PW_{12}O_{40}]$ and $H_4[PW_{11}VO_{40}]$ are fully dissociated and the third proton is partly dissociated. In the less polar acetic acid, the HPA behave as comparatively weak 1–1 electrolytes.[4,41,42] Table 2 presents the stepwise dissociation constants of the HPA in acetone and acetic acid and for comparison also the dissociation constants of the usual inorganic acids. Evidently, the HPA are much stronger than the usual inorganic acids such as H_2SO_4, HBr, HCl, HNO_3, and even $HClO_4$. This is of fundamental importance for the application of HPA in acid catalysis. Attention should be drawn to the fact that, in terms of acidity, sulphuric acid, which is a traditional acid catalyst, is inferior to HPA by 2–5 pK units. The dependence of the acidity of HPA on their composition is strikingly weak. It is remarkable that the nature of the central atom has almost no influence despite the fact that the strengths of the corresponding simple acids differ appreciably (thus H_3PO_4 and H_4SiO_4 have pK_1 = 2.12 and 9.7 respectively in water[45]). Heteropolyacids are significantly stronger than the corresponding simple acids, which are weak or moderately strong.

Table 2. The dissociation constants of heteropolyacids in acetone and acetic acid.

Acid	Acetone			Acetic acid
	pK_1	pK_2	pK_3	pK_1
$H_3[PW_{12}O_{40}]$	1.6	3.0	4.0	4.8
$H_4[PW_{11}VO_{40}]$	1.8	3.2	4.4	4.7
$H_5[PW_{10}V_2O_{40}]$	—	—	—	4.8
$H_4[SiW_{12}O_{40}]$	2.0	3.6	5.3	5.0
$H_3[PMo_{12}O_{40}]$	2.0	3.6	5.3	4.7
$H_4[PMo^{VI}_{11}Mo^{V}O_{40}]$	2.1	3.7	5.5	—
$H_4[PMo_{11}VO_{40}]$	2.1	3.7	5.6	4.7
$H_4[SiMo_{12}O_{40}]$	2.1	3.9	5.9	4.8
$H_4[GeW_{12}O_{40}]$	—	—	—	4.3**
$H_5[GeW_{11}VO_{40}]$	—	—	—	4.7**
$H_6[GeW_{10}V_2O_{40}]$	—	—	—	4.6**
$HClO_4$	—	—	—	4.9***
HBr	—	—	—	5.6***
H_2SO_4	6.6*	—	—	7.0***
HCl	4.3*	—	—	8.4***
HNO_3	9.4*	—	—	10.1***

*From Pawlak et al.[43]

**From Polotebnova et al.[44]

***From Porcham and Engelbrecht.[46] The pK not marked with asterisks were taken from Kozhevnikov and co-workers.[41,42]

The difference between the strengths of the HPA and the usual acids can be most simply explained within the framework of the electrostatic theory taking into account the size of the anions and the number of oxygen atoms available for the delocalisation of the charge of the anion.[4,41,42] Since the HPAN are much larger than the anions of the usual acids, the energy of the proton bond in the HPA should be lower and their dissociation constants should be higher compared with the usual acids. Furthermore, the greater the degree of delocalisation of the charge of the anion, the smaller the effective negative charge on its individual basic proton-accepting centres, and hence the weaker the attraction of the proton to the acid anion. The formal negative charges of the HPAN $PM_{12}O_{40}^{3-}$ and $SiM_{12}O_{40}^{4-}$ are identical with the charges on the anions of the corresponding simple acids PO_4^{3-} and SiO_4^{4-}, but the charge per outer oxygen atom is 9 times smaller in the HPA than in the phosphate and silicate ions. As a result of this, the acids $H_{8-x}[XM_{12}O_{40}]$ are much stronger than $H_{8-x}[XO_4]$. An interesting analogy between the properties of the HPA and inorganic acids having the general formula $XO_n(OH)_m$, where X is a group IVA–VIIA element, is noteworthy. These acids are remarkable because their strength increases with increase in n and depends little on m for constant n.[47]

The weak influence of the composition of the HPA on their acidity nevertheless obeys a definite rule, which is clearer in polar solvents. In solvents of low polarity, for example, in acetic acid, there is a possibility of the influence by ion association. The series based on the acid strengths of the HPA in acetone is:[4,42]

$$H_3[PW_{12}O_{40}] > H_4[PW_{11}VO_{40}] > H_4[SiW_{12}O_{40}] \simeq H_3[PMo_{12}O_{40}] > > H_4[PMo^{VI}_{11}Mo^{V}O_{40}] \simeq H_4[PMo_{11}VO_{40}] > H_4[SiMo_{12}O_{40}] .$$

A similar sequence has been observed from the variation of the chemical shifts of the proton of chloral hydrate in the presence of HPA, obtained using nitrobenzene as the solvent. Thus the acidity series in solutions agrees well with the series found for solid acid hydrates. This agreement is reasonable, because the HPA behave in approximately the same way in the solid state and in solution.

The acidity diminishes when the HPA is reduced and when Mo or W is replaced by V and also on replacement of the central P atom by Si.

In all the cases enumerated, the decrease in acidity when the composition of the HPA is altered is accompanied by an increase in its basicity (the number of equivalent protons bound to the HPAN). The above dependence of the dissociation constants of HPA on their basicity agrees with the prediction of the electrostatic theory. By treating the HPAN as conducting spheres, with a charge equal to the basicity of the HPA, and the protons as positive point charges, it can be shown that any change in composition leading to an increase in the basicity of the HPA entails a decrease in the dissociation constants.[42] We may note that the substitution of Mo by W in the HPAN increases the dissociation constant but does not alter the basicity of the acid. However, in this case there is a correlation between the acidity and the effective charge on the peripheral oxygen atoms of the anion.

The splitting off of a proton from the acid can be represented as an ionisation process—dissociation with the intermediate formation of an ion pair:[48]

$$HPA \overset{K_i}{\rightleftarrows} HPAN^- \| H^+ \overset{K_d}{\rightleftarrows} HPAN^- + H^+ .$$

It has been established that the HPA in solution are almost fully ionised ($K_i \gg 1$) and exist in the form of solvate-separated ion pairs.[41,42] Thus the specific features of the acid properties of the HPA are determined by the weak electrostatic bond between the proton and the anion in the ion pair. The fruitfulness of electrostatic ideas in the chemistry of HPC, owing to the large amount of ionic character in the bond between the cations and the polyanions and the weak solvation of the HPC, must be emphasised.

Concentrated HPA solutions are of great interest for catalysis. The acidity of concentrated $H_3[PW_{12}O_{40}]$ solutions is greater than the acidity of solutions of sulphuric and perchloric acids having the same concentration. The difference between the H_0 is 1–1.5 units.[49] Presumably the values of H

are similar for acids of different composition, because in dilute solutions the dissociation constants of HPA depend only slightly on composition.

Using the concepts of hard and soft acids and bases, one can say that the HPAN are soft bases, which interact weakly with the hard acid H^+. According to Izumi et al.,[19] acids can be arranged in the following sequence in terms of their softness:

$$SiW_{12}O_{40}^{4-} > GeW_{12}O_{40}^{4-} > PW_{12}O_{40}^{3-} > PMo_{12}O_{40}^{3-} > \\ > SiMo_{12}O_{40}^{4-} > NO_3^- > p\text{-}MeC_6H_4SO_3^- > SO_4^{2-}.$$

3. Relation between the Oxidative and Acid Properties of Heteropolycompounds

HPC are many-electron oxidants. The addition of electrons increases the basicity of the HPAN and may be accompanied by protonation. The reduction of the Mo and W HPAN can be represented by the following equation taking into account protonation:

$$XM_{12}^{VI}O_{40}^{x-s} + ne^- + mH^+ \rightarrow H_mXM_{12-n}^{VI}M_n^{V}O_{40}^{x+m-n-s}$$

where $m \leq n$.[4,10,50] Hence the oxidation potential of the HPAN is

$$E = E_0 + \frac{RT}{nF} \ln \{XM_{12}^{VI}O_{40}^{x-s}\} \{H^+\}^m / \{H_mXM_{12-n}^{VI}M_n^{V}O_{40}^{x+m-n-s}\},$$

where E_0 is the standard redox potential, F is the Faraday, and the formulae in braces represent the ionic activities.

Table 3. The redox potentials of Keggin's structure of heteropolycompounds in aqueous solution.

Redox system	n_e	E_0, V	Refs.
V (V) → V (IV)			
$PV^{V}W_{11}/PV^{IV}W_{11}$	1	0.78	[53]
$PV^{V}Mo_{11}/PV^{IV}Mo_{11}$	1	0.68	[54]
$PV_2^{V}Mo_{10}/PV_2^{IV}Mo_{10}$	2	0.71	[54]
$PV_3^{V}Mo_9/PV_3^{IV}Mo_9$	3	0.71	[54]
$PV_4^{V}Mo_8/PV_4^{IV}Mo_8$	4	0.71	[54]
Mo (VI) → Mo (V)			
$PMo_{12}^{VI}/PMo_9^{VI}Mo_3^{V}$	3	0.65	[55]
$SiMo_{12}^{VI}/SiMo_9^{VI}Mo_3^{V}$	3	0.63	[55]
W (VI) → W (V)			
$BW_{12}^{VI}/BW_{11}^{VI}W^{V}$	1	−0.36	[56]
$GeW_{12}^{VI}/GeW_{11}^{VI}W^{V}$	1	−0.02	[56]
$SiW_{12}^{VI}/SiW_{11}^{VI}W^{V}$	1	−0.05	[56]
$PW_{12}^{VI}/PW_{11}^{VI}W^{V}$	1	0.15	[56]
Co (III) → Co (II)			
$Co^{III}W_{12}/Co^{II}W_{12}$	1	1.0	[57]

Remarks. The O atoms and charges have been omitted from the formulae; n_e is the number of electrons transferred and E_0 is expressed relative to the normal hydrogen electrode.

The quantities E_0 are as a rule unknown owing to the lack of data on the HPAN equilibria in solution. One uses instead the corresponding formal redox potentials, which depend on the pH and the HPAN concentration.[50] It is seen from the last equation that the oxidation potential of the HPAN depends on the acidity of the medium, at least in the pH range where the anion is protonated on reduction. Tungsten anions with Keggin's structure may have a charge up to −6 without the addition of protons on reduction in an acid aqueous solution (pH ≤ 1) by virtue of the high acidity of the corresponding acids.[51] In non-aqueous media, their charge is much smaller.

The oxidation potential of the HPC depends on the nature of both the metals and the central atom[4,50,52] (Table 3). The oxidation potential diminishes in the series of metals V > Mo > W. The central atom (a constant electrovalence ion) influences the redox potential via the change in the charge of the HPAN: the higher the charge of the anion, the lower the oxidation potential.[4,50,52] The dependence of the redox potential on the charge of the anion is frequencly linear and can be predicted with the aid of electrostatic theory.[52]

It has been demonstrated by the temperature-programmed reduction method that the ease of reduction of solid HPA by hydrogen diminishes in the sequence $PMo_{10}V_2 \cong SiMo_{12} \geq PMo_{12} \cong PMo_6W_6 > PMo_2W_{10} > PW_{12} \cong SiW_{12}$, and the ease of reduction of salts of 12-molybdophosphoric acid diminishes in the sequence $Ag^+ > Cu^{2+} > Ni^{2+}$.[5,58] The process is appreciably facilitated if a mixture of the acids with the Pd/C catalyst is reduced. Thus the capacity of solid HPA for reduction is fairly well correlated with the redox potentials in solution.

The question of the relation between the oxidative and acid properties of HPA is important for their use as acid catalysts. Comparison of the dissociation constants and oxidation potentials of HPA (Tables 2 and 3) shows that there is no correlation between them. At the same time, one must bear in mind that the dissociation constants of HPA diminish when they are reduced. Thus the catalytic activity of HPA should depend on the reducing capacity of the reaction medium.

Data on the kinetics of the redox reactions of HPAN with various one-electron reductants and oxidants are of interest in this connection. It has been established[59] that the observed kinetics agree satisfactorily with the Marcus theory. Thus this theory can be used to predict the stability of HPA in a reducing medium under the conditions of acid catalysis.

IV. ACID CATALYSIS BY HETEROPOLYACIDS

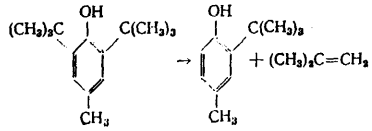
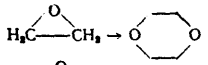
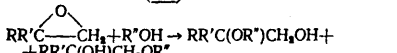
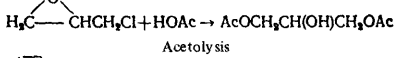
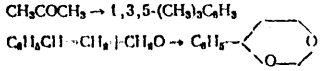
Heteropolyacids have long been used in catalysis,[3,10,11] but systematic studies in this field began comparatively recently. The likely usefulness of HPA as acid catalysts is due to their high Brønsted acidity, which is superior to that of the usual catalysts. Since HPA are readily soluble in water and oxygen-containing solvents and their stability in the solid state is fairly high, they are used as both homogeneous and heterogeneous catalysts. The W and Mo HPA have acceptable technological characteristics. In contrast to the usual inorganic acids, they are non-toxic and involatile, have no smell, and are stable on prolonged storage. Although HPA are much more expensive than acids such as sulphuric and hydrochloric, their use is frequently economically justified because of the high efficiency of their catalytic action.

Tungstic acids are the preferred catalysts in the series of HPA[4] because of their higher acidity, hydrolytic and thermal stability, and lower oxidation potentials compared with the Mo and V acids. In heterogeneous catalysis, one uses, together with HPA, their salts with cations such as Ag^+, Cu^{2+}, Pd^{2+}, Al^{3+}, etc.[7] The mechanism of the formation of acid centres in such systems is examined below. The strength and number of acid centres of HPA catalysts can be regulated by selecting the outer-sphere cation, by replacing the central atom and the metal in the structure of the polyanion, and also by employing carriers of different nature and by varying the concentration of the acid on the carrier.[5] In both homogeneous and heterogeneous catalysis by heteropolyacids, the

Brønsted rule usually holds satisfactorily: the catalytic activity is correlated with the strength of the acid centres of the catalyst.

Table 4 presents examples of reactions catalysed by HPA, many of which are of practical interest. HPA are frequently superior to the traditional acid catalysts as regards not only activity but also selectivity. This is because they make it possible to carry out the process under milder conditions. Furthermore, by virtue of the inertness of the anion, HPA do not enter into side reactions with organic reagents, in the manner characteristic of the usual inorganic acids (sulphonation, chlorination, etc.).[4]

Table 4. Acid catalystis by heteropolyacids.

Reaction	Catalyst	T, °C	α, %	A	Refs.
Hydration–dehydration					
$RCH{=}CH_2+H_2O \rightarrow RCH(OH)CH_3$	PW_{12}, SiW_{12}, PMo (hom.)	170—350	95—99	2—4	[9]
$C_6H_5C{\equiv}CH+H_2O \rightarrow C_6H_5COCH_3$	PW_{12}, PMo_{12} (hom.)	60	—	100	[3, 60]
$CH_3CH(OH)CH_3 \rightarrow CH_2{=}CHCH_3+H_2O$	PW_{12} (het.)	150	100	100	[61]
Esterification					
$RCH{=}CH_2+R'COOH \rightarrow R(OOCR')CH_3$	PW_{12} (hom.)	20—140	100	30—90	[62]
$(CH_3)_2C{=}CH_2+CH_3OH \rightarrow (CH_3)_3COCH_3$	PW_{12}/SiO_2, PW_{12}/C, SiW_{12}/C	90	100	300	[63, 64]
$t\text{-}C_4H_9OH \rightarrow (t\text{-}C_4H_9)_2O + H_2O$	PW_{12}/C, SiW_{12}/C	106	—	—	[65]
$HOCH_2CH_2CH_2CH_2OH \rightarrow$  $+ H_2O$	SiW_{12}, PW_{12}, PMo_{12} (hom.)	160	—	3	[66]
$C_2H_5OH+HOAc \rightarrow C_2H_5OAc + H_2O$	PW_{12}/C, SiW_{12}/C	120—150	96—100	>2	[36]
$n\text{-}C_4H_9OAc + C_2H_5OH \rightarrow C_2H_5OAc + n\text{-}C_4H_9OH$	PMo_{12}, PW_{12} (hom.)	110	—	4—10	[67]
Decomposition					
$C_6H_5(CH_3)_2COOH \rightarrow C_6H_5OH+CH_3COCH_3$	PMo_{12} (hom.)	25—60	>99	>100	[68]
$HCOOH \rightarrow CO + H_2O$	PW_{12} (het.)	150	100	—	[69]
$CH_3CH(CH_3)COOH \rightarrow CH_2{=}CHCH_3+CO+H_2O$	PW_{12}, SiW_{12} (het.)	240	100	4	[70]
Nitration					
$C_6H_6+NO_2 \rightarrow C_6H_5NO_2+NO+H_2O$	PW_{12}/SiO_2	270	—	—	[66]
Alkylation–dealkylation					
$C_6H_6+CH_2CH{=}CH_2 \rightarrow C_6H_5CH(CH_3)_2$	SiW_{12}/SiO_2	150	73	60	[71]
$C_6H_5HC(CH_3)_2 \rightarrow C_6H_6 + CH_3CH{=}CH_2$	PW_{12} (het.)	250	—	—	[69]
$C_6H_5CH_2+CH_3OH \rightarrow C_6H_4(CH_3)_2+H_2O$	PW_{12} (het.)	250	—	—*	[5, 72]
	PW_{12}, SiW_{12} (hom.)	118	97	>100	[73]
Reactions of epoxides					
	SiW_{12}/SiO_2, $SiMo_{12}/SiO_2$	100—260	—	—	[74]
	PW_{12}, PMo_{12}, SiW_{12} (hom.)	50	95—97	—	[75]
	PW_{12}, PMo_{12}, SiW_{12}, GeW_{12} (hom.)	30	~100	10^{3}**	[19]
Acetolysis					
 $+ HOAc \rightarrow AcOCH_2CH_2CH_2CH_2OAc+H_2O$	PW_{12}, SiW_{12}, PMo_{12} (hom.)	95	—	>100**	[19]
$(C_4H_9)_2O+HOAc \rightarrow C_4H_9OAc + H_2O$	PW_{12}, SiW_{12}, PMo_{12} (hom.)	118	—	100**	[19]
 $+ Ac_2O \rightarrow (AcOCH_2CH_2CH_2CH_2)_2O$	SiW_{12}, PW_{12}, GeW_{12} (hom.)	50	89—95	$>10^{3}$	[19]
Isomerisation					
But-1-ene → but-2-ene	PW_{12} (het.)	—	—	—	[61]
cis-But-2-ene → *trans*-but-2-ene	PW_{12} (het.)	25—100	—	—	[69]
o-Xylene → *p*-xylene + *m*-xylene	PW_{12} (het.)	300	—	—	[76]
n-Alkane → isoalkane	Pd — PW_{12}/SiO_2	210	87	—	[77]
Condensation					
$CH_3COCH_3 \rightarrow 1,3,5\text{-}(CH_3)_3C_6H_3$	PW_{12}, PMo_{12}, SiW_{12} (hom.)	25	40—55	—	[78]
	PMo_{12}, PW_{12} (hom.)	45	—	50	[79]
$n\,C_6H_5CH_2OH \rightarrow -(-C_6H_4CH_2-)_n- + (n-1)H_2O$	PW_{12} (hom.)	25	—	—	[5, 80]
Reactions of methanol and CO					
$CH_3OH \rightarrow$ olefin + alkane	PW_{12}, SiW_{12} (het.)***	300	—	—	[2, 7]
$CO + H_2O \rightarrow HCOOH$	PMo_{12}, SiW_{12} (het.)	200—300	—	—	[81]
$CO + ROH \rightarrow RCOOH$	PMo_{12}, SiW_{12} (het.)	200—300	—	—	[81]
Polymerisation and oligomerisation					
$n\,RCH{=}CH_2 \rightarrow -(-CHR-CH_2-)_n-$	PW_{12}/Al_2O_3	300	—	—	[82]

Notation: XM_{12} are the heteropolyacids $H_{8-x}[XM_{12}O_{40}]$ and in certain cases their salts; hom. = homogeneous catalytic systems and het. = heterogeneous catalytic systems; T is the temperature; A is the ratio of the catalytic activity of the HPA to the activity of an inorganic acid (H_2SO_4) in homogeneous reactions or of aluminosilicate in heterogeneous reactions; α is the selectivity.

*The aluminosilicate exhibits an appreciable activity only above 400 °C.[5,72]

**The activity of the HPA in relation to toluene-*p*-sulphonic acid.

***Together with the acids, the Ag^+, Cu^{2+}, and Al^{3+} salts are active.

1. Homogeneous Acid Catalysis

In this Section attention is concentrated on the following questions: (a) comparison of HPA and the usual inorganic acids in terms of their catalytic activity and selectivity; (b) dependence of the activity of HPA on their composition; (c) relation between the activity of HPA and their acidity; (d) the influence of the oxidative properties of HPA on their catalytic action.

The hydration of lower olefins is the first example of the practical application of HPA in an acid catalysed process.[9] The application of HPA on carriers as heterogeneous catalysts of the hydration of olefins has been known for a long time. They are more active than the industrial H_3PO_4/SiO_2 catalyst and are not removed by entrainment.[83] In the homogeneous process developed comparatively recently,[9] olefins ranging from ethylene to butene are converted into alcohols with a selectivity of 95–99% at 170–350 °C and pressures in the range 10–30 MPa in the presence of 10^{-5}–10^{-3} M aqueous solutions of $H_4[SiW_{12}O_{40}]$, $H_3[PW_{12}O_{40}]$, $H_5[BW_{12}O_{40}]$, $H_3[PMo_{12}O_{40}]$, $H_4[SiMo_{12}O_{40}]$, and their soluble salts. In conformity with their strength, the catalytic activity of HPA is higher than those of sulphuric and nitric acids.[79] The main advantage of the homogeneous hydration of olefins compared with the heterogeneous process is the attainment of higher degrees of conversion of the olefin as a result of the increased concentration of water and the use of a higher pressure. Data concerning industrial liquid-phase hydration of propene under the influence of HPA have been published recently.[9]

The addition of carboxylic acids to olefins (esterification of olefins) proceeds smoothly in solution in the presence of 10^{-4}–10^{-2} M tungsten and molybdenum HPA at 20–140 °C with a selectivity of ~100% in relation to esters of secondary alcohols.[4,62] Sulphuric acid, whose acidity is lower, is less active than HPA by a factor of 30–90.[62] The activity of tungstic acid is higher by a factor of 2–2.5 than that of molybdic acids, despite the virtual identity of their dissociation constants, which is due to the difference between the oxidation potentials of the acids. Molybdic acids, which are stronger oxidants, are reduced during the reaction by the components of the reaction mixture and lose their acidity, while tungstic acids are not reduced, because their oxidation potentials are significantly lower.

The dealkylation of derivatives of 2,6-di-t-butylphenol to 2-t-butylphenols is a key stage in the synthesis of widely used phenolic antioxidants. The acids PW_{12} and SiW_{12} are highly active homogeneous and heterogeneous catalysts of this reaction.[73,84,85] The heterogeneous process proceeds at 130–150 °C in the presence of the catalyst (less than 1%) in the melt of the substrate.[84,85] Molybdic acids are raidly deactivated as a result of their reduction by the reaction medium. HPA are tens of times more active than heterogeneous catalysts such as ion-exchange resins, aluminosilicates, aluminium sulphate, etc. The homogeneous process is even more effective. In solutions in acetic acid, dealkylation takes place already at 80 °C.[73] The catalytic activity of HPA is correlated with the acidity and exceeds by a factor greater than 100 the activity of sulphuric acid.

The transesterification of butyl acetate to form ethyl acetate takes place in solution in ethanol at 110–130 °C in the presence of 10^{-4}–10^{-2} M tungsten or molybdenum HPA.[67] In this reaction, the HPA is 4–10 times more active than sulphuric acid. Contrary to expectation, molybdic acids proved to be more active in this instance than tungstic acids. In the course of the reaction, the Mo acids are reduced and probably partly decompose. The true catalyst apparently consists of alkoxide complexes of molybdenum formed on decomposition of the HPA. In conformity with this hypothesis, the order of the reaction with respect to the molybdenum HPA is less than unity (the order with respect to tungstic acids is unity). We may note that titanium and zirconium alkoxide complexes are known to catalyse effectively esterification reactions.[86] The reduction and decomposition of molybdic acids have also been observed in the acetolysis reactions of esters.[19]

The acid decomposition of cumenyl hydroperoxide is the basis of the commonest industrial method of synthesis of phenol and acetone. Many homogeneous and heterogeneous catalysts have been proposed for this reaction, but only sulphuric acid has found practical application, although in its presence the process is insufficiently selective and yields phenolic waste water.[87] HPA are very active and selective homogeneous catalysts of the decomposition of cumenyl hydroperoxide.[68,88] Compared with sulphuric acid, they reduce the yield of the phenolic resin and the amount of waste water and increase the quality of the phenol obtained. The reaction rate constants k is correlated with the acidity of the HPA (in acetone at 25 °C [68]):

Catalyst	PW_{12}	$PW_{11}V$	PMo_{12}	SiW_{12}	$PMo_{11}V$	$SiMo_{12}$
$10^4 k, s^{-1}$	8.0	6.4	6.3	5.8	4.2	3.5
pK_a	3.0	3.2	3.6	3.6	3.7	3.9

Sulphuric acid is less active by 2–3 orders of magnitude than HPA.

The most selective catalyst of the decomposition of cumenyl hydroperoxide is 12-molybdophosphoric acid.[88] Tungstic acids are significantly less selective. It is most probable that this is due to the difference between the oxidative properties of the molybdic and tungstic acids. The point is that, in the presence of the hydroperoxide, which is a powerful oxidant, the HPA are in the oxidised state. After the completion of the decomposition of the hydroperoxide, the reaction medium becomes reducing and the molybdenum HPA are rapidly reduced in it and lose their catalytic activity. Tungsten HPA and the usual inorganic acids are not reduced and continue to catalyse side condensation reactions after the decomposition of the hydroperoxide has been completed. Thus the oxidative properties of HPA may also play a positive role in acid catalysis under certain conditions.

A selective semi-industrial method of synthesis of methyl methacrylate by the homogeneous esterification of methacrylic acid with t-butyl methyl ether (TBME) in the presence of Mo and W heteropolyacids at 110–150 °C has been developed:[89]

$$H_2C{=}C(CH_3)COOH + (CH_3)_3COCH_3 \rightarrow$$
$$\rightarrow H_2C{=}C(CH_3)COOCH_3 + H_2C{=}C(CH_3)_2 .$$

The initial stage is the decomposition of TBME to methanol and isobutene. The isobutene dimer is formed as a side product, but its yield can be appreciably reduced by the continuous removal of isobutene from the reactor.

A new interesting aspect of catalysis by HPA is asymmetric synthesis. It has been found recently that the chiral acid $H_6[P_2Mo_{18}O_{62}]$ can be used as the catalyst of the asymmetric polycondensation of benzyl alcohol.[90] In the presence of the l-brucine-$H_6[P_2Mo_{18}O_{62}]$ homogeneous system, benzyl alcohol is converted into an optically active polybenzyl:

$$nC_6H_5CH_2OH \rightarrow -(-C_6H_4CH_2-)_n-+(n-1)H_2O .$$

In the presence of the non-chiral acid $H_6[P_2W_{18}O_{62}]$, an optically inactive polybenzyl is formed.

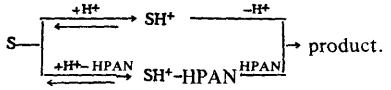
The homogeneous reactions catalysed by HPA are usually of first order with respect to the substrate S. The order with respect to the catalyst depends on the ionising capacity of the solvent. Thus, in media where the degree of dissociation of the HPA is low, the reactions are of first order. For example, the rates of the reactions involving the esterification of olefins and the dealkylation of derivatives of 2,6-di-t-butylphenol in acetic acid[62,73] are described by the expression:

$$v = k[HPA][S] .$$

In more polar solvents, where the degree of dissociation of the HPA is appreciable, the process frequently takes place in accordance with the kinetic equation

$$v = (k_1[H^+] + k_2[H^+ - HPAN])[S],$$

where H^+–HPAN is the acid heteropolyanion. Examples of such reactions are the decomposition of cumenyl hydroperoxide into phenol and acetone in acetone (H^+–HPA = $H_2PMo_{12}O_{40}^-$),[68] the hydration of isobutene,[3,79] and the cyclisation of butane-1,4-diol to tetrahydrofuran[66] in aqueous solution (H^+–HPA = $HSiW_{12}O_{40}^{3-}$). In this case, the reaction proceeds via two pathways: specific catalysis by the H^+ ion and general catalysis by the HPAN:



Thus HPA are more active as homogeneous catalysts than the usual acids, especially sulphuric acid. This makes it possible to carry out the catalytic processes at a lower catalyst concentration, which frequently increases the selectivity and makes it possible to reduce the amount of waste water in the neutralisation of the catalyst.

2. Heterogeneous Catalysis

(a) *General characteristics.* In heterogeneous catalysis, HPA and their salts are used as massive and deposited catalysts. The best carriers are neutral supports—silica gel and activated charcoal. Basic carriers, such as Al_2O_3 and MgO, are unsuitable, because they neutralise the HPA.[36] The properties of catalysts based on the salts depend significantly on the nature of the metal cation, the degree of substitution of hydrogen in the acid by the metal, and the solubility of the salt. The temperature at which the HPA catalysts are used does not as a rule exceed 300–350 °C, which is within the limits of the thermal stability of tungstic acids. Since HPA and the water soluble salts are highly hydrated, they are subjected to a preliminary heat treatment *in vacuo* at 100° to 300 °C in order to remove the water of crystallisation. Such heat treatment does not disrupt the structure of the HPAN. Evacuation of the HPC at 130 °C for 1 h lowers the amount of water to 1–2 molecules per HPAN.[69] The insoluble salts are hydrated to a much lesser extent. Their water is zeolitic in character and is readily removed by evacuation at 25 °C.[14]

The acids in massive form and their soluble salts are characterised by a low specific surface (1–5 $m^2\ g^{-1}$), which depends little on the heat treatment conditions.[69,91] The specific surface of insoluble caesium salts reaches 100–200 $m^2\ g^{-1}$ The acid caesium salts $Cs_{3-x}H_x[PW_{12}O_{40}]$ (x = 0.15 to 0.5), which have a large surface area, are of interest as insoluble acid catalysts.[5,92] They are distinguished by a higher thermal stability than the initial acids.[5]

The porosity of massive specimens of the PmO_{12} and PW_{12} acids is insignificant. Thus $H_3[PMo_{12}O_{40}]$ has a pore volume of 0.026 $cm^3\ g^{-1}$ at 25 °C and a wide distribution of the pore sizes with respect to radius. After vacuum treatment at 110 °C, the pore volume remains unchanged but a narrow peak, corresponding to a radius of ~2 nm, appears on the pore size distribution curve. Such pores are formed as a result of the change in the crystal structure of the acid on dehydration, which leads to the appearance of cavities and the contraction of the unit cell. After evacuation at 450 °C, the peak vanishes; the pore distribution again becomes broad, which can be accounted for by the further mutual approach of the HPAN.[93]

The study of the PW_{12} and SiW_{12} acids deposited on silica gel by X-ray diffraction showed that the HPA phase on the carrier surface is formed when its content is ~20 wt.%.[36] According to ammonia thermal desorption data, the strength of the HPA on silica gel diminishes, as for the massive acids, on passing from PW_{12} to SiW_{12}, and is independent of its concentration on the carrier.[36] HPA on activated charcoal exhibit high activity and are not washed off by water and organic solvents.[65] Such catalysts are promising for processes in suspension. The decomposition of tungsten HPA was observed when these were deposited on alumina even when the basicity of the Al_2O_3 had been reduced by preliminary treatment with HCl.[36]

The activity of deposited catalysts usually increases with increase in the content of the HPA to 15–30 wt.% (which corresponds to approximately monolayer coverage) and is subsequently independent of the latter.[36,66] The activity of the deposited catalysts calculated per acid molecule is much lower than the activity of the massive acid specimens. This applies to reactions such as the alkylation of benzene with ethylene, the esterification of acetic acid with ethanol, the dehydration of 2-propanol,[36] the vapour-phase nitration of benzene,[66] etc.

(b) *The "pseudo-liquid phase".* The water-soluble HPC exhibit a high affinity for the molecules of polar substances such as alcohols, ketones, ethers, esters, amines, etc. Large amounts of these substances are sorbed in the bulk of the crystalline HPC with formation of solvates. This phenomenon should not be confused with adsorption in the micropores of the usual sorbents.[1,5,7] Table 5 presents data for the absorption and adsorption of polar and non-polar substances by the acid $H_3[PW_{12}O_{40}]$. The total degree of sorption of the substance at 25 °C and the amount which is irreversibly retained after evacuation at 25 °C are indicated. For polar molecules, the latter corresponds to the presence of 50–100 layers of the sorbate on the $H_3[PW_{12}O_{40}]$ surface. Oxygen-containing compounds are almost fully desorbed at 100–150 °C, while nitrogen derivatives require the use of higher temperatures. The degree of sorption of non-polar hydrocarbons (alkanes, olefins, arenes) is insignificant. They are adsorbed only on the HPA surface.

Table 5. The sorption of different substances by the acid $H_3[PW_{12}O_{40}]$ at 25 °C.[5]

Substance	Sorption*	
	irreversible	total
Pyridine	6.0	9
Ammonia	3.2	4.3
Methanol	2.2	>10
Isopropyl alcohol	6.3	>10
Ethylene	0.03	0.04
But-1-ene	0.2	0.25
Benzene	0.1	0.5

*The number of sorbed molecules of the given substance per HPA molecule.

By virtue of the rapid absorption of polar molecules, the catalytic reactions can occur not only on the surface but also on the bulk of the massive HPA. In relation to polar substances, solid HPA behave similarly to highly concentrated solutions, i.e. all the acid protons and not only the surface

protons participate in the catalytic reaction. This phenomenon, which is unusual for heterogeneous acid catalysis and is characteristic of massive HPA, is described by the term "pseudo-liquid phase".[1,5] The ability of crystalline HPA to effect the catalytic reactions of polar substances in the bulk of the catalyst, like the reactions in homogeneous systems, is implied.

In contrast to polar molecules, non-polar reagents are incapable of being absorbed in the bulk of the HPA; they interact only with the surface of the catalyst. Soluble salts of HPA also possess the property of the "pseudo-liquid phase". Insoluble salts, which do not absorb polar molecules, possess no such property.

In terms of the catalytic properties in relation to the molecules of polar substances, massive HPA resemble zeolites to some extent. In both cases, virtually all the acid centres of the catalyst are accessible: in the HPA as a result of the absorption of the substrate in the bulk phase and in zeolites as a result of the high internal surface area. However, whereas in the case of HPA this is true only of polar molecules, in a zeolite this is true of any molecules whose dimensions do not exceed the diameter of the zeolite channels. In contrast to zeolites, HPA do not have sufficiently pronounced molecular-sieve properties, because they do not have a rigorously ordered porous structure.

Several studies have been devoted to the "pseudo-liquid phase".[1,5,7,94-98] The dehydration of alcohols (ethanol, 2-propanol, 2-butanol),[69,94] the conversion of methanol into hydrocarbons,[7,95] the decomposition of formic acid,[69] and other reactions have been included amongst pseudo-homogeneous reactions. The "pseudo-liquid phase" is manifested kinetically by the fact that the rate of the reaction catalysed by the deposited HPA is proportional to the concentration of the active component and not its surface area. Such relations have been found in the study of the conversion of methanol on deposited silver and copper salts of PW_{12}.[97,98] However, in the case of the HPA themselves, the rate, which initially increases with increase of the amount of acid on the carrier, subsequently reaches a plateau; thus the specific catalytic activity calculated per HPA molecule diminishes. This can be explained by the fact that, on increasing the amount of deposited acid, the absorption of the substrate in the bulk of the catalyst becomes the rate-limiting stage of the catalytic process. The latter is analogous to the internal diffusion inhibition in the case of the usual porous catalysts. Another possible explanation is a considerable contribution of the surface reaction.

The correlation of the catalytic activity with the acidity of the massive HPA specimens may serve as evidence for pseudo-homogeneity. Thus the rates of the above reactions decrease almost linearly as the H^+ in $H_3[PW_{12}O_{40}]$ is substituted by sodium or pyridine is added, falling almost to zero after the introduction of three pyridine molecules or three sodium ions per PW_{12} anion.[7,69,94,95] In the case of surface reactions, the specific surface of the catalyst plays a decisive role. For example, in the conversion of dimethyl ether into hydrocarbons, the insoluble salt $Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$ (specific surface 101 $m^2\ g^{-1}$) shows a higher activity per unit mass of the catalyst than $H_3[PW_{12}O_{40}]$ (specific surface 5 $m^2\ g^{-1}$).[92]

By virtue of the similarity of the properties of crystalline and dissolved HPA, their acidities in the solid state and in solution depend on the composition of the acid in virtually the same way. As a result of this, the rates of pseudo-homogeneous reactions catalysed by solid HPA are usually well correlated with the dissociation constants of the acids in solution and with the strengths of the solid acids measured by the method involving the thermal desorption of ammonia or pyridine. Thus the activity of massive HPA in the dehydration of 2-propanol at 100 °C diminishes in the sequence $PW_{12} > SiW_{12} > PW_{10}P_2 > PMo_{12} \cong PMo_{10}V_2 \cong SiMo_{12}$,[1,5] which is close to the acidity series in solution (Table 2). The lower activity of PMo_{12} compared with SiW_{12} can be explained by the reduction of PMo_{12} during the reaction.[5]

The absorption of 2-propanol in the bulk of the catalyst during dehydration on $H_3[PW_{12}O_{40}]$ has been demonstrated by the rapid replacement of 2-propanol-d_0 in the gas stream by 2-propanol-d_8.[94] In the absence of the catalyst, the d_0 molecules were rapidly (in the course of 2 min) replaced by the d_8 molecules at the outlet from the reactor. In the presence of the catalyst, the exchange took a much longer time (~20 min) which confirms the sorption of the alcohol in the bulk of the HPA. These data made it possible to estimate the amount of alcohol in the catalyst, which was ~7 molecules per anion, corresponding to the coverage of the $H_3[PW_{12}O_{40}]$ surface by approximately 100 alcohol monolayers. This demonstrates convincingly the presence of 2-propanol in the bulk of the catalyst. It has also been found that the rate of absorption is 50 times higher than the rate of dehydration of propanol and absorption does not therefore limit the rate of the catalytic reaction under these conditions (80 °C).

The question of the relative contributions of the bulk and surface reactions to the observed catalytic activity of HPA catalysts naturally arises. It can be answered by comparing the activities of massive specimens of the acids and the dispersed acids on carriers with respect to reactions characterised by pseudo-homogeneity. As already mentioned, in many reactions the catalytic activity of HPA deposited on inert carriers, calculated per acid molecule, is much higher than for massive specimens of the acids. This has been observed both in surface reactions (alkylation of benzene by ethylene,[36] isomerisation of but-1-ene [94]) and in the typical bulk-phase 2-propanol dehydration reaction.[36] The specific catalytic activity is independent of the concentration of deposited HPC only in the conversion of methanol on the silver and copper salts of PW_{12}.[97,98] However, this may be associated with the characteristic features of the formation of the acid centres in the HPA salts (see below). Thus the impression is created that in pseudo-homogeneous reactions the activity of solid HPA catalysts is determined to a larger extent by the degree of dispersion of the acid than by its bulk-phase properties. This may be associated with the difference between the strengths of the surface and bulk-phase protic centres of the HPA (see below) or with the slow course of absorption, as a result of which the reaction proceeds preferentially in the layer near the surface.

Pseudo-homogeneity apparently plays a significant role in low-temperature reactions of polar substances, i.e. under conditions where the degree of sorption of the substrate in the bulk of the catalyst is high. In high-temperature reactions, the contribution of the bulk-phase reaction is probably not so great. However, the available data are still too few to reach a final conclusion. Detailed kinetic studies of catalysis by deposited HPA are necessary.

The practical value of the phenomenon of the "pseudo-liquid phase" arises because it becomes possible to regulate specifically the selectivity of the catalytic process by differentiating the acid reactions of polar and non-polar substances on coarsely dispersed soluble and finely dispersed insoluble HPC—for example, $H_3[PW_{12}O_{40}]$ and $Cs_{3-x}H_x[PW_{12}O_{40}]$.[55,99] The selectivity can also be altered by employing the difference between the rate of desorption of the intermediates from the surface of the catalyst and from its bulk phase.

An example of such regulation of selectivity is provided by the conversion of dimethyl ether into a mixture of C_1–C_6 alkenes and alkanes on massive PW_{12} HPC at 290 °C.[99] The alkenes are the primary products from which alkanes are formed. The alkene/alkane ratio is clearly correlated with the absorption capacity of the catalyst. Thus, in the case

of the acid $H_3[PW_{12}O_{40}]$, which absorbs the ether in an amount corresponding to approximately 40 monolayers (28 °C), the propene/propane ratio is approximately unity. The salt $Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$ sorbs less than one monolayer and we have the ratio propane/propane ≅ 12. These data have been explained as follows.[97] The alkenes formed on the surface of the $Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$ catalyst are readily desorbed. The alkenes obtained in the bulk of the catalyst, namely the acid $H_3[PW_{12}O_{40}]$, its sodium salts, etc. undergo hydrogen transfer reactions with formation of alkanes before being desorbed. Other examples of the regulation of selectivity have been published.[69]

Theoretically the HPA capable of behaving as a "pseudo-liquid phase" are unique objects for the study of one of the main problems of catalysis—the relation between homogeneous and heterogeneous catalysis.

(c) *The acid centres of heteropolyacid catalysts.* As already mentioned, massive HPA exhibit purely Brønsted acidity.[1,5,7] In terms of its strength, they are superior to aluminosilicates[5] and are much more active than the zeolite HY in the dehydration of 2-propanol.[100] It is believed that the protic centres of the HPA are fairly uniform, at least as regards the bases sorbed in the bulk phase (ammonia, pyridine).[93] These conclusions can be extended also to HPA on inert carriers.

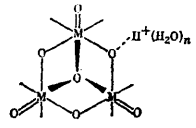
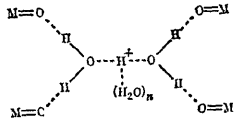
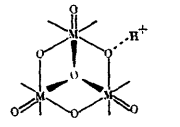
Data on the crystal and proton structures of HPA permit a series of hypotheses about the structure of the acid centres of the catalyst considered. The protons in the free HPA molecules (in solution and probably on the surface of the inert carrier for a low coverage) are localised predominantly at the oxygen atoms of the angular bridges M–O–M.[12] In massive acids, the protons participate in the formation of the crystal structure, linking together the HPAN by hydrogen bonds.[12] In the crystals, the positions of the protons may be different because they are determined not only by the negative charge on the oxygen atoms of the polyanion but also by the character of the packing and the unit cell parameters. Indeed, a structural study[34] has shown that the protons in the hexahydrate $H_3[PW_{12}O_{40}]$ enter into the composition of the dioxonium ions $H_2O...H^+...OH_2$, each of which links four neighbouring HPAN by forming hydrogen bonds between the protons of the water molecules and the terminal oxygen atoms of the W=O group. On dehydration, the size of the unit cell diminishes.[14] The exact data concerning the positions of the protons in the dehydrated acids are lacking, but, by analogy with hydrates, one may assume that the crystal structure is determined by the presence of a hydrogen bond between the HPAN via the terminal oxygen atoms, $M{=}O...H^+...O{=}M$, where the non-hydrated proton assumes the role of the binder.

Thus the structure of the Brønsted acid centres in HPA catalysts should depend on their phase state (homogeneous, heterogeneous, massive, or deposited) and the degree of hydration. On the basis of the available structural data, we shall now attempt to represent the structure of the proton centres of the main types of catalysts of this kind (Table 6).

In homogeneous systems the HPA molecules exist in a free state in solution. Their acid centres are homogeneous; they include hydrated (solvated) protons, which are most probably localised at the oxygen atoms of the angular bridges M–O–M, linking the metal atoms in the M_3O_{13} triads. The structure of such centres can be represented as structure (I), where three equivalent bridging oxygen atoms in the six-membered metallocycle serve as centres at which the hydrated protons are localised. In the middle of the skeleton of the triad there is an internal oxygen atom through which the triad is linked to the heteroatom.

The heterogeneous catalysts include bulk-phase and surface acid centres. Their structures may be different for the massive and deposited forms. According to some data,[34] the bulk-phase proton centres of the massive hexahydrate of the PW_{12} acid have the structure (II), which incorporates a dioxonium ion linked via hydrogen bonds to the terminal oxygen atoms of the four anions in the unit cell. In highly hydrated acids, the $H_5O_2^+$ ion may be additionally hydrated and the water molecules can also participate in the formation of hydrogen bonds between the anions.[12,34] Such protons centres are apparently responsible for the occurrence of the low-temperature psuedo-homogeneous reactions involving the liberation of water, for example, the dehydration of 2-propanol at 80–150 °C. In vapour-phase reactions at a higher temperature, they are hardly retained as a consequence of the dehydration of the acid.

Table 6. The proton centres of catalysts based on heteropolyacids.

No.	Structure of proton centre*	Type of catalyst	Characteristics of the proton centre
(I)		Homogeneous	Centre in isolated HPA molecule in solution
(II)		Massive heterogeneous	Bulk-phase centre in highly hydrated HPA
(III)	$M{=}O\cdots H^+\cdots O{=}M$	Massive heterogeneous	Bulk-phase centre in dehydrated HPA
(IV)		Deposited heterogeneous	Centre in highly dispersed acid on a carrier or surface centre in the massive acid

*M = Mo or W.

The bulk-phase centres of the dehydrated HPA can be represented by the structure (III). It is natural to suppose that the structures (II) and (III) can be reversibly interconverted in the course of the acid hydration–dehydration process. The bulk-phase proton centres (III) probably play a significant role in high-temperature pseudo-homogeneous reactions such as the conversion of methanol and dimethyl ether into hydrocarbons at 250–350 °C.

The structural characteristics of the deposited HPA have so far been inadequately investigated. The structure (IV) may be adopted for the proton centres of highly dispersed HPA on the surfaces of inert carriers. It is analogous to the structure of the HPA centres in solution. The difference consists only in the fact that in the deposited catalyst the water content has been reduced to a minimum as a result of heat treatment. If the HPA concentration on the carrier is

sufficient for the formation of a two-dimensional or three-dimensional phase, the proton centres of the deposited catalyst may be represented by the set of structures (II)–(IV) depending on the degree of hydration. As regards the surface proton centres of massive HPA, the structure (IV) can be adopted for them although one cannot rule out the additional involvement in the surface reactions of the bulk-phase centres (II) and (III) in the layer near the surface.

The ideas about the structure of the acid centres of the HPA examined may be extended also to acid alkali metal salts.

The question of the realtive activities of different acid centres is very important. Unfortunately, there are as yet insufficient data for a detailed comparison, but certain estimates are possible. It has been found that the activity of the surface acid centres of massive $H_3[PW_{12}O_{40}]$ in the heterogeneous dealkylation of 2,6-di-t-butyl-4-methylphenol in the substrate melt is close to the activity of the centres in the corresponding homogeneous process in solution in acetic acid.[73] This result appears to be entirely natural, since the structures of the centres (I) and (IV) are identical, but it would be too early to treat it as a general rule.

There are not yet any reliable experimental data for the comparison of the activities of the bulk-phase centres (II) and (III), but they can be compared with the centres (IV) in highly dispersed acids on the surface of an inert carrier. As already mentioned, the deposited acids are a little more active than the massive specimens per one acid molecule in typical bulk-phase reactions such as the dehydration of 2-propanol and the esterification of acetic acid by ethanol.[36] This shows that the surface centres (IV) are more active than the bulk-phase centres (II) and (III). This is evidently caused by their different strengths and accessibilities. The more accessible centres (IV), incorporating isolated protons, undoubtedly exhibit a stronger protonating capacity than the centres (II) and (III) in which the protons are bound more strongly, because they participate in the formation of the crystal structure. The surface centres (IV) apparently play the main role in heterogeneous catalysis in many instances.

The structure may be refined and the strength of various proton centres may be estimated in principle by quantum-chemical methods. A semi-empirical calculation has been carried out for the cluster $M_3O_{16}X$ modelling the acid centre (IV), within the framework of the extended Hückel method.[37] The electronic structure of $PMo_{12}O_{40}^{3-}$ has been calculated in terms of the LCAO-MO approximation.[101]

(d) *The formation of acid centres in the salts of heteropolyacids.* Many neutral HPA salts catalyse reactions occurring on Brønsted acid centres and the activity of the salts of certain metals greatly exceeds the activity of the initial acids.[7,64,76,102,103] The neutral salts themselves do not possess an appreciable acidity. This is evident, for example, from the fact that, when pyridine is adsorbed on them, pyridinium ions are not formed and they totally fail to catalyse reactions such as the cracking of cumene and the isomerisation of *o*-xylene, which occur on proton centres, including HPA.[76] It has been established that the salts acquire a strong Brønsted acidity and a high catalytic activity on interaction with the reaction medium. Depending on the nature of the metal cation, one of two mechanisms of the generation of acid centres operates: the hydrolytic[104] or oxidation-reduction[76] mechanisms.

The hydrolytic mechanism is characteristic of metal cations with a high electronegativity (Al^{3+}, La^{3+}, Zn^{2+}, etc.). The Brønsted acid centres are formed as a result of the dissociation of water molecules in the coordination sphere of the metal ion in accordance with the equation

$$M^{n+}+H_2O\rightleftarrows M(H_2O)^{n+}\rightleftarrows M(OH)^{(n-1)+}+H^+.$$

The correlation between the catalytic activity and the electronegativity of the metal cation is a sign of the hydrolytic mechanism because the acid dissociation constants of the aquo-complexes are well correlated with the electronegativities.[105] Such correlation has been found in the dehydration of 2-propanol on PMo_{12} salts.[104]

The oxidation-reduction mechanism predominates for salts with metal cations having a fairly high oxidation potential (Ag^+, Cu^{2+}, Pd^{2+}, Pt^{4+}, etc.).[7,76] The acid centres are formed as a result of the reduction of the metal cations by the components of the reaction medium. A typical example is provided by the conversion of methanol into hydrocarbons in the presence of the silver and copper salts of PW_{12}.[7,103] The hydrogen formed as a result of the dehydrogenation of the alcohol then plays the role of the reductant. Traces of H_2 have indeed been detected in the methanol conversion products. The proton centres are formed in accordance with the equations

$$Ag^+ + {}^1/_2H_2 \rightarrow Ag^0 + H^+,$$
$$Cu^{2+} + {}^1/_2H_2 \rightarrow Cu^+ + H^+.$$

The conversion of methanol in the presence of PW_{12} salts has a long induction period, during which the acid centres are produced. When H_2 is introduced into the system, the induction period vanishes. The activity of the salts after treatment with hydrogen at 300 °C exceeds the activity of the initial acid. Small amounts of added O_2 reversibly suppress the catalytic activity of the salt, probably as a result of the reaction:

$$2Ag^0 + 2H + {}^1/_2O_2 \rightarrow 2Ag^+ + H_2O.$$

We may note that, in the hydrolytic formation of acid centres, the catalytic activity of the salts is independent of the presence of H_2 in the system. It is not yet clear why the salts reduced with hydrogen are more active than the initial acids. In our view, this may be accounted for by the activation of the substrate by metal cations or other metal species.

Active catalysts of the conversion of methanol have been prepared by treating with hydrogen the silver salt of PW_{12} deposited on Pd/SiO_2.[66] The mechanism of the formation of the acid catalyst probably involves the dissociation of the hydrogen molecule by metallic palladium. Next, the H atoms, migrating on the surface as a result of spill-over, reduce the silver salt of PW_{12}.

After treatment with hydrogen, the silver and copper salts of PW_{12} catalyse the cracking of cumene and the isomerisation of *o*-xylene.[76] The palladium salt of PW_{12} reduced with hydrogen is an active catalyst of the isomerisation of alkanes.[77] A bifunctional catalyst, incorporating zerovalent palladium and the HPA, is formed in this system via the oxidation-reduction mechanism. The catalytic process involves the dehydrogenation of the alkane on the zerovalent palladium and the subsequent acid skeletal isomerisation. An analogous catalyst has been obtained from a platinum(IV) salt.[66]

(e) *Certain catalytic reactions with participation of heteropolyacids and their salts.* Recently, much attention has been devoted to the synthesis of hydrocarbons from coal in connection with the limited availability of petroleum resources. One of the main aspects of the solution of this problem is the synthesis of hydrocarbons from methanol. Methods have been developed for the conversion of methanol into an artificial liquid fuel containing paraffinic and aromatic hydrocarbons, ranging from C_7 and above, using high-silicon zeolites as catalysts.[106] However, the HPA PW_{12} and SiW_{12} as well as their salts also catalyse the conversion of methanol into hydrocarbons.[2,95,102] A mixture of olefins and alkanes ranging from C_1 to C_7 as well as water and dimethyl ether are formed in the reaction occurring at atmospheric pressure and 250–350°C.

The C_3–C_5 compounds predominate among the hydrocarbons. In contrast to the reaction on zeolites, the yield of compounds above C_7 and aromatic hydrocarbons is very low. This difference is probably due to the molecular sieve effect of zeolites, as a result of which the reaction of hydrocarbons within the zeolite pores is more extensive than on the HPA.

The composition of the products renders HPA unsuitable for the synthesis of motor fuel. However, they are of interest for the selective synthesis from methanol of hydrocarbons such as ethylene and propene. The preferred catalysts for this purpose are the insoluble PW_{12} salts with organic and inorganic cations, which have a large surface area.[99] Vigorous research is being prosecuted on these lines.

The activity of PW_{12} salts in the conversion of methanol decreases in the following sequence (the yields of hydrocarbons, expressed as percentages, at 300 °C are indicated in brackets):[102] Ag(98) > Cu(60) ≅ H(60) > Fe(48) > Al(36) > Pd(26) > La(24) > Zn(13). An analogous series has been obtained for the SiW_{12} salts: Ag(79) > Cu(61) > H(39) > Fe(24) > Al(15) > Zn(7) > La(2). The proportions of different hydrocarbons in the methanol conversion products on HPA and their salts are the same,[102] which indicates that a common mechanism of the catalytic process operates. It has been suggested that the conversion of methanol occurs in the bulk of the catalyst via a carbonium ion mechanism.[2,95]

The alkylation of aromatic compounds by olefins is a large-scale industrial process. Tungsten HPA, which catalyse this reaction, are much more active than the usual heterogeneous catalysts (aluminosilicates, H_3PO_4/SiO_2, etc.). The optimum efficiency in the alkylation of benzene by propene has been achieved when the HPA was used at 150 °C and a pressure of 15 atm, while in the case of the aluminosilicate catalyst the highest efficiency was at 300 °C and 30 atm.[71]

The industrial synthesis of t-butyl methyl ether, an additive which increases the octane number of motor fuel, is carried out by the reaction of isobutene with methanol in the liquid phase in the presence of a cation-exchange resin:[107]

$$(CH_3)_2C{=}CH_2 + CH_3OH \rightarrow (CH_3)_3COCH_3 .$$

HPA catalyse this reaction in both liquid and vapour phases.[63,108–110] The activity of solid acids in the vapour-phase synthesis of TBME at 90 °C decreases in the sequence $H_3[PW_{12}O_{40}] \cong H_4[SiW_{12}O_{40}] > H_3[PMo_{12}O_{40}] \cong$ zeolite HY > SiO_2–Al_2O_3 > $H_4[SiMo_{12}O_{40}]$. Alumina is completely inactive.[110]

The PW_{12} and SiW_{12} acids and their silver and copper salts, deposited on activated charcoal (30 wt.%), ensure a process selectivity of 100% at 50–110 °C for degrees of conversion of isobutene in the range 30–40%.[64] The activity of the salts increases after treatment with hydrogen. The salt $Ag_3[PW_{12}O_{40}]$, reduced with hydrogen at 200–300 °C, is more active than $H_3[PW_{12}O_{40}]$. The rate of reaction increases with increase in the concentration of $Ag_3[PW_{12}O_{40}]$ on the carrier to 50 wt.% and then remains constant. The yield of TBME increases with decrease of temperature as a consequence of the displacement of the reaction equilibrium towards the product. At 50 °C and for the volume ratio methanol/isobutene = 1, the yield of TBME on the 30% $Ag_3[PW_{12}O_{40}]/C$ catalyst was 76% for a selectivity of 100%. This catalyst is three times more active than the industrial catalyst (the Amberlite 15 cation-exchange resin)[64] and 100 times more active than aluminosilicates.[5]

Using solid HPA, certain traditional liquid-phase processes can be carried out in the vapour phase. An excellent example is provided by the nitration of benzene. The industrial process involving nitration with a mixture of concentrated nitric and sulphuric acids was developed a very long time ago but hitherto problems of the processing of the acid employed and of the waste water have not been finally solved. In the presence of the $H_3[PW_{12}O_{40}]/SiO_2$ catalyst benzene is nitrated with nitrogen dioxide in the vapour phase at 270 °C.[66] The reaction takes place in accordance with the equation

$$C_6H_6 + NO_2 \rightarrow C_6H_5NO_2 + NO + H_2O .$$

Dinitrobenzene is not formed. The rate of the process increases with increase in the $H_3[PW_{12}O_{40}]$ content to 30% and then remains constant. The yield of nitrobenzene, reaching 56%, increases in the presence of water vapour, which probable stabilises the HPA structure.

The number of examples illustrating the high efficiency of HPA catalysts could be greatly increased. In many instances they are more active than the usual acid catalysts and satisfy to a greater extent the energy and ecological requirements which must be met by modern chemical industry.

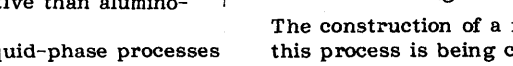
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Extensive information about the catalytic properties of HPA has now accumulated. Many new catalytic processes have been developed and some of them have already begun to be used in industry. However, much still remains to be done both as regards the development of the theoretical principles of catalysis by HPA and as regards its practical application.

HPA are extremely interesting as model objects for the study of the elementary steps in heterogeneous acid catalysis. Together with the experimental methods, quantum-chemical calculations in terms of the cluster approximation can be used effectively for this purpose. The behaviour of solid HPA as the "pseudo-liquid phase" leads to unique possibilities for the study of the relation between homogeneous and heterogeneous catalysis.

The synthesis and study of the catalytic properties of new HPC, incorporating different elements as central atoms, ligands, and outer-sphere cations, constitutes an urgent problem. An interesting application of HPC is bifunctional catalysis with simultaneous transfer of protons and electrons, which has so far been little investigated. The employment of HPC as catalysts of a wide variety of processes in fine organic synthesis, including asymmetric synthesis, is promising. Because of the high price of the products, the gain in selectivity in this instance as a result of the introduction of the more effective catalyst frequently greatly exceeds the expenditure on the catalyst.

During the preparation of the review for the press, the VIIIth Japanese–Soviet Seminar on Catalysis, "Catalysis by New Materials", was held in Tokyo. Studies on catalysis by HPA, including the practical utilisation of these catalysts, were widely represented.[111–116] At the present time, tungsten HPA are used in Japan in the industrial manufacture of 2-propanol, 2-butanol, and t-butyl alcohol by the liquid-phase hydration of the corresponding olefins. A process leading to the polymerisation of tetrahydrofuran in the presence of $H_3PW_{12}O_{40}$ has been developed:[115]



The construction of a factory in Japan for the application of this process is being completed.

The vapour-phase oxidation of methacrolein to methacrylic acid in the presence of a heterogeneous catalyst based on PMo_{12} is used on a large scale (80 000 tonnes annually).[111] Thus the industrial application of HPA catalysts abroad is increasing at a high rate, which confirms the urgent need to develop this field in our country.

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