



## Review

## The role of water in the catalysis on solid heteropolyacids

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## ABSTRACT

Heteropolyacids (HPAs) are used as catalysts for many acid reactions in both homogeneous and heterogeneous systems. For such systems water, as a vapour and/or the crystallization water, plays an essential role. The review surveys the structure of HPA hydrates and the physicochemical properties of HPA–water system. Especially, tendency to the formation of protonated water clusters in the bulk of the solid, together with acid strength and sorption properties are described. The catalytic part of the paper includes following topics: the role of water as a substrate (hydration of olefins), product (dehydration of alcohols) and as water formally not participating in the catalytic reaction (etherification).

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## 1. Introduction

Due to their specific physicochemical properties: high acidity and also – in some cases – oxidizing properties, heteropolyacids are effective catalysts in a number of acid–base or redox type catalytic reactions. In last decades they have been used in several industrial processes: hydration of propene, n-butene, isobutene [1],

polymerization of tetrahydrofuran [2] as well as the oxidation of methacrolein to methacrylic acid [3].

Heteropolyacids (HPA) the most frequently used in catalysis are Keggin type dodecaheteropolyacids such as  $H_4SiW_{12}O_{40}$ ,  $H_3PW_{12}O_{40}$  containing anions  $[XM_{12}O_{40}]^{n-}$  ( $X=P, Si$ ;  $M=Mo, W, V$ , etc.) [4,5]. Recently the interest in the Wells–Dawson type HPAs [6–12] with  $[X_2M_{18}O_{62}]^{n-}$  anions (where  $X=P, As$  and  $M=Mo, W$ ) is growing. In both HPAs, polyanions are forming so-called primary structure. In the solids anions, countercations and also some polar molecules, such as water or alcohols, are forming secondary structure.

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Heteropolyacids, belonging to the strongest mineral acids, exhibit both in the solid-state and in solution very high acid strength, comparable to that of the so-called superacids. Solid heteropolyacids devoid of crystallization water absorb easily polar molecules, penetrating the bulk of their crystallites and forming there protonated monomers or oligomeric clusters. Water is playing a special role in the chemistry of heteropolyacids, which are usually obtained in hydrated forms. The amount of crystallization water can be varied significantly from about 20 up to 30H<sub>2</sub>O molecules per one anion (called also Keggin or Wells–Dawson unit, KU or DU). Water in HPAs participates in the formation of secondary structure, influences the acidity and sorption properties [13,14]. It may also participate in catalytic reactions like dehydration of alcohols or hydration of olefins, where water is either the substrate or the product of the catalytic reaction. The more, being able to alter the acidity, it may also influence catalytic reactions in which it does not manifestly participate.

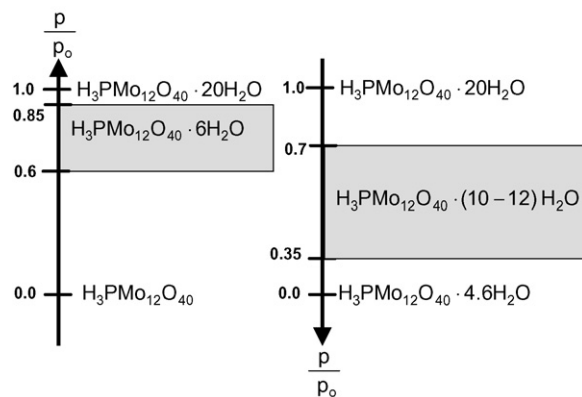
The aim of the present publication is to review the role of water in altering of the structure and the acidity of heteropolyacids and to discuss selected cases of catalytic reactions with direct participation of water molecules or influencing indirectly their course.

## 2. Heteropolyacid–water system

As already said, heteropolyacids are usually obtained in the hydrated forms. When crystallized from aqueous solution or equilibrated with water vapour at room temperature over water or water-salt solution they contain as much as 20 to nearly 30 water molecules per one anion. Depending on the pressure and temperature and also heating rate different lower hydrates can be obtained [15].

The literature concerning, the water vapour–heteropolyacid hydrates equilibria is scarce. Rykova et al. [15] measured ascending and descending branches of water vapour isotherms using H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> recrystallized from water and then preheated in vacuum at 120 °C at 0.1 Pa up to the constant weight. It was assumed by the authors that the initial sample of H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> was completely devoid of crystallization water. The isotherm was taken at 20 ± 2 °C. The ascending isotherm indicated the formation of hexahydrate H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>·6H<sub>2</sub>O stable in the vast region of pressures (plateau at  $p/p_0 = 0.6–0.85$ ) which could be practically extended up to the near-saturated pressure  $p/p_0 = 0.9$ . Above this pressure a rapid increase in the content of water was observed up to the formation H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>·20.5H<sub>2</sub>O. The authors observed that water incorporated in the bulk hydrates was retained fairly strongly. In the course of isothermal dehydration long hysteresis delays were observed. Therewith gradual transition to a stable, medium-water state ( $n = 10–12$ ) takes place and then to the hydrate H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>·4.6H<sub>2</sub>O that exists at 0.1 Pa. The experiment was presented by the authors on the following Scheme 1.

Phase changes observed on gradual increase and decrease of water vapour pressure indicating the deep hysteresis of sorption–desorption equilibrium isotherms. However it should be observed that the most stable hexahydrate, the existence of which has been observed by the authors, corresponds to the situation in which two water molecules per one proton are present. This suggests the formation of H<sub>5</sub>O<sub>2</sub><sup>+</sup> in the secondary structure. The information concerning the stability range of different heteropolyacids hydrates is scattered in the literature. Here only few examples will be given. In particular, Nakamura et al. [16] found that Keggin hydrates H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>·29H<sub>2</sub>O and H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>·29H<sub>2</sub>O were stable at 15–80 °C at the humidity range 70–95% and 80–95%, respectively. It has been also indicated [12] that Wells–Dawson type heteropolyacids H<sub>6</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>·28.8H<sub>2</sub>O kept at room temperature over saturated solution of Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O ( $p = 450$  hPa) was obtained.



Scheme 1.

In contrast to the rare studies of water vapour–heteropolyacid equilibria the investigation of HPA hydrates decomposition under the dynamic conditions of increasing temperature, different heating rate and gas pressures were undertaken by many authors.

Hodnett and Moffat [17] investigated this process using temperature-programmed desorption (TPD) of water from the differently hydrated samples of heteropolyacids  $H_n[XM_{12}O_{40}]^n$  where: X = P, Si, and M = Mo, W. Samples, recrystallized from water were standardized for 16 h at 25, 190, 320 and 450 °C in a current of dry helium gas. The TPD profiles of non-treated heteropolyacids could not be determined due to the large amounts of water desorbing at room temperature in the helium flow. The evolution of such loosely bonded water was observed also by Tsigdinos [18] who considered it to be “zeolitic”-type water. Heteropolyacids activated by Hodnett and Moffat at 25 and 190 °C desorbed water in two temperature regions. According to the authors, first of them (150–200 °C) corresponded to the departure of water molecules held by multiple hydrogen bonds to the acid. The second temperature region (350–500 °C) was assumed to be connected with the deprotonation of dehydrated heteropolyacid (already free from crystallization water: H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>) connected with the concurrent nonreductive loss of lattice oxygens. The X-ray investigation of such dehydrated heteropolyacid indicated that it not decomposed to its constituent oxides as it was suggested in the literature. According to the authors their results supported also by IR investigation indicated that H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> is capable of loosing some lattice oxygen without the collapse of its primary Keggin structure with only slight rearrangement of its secondary structure. The TPD profiles [17] obtained for the heteropolyacid samples activated over 190 °C did not exhibit desorption peak in the lower temperature region, i.e. they did not contain hydrogen-bonded water between heteropolyacid anions. In the higher temperature region (about 200 °C), an identical peak as that appearing in the case of the sample activated at 25 °C (and corresponding to the HPA dehydroxylation), was observed. The above results were also confirmed by Jozefowicz et al. [19]. Temperature-programmed desorption of water species from H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> outgassed at 27 °C for 12 h have exhibited two desorption peaks. The weaker one was centred at about 182 °C and consisted in the emission of monomeric water molecules (mass 18). The stronger peak centred about 327 °C could be ascribed to the emission of water contained in the form of H<sub>5</sub>O<sub>2</sub><sup>+</sup> protonated water dimers.

### 2.1. Thermogravimetric analysis: dehydration and thermal stability

The method, the most frequently used for the dynamical study of heteropolyacid hydrates decomposition is thermogravimetric,

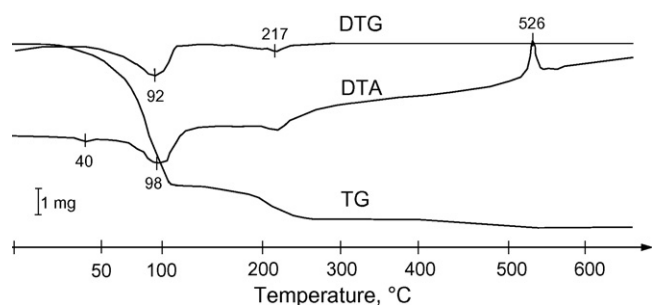


Fig. 1. TG, DTG and DTA thermal analysis of  $H_4SiW_{12}O_{40}$ . Heating rate  $5^\circ C/min$  [20].

comprising TG, DTA and DTG curves. A typical example of such analysis is presented in Fig. 1 [20]. It concerns a sample of dodecatungstosilicic acid  $H_4SiW_{12}O_{40} \cdot 24.8H_2O$  recrystallized from water and kept at room temperature over a saturated solution of NaCl. It is seen from the TG curve that slow decrease of the sample weight begins already close to the ambient temperature. The departure of the most of loosely bonded water becomes faster over  $50\text{--}60^\circ C$  and reaches its maximum rate at about  $92\text{--}98^\circ C$ , as indicated by DTG and endothermic DTA peaks. This process is finished at about  $115^\circ C$  after the loss of  $20.6H_2O$  molecules per one HPA anion. As already mentioned, this kind of loosely bonded water was called by Tsigdinos [5] “zeolitic”-type water. In fact, Wada [21] has shown by  $^1H$  NMR measurements that water in the highly hydrated  $H_3PW_{12}O_{40} \cdot 29H_2O$  acid exhibits the chemical shift very much similar to that observed for water in zeolites. A small endothermic DTA peak appeared at  $40^\circ C$  which was attributed to the fusion of heteropolyacid in its own crystallization water [20]. This peak was not observed by the author if the pristine sample was partly dehydrated by vacuum treatment or the storage over concentrated  $H_2SO_4$ . The mass of the sample remained virtually constant on heating from 250 to  $500^\circ C$ . The plateau above  $\sim 250^\circ C$  on TG curve can be attributed to the presence of fully dehydrated heteropolyacid  $H_4SiW_{12}O_{40}$ . Between 400 and  $500^\circ C$  TG shows again slow weight decrease, indicating sample dehydroxylation (departure of the water of constitution). No further changes in weight were observed during the consequent heating up to  $650^\circ C$ . An exothermic DTA peak indicat-

ing some phase transformation, most probably the recrystallization of the dehydration product, was observed at  $526^\circ C$ .

The general course of derivatographic analysis in the case of hydrates of some other Keggin and Wells–Dawson heteropolyacids is similar to that presented in Fig. 1. However, the exact positions of DTA peaks depend on the hydration degree of the initial sample, the rate of heating and the composition of heteropolyacid anions as it is shown by the data collected in Table 1. According to Furuta et al. [22] infrared investigations, the thermal stability of the heteropolyacids increases at the presence of water vapour.

Only in a few cases, the dynamic derivatographic investigation of HPA hydrates the thermal behaviour was supplemented by the static experiments in which the samples were isothermally heated at temperatures chosen on the basis of the TG–DTA analysis and subsequently examined by XRD. Fournier et al. [23] studied in this way thermal stability of vanadium-containing heteropolyacids  $H_{3+x}PM_{12-x}V_xO_{40} \cdot (13\text{--}14)H_2O$  ( $M = Mo, W; x = 0\text{--}1$ ). The HPA samples were obtained from the solid acids containing  $29H_2O$  molecules only by the flow of the air, without the thermal pretreatment. After that, samples were heated at selected temperatures in situ in an X-ray diffractometer under gas flow ( $O_2$  or  $N_2$ ) for 1 h in each temperature. Some of the results are given in Table 2.

In a similar way, Bondarieva et al. [25] investigated thermal behaviour of  $H_3PMo_{12}O_{40} \cdot 13H_2O$  prepared by heating at  $120^\circ C$ . According to the scheme given by these authors water departed at temperatures up to  $350^\circ C$  and the anhydrous acid dehydroxylated at  $385^\circ C$  thus giving the product of the composition  $H_xPMo_{12}O_{(38.5+(x/2))}$  ( $x = 0.01$ ).

Generally, dodeca- and octadecaheteropolyacids, recrystallized from water, contain up to 28–30 water molecules per one HPA anion. They are not stable at ambient atmosphere and gradually lose water, turning into lower hydrates. In order to obtain highly hydrated HPAs it is necessary to keep them over saturated solution of the highly soluble salts, NaCl or  $Mg(NO_3)_2$ . On heating from room temperature to  $100\text{--}110^\circ C$  the most loosely bonded water departs giving rise to hydrates, containing usually  $13\text{--}14H_2O$  molecules. These hydrates show the composition in which the number of water molecules is close to the number of protons or twice of the number of protons as  $H_4SiW_{12}O_{40} \cdot 4H_2O$ ,  $H_3PW_{12}O_{40} \cdot 6H_2O$ , etc. The latter decompose at temperatures  $150\text{--}200^\circ C$ , giving anhydrous

Table 1  
DTA endothermic and exothermic peaks of different HPAs: (\*) unstable hydrate.

Sample	DTA endothermic peaks, $^\circ C$	Intermediate hydrates	Dehydroxylation of anhydrous HPA, $^\circ C$	Exothermic peaks, $^\circ C$	Refs.
$H_3PW_{12}O_{40} \cdot 14H_2O$	30–200	$H_3PW_{12}O_{40} \cdot 6H_2O$	315–470	553	[23]
$H_3PW_{12}O_{40} \cdot 24H_2O$	–	$H_3PW_{12}O_{40} \cdot 5H_2O$	–	500–600	[24]
$H_4PW_{11}VO_{40} \cdot 14H_2O$	30–200	$H_3PW_{11}VO_{40} \cdot 6H_2O$	270–435	509	[23]
$H_6P_2W_{18}O_{62} \cdot 24H_2O$	66–72 97–114 308–318	$H_6P_2W_{18}O_{62} \cdot 17H_2O$ $H_6P_2W_{18}O_{62} \cdot 5H_2O$ $H_6P_2W_{18}O_{62} \cdot 2H_2O$	–	600	[9]
$H_6P_2W_{18}O_{62} \cdot 28.8H_2O$	68, 105, 148	$H_6P_2W_{18}O_{62} \cdot 6H_2O$ $H_6P_2W_{18}O_{62} \cdot 12H_2O$ $H_6P_2W_{18}O_{62} \cdot 12H_2O$	$\sim 250$	600	[12]
$H_3PMo_{12}O_{40} \cdot 13H_2O$	30–165	$H_3PMo_{12}O_{40} \cdot 7\text{--}8H_2O$ (*)	245–395	426	[23]
$H_3PMo_{12}O_{40} \cdot 13H_2O$	185	$H_3PMo_{12}O_{40} \cdot 7\text{--}8H_2O$ (*)	385	450	[25]
$H_3PMo_{12}O_{40} \cdot 16.5H_2O$	25–75 80–105 120–150	$H_3PMo_{12}O_{40} \cdot 1.5H_2O$	–	400–420	[5]
$H_4PMo_{11}VO_{40} \cdot 13H_2O$	30–180	$H_4PMo_{11}VO_{40} \cdot 7\text{--}8H_2O$	220–380	463	[23]
$H_4SiW_{12}O_{40} \cdot 23.7H_2O$	73, 84, 121, 237	$H_4SiW_{12}O_{40} \cdot 17.3H_2O$ $H_4SiW_{12}O_{40} \cdot 6H_2O$	237–507	520	[26]
$H_4SiW_{12}O_{40} \cdot 24.8H_2O$	40, 98, 217	$H_4SiW_{12}O_{40} \cdot 4H_2O$	400–500	526	[20]
$H_4SiMo_{12}O_{40} \cdot 13.5H_2O$	25–130	–	–	310–340	[5]

**Table 2**  
Thermal pathways for the selected hydrated heteropolyacids [23].

$\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot 29\text{H}_2\text{O}$	$\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 29\text{H}_2\text{O}$	$\text{H}_4\text{PW}_{11}\text{VO}_{40}\cdot 29\text{H}_2\text{O}$
cubic ↓ 25 °C	cubic ↓ 25 °C	cubic ↓ 25 °C
$\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot 13\text{H}_2\text{O}$	$\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 13\text{H}_2\text{O}$	$\text{H}_4\text{PW}_{11}\text{VO}_{40}\cdot 13\text{H}_2\text{O}$
triclinic T ↓ 60–80 °C	triclinic T ↓ 40–60 °C	triclinic T ↓ 40–60 °C
$\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot 7\text{--}8\text{H}_2\text{O}$	$\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 6\text{H}_2\text{O}$	$\text{H}_4\text{PW}_{11}\text{VO}_{40}\cdot 6\text{H}_2\text{O}$
unstable (cubic ?) ↓ 100–350 °C	cubic C ↓ 180–350 °C	cubic C ↓ 150–410 °C
$\text{H}_3\text{PMo}_{12}\text{O}_{40}$	$\text{H}_3\text{PW}_{12}\text{O}_{40}$	$(\text{H}_2\text{VO}_2\text{PW}_{12}\text{O}_{40})$
tetragonal Q ↓ 450 °C	tetragonal Q ↓ 550 °C	cubic C ↓ 550 °C
$(0.5\text{P}_2\text{O}_5) + 12\text{MoO}_3$ undetected orthorhombic	$(0.5\text{P}_2\text{O}_5) + 12\text{WO}_3$ undetected orthorhombic	$(0.5\text{P}_2\text{O}_5 + 0.5\text{V}_2\text{O}_5) + 12\text{WO}_3$ undetected orthorhombic

heteropolyacids  $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ ,  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ , etc. The final stage of decomposition consists of the departure of the water of constitution (dehydroxylation) connected with the non-reducible decrease of the number of oxygen atoms:  $\text{H}_4\text{SiW}_{12}\text{O}_{40} \rightarrow \text{SiW}_{12}\text{O}_{38} + 2\text{H}_2\text{O}$ .

All these transformations are connected with DTA endothermic peaks, mostly between 200 and 400 °C (Table 1). The properties of the dehydroxylation products are not well described. However, on further heating they suffer exothermic phase transformation indicated by DTA peak and not accompanied by the changes of sample mass. On the basis of the dehydroxylation temperature, the sequence of anhydrous heteropolyacids in terms of thermal stability is observed:  $\text{H}_3\text{PW}_{12}\text{O}_{40} > \text{H}_4\text{SiW}_{12}\text{O}_{40} > \text{H}_3\text{PMo}_{12}\text{O}_{40} > \text{H}_4\text{SiMo}_{12}\text{O}_{40}$  [27].

## 2.2. Structure of hydrated and dehydrated solid heteropolyacids

The particular hydrates of heteropolyacids differ by their crystallographic point group and hence by their structure:  $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 29\text{H}_2\text{O}$  is cubic ( $\text{Fd}\bar{3}\text{m}$ ) [28,31],  $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 21\text{H}_2\text{O}$  orthorhombic (Pcca) [29],  $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 14\text{H}_2\text{O}$  [23] triclinic ( $P_1$ ) and  $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 6\text{H}_2\text{O}$  cubic ( $\text{Pn}3\text{m}$ ) [4,30].

Keggin [4], in his fundamental X-ray research in 1934 in which he determined the structure of the anion in  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ , used the sample of the highly hydrated dodecatungstophosphoric acid, obtained by the dehydration over  $\text{P}_2\text{O}_5$  in vacuum. Its approximate composition was  $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 5\text{H}_2\text{O}$ . According to Keggin, anions forming roughly spherical units, even when arranged in a close packing will still leave a considerable volume of an unoccupied space filled by the crystallization water. However, at the time of his experiments, he was unable to determine the exact positions of water molecules.

An attempt to give more precise idea of the arrangement of water molecules in highly hydrated  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  was undertaken by Bradley and Illingworth [31]. For their calculations they used the X-ray diffraction data obtained by Keggin for  $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 29\text{H}_2\text{O}$ . According to them, the hydrate containing 29  $\text{H}_2\text{O}$  molecules, may be regarded as built up of equal numbers of oppositely charged ions  $(\text{PW}_{12}\text{O}_{40})^{3-}$  and  $(\text{H}_3\cdot 29\text{H}_2\text{O})^{3+}$ , lying on two, interpenetrat-

ing diamond lattices. On the bases of the symmetry considerations, the authors proposed the structure of the  $(\text{H}_3\cdot 29\text{H}_2\text{O})^{3+}$  clusters.

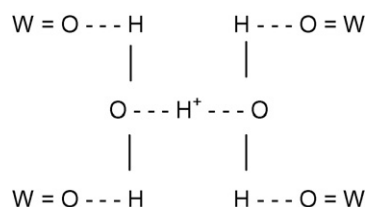
Much more precise results were obtained by Brown et al. [30], using X-ray and neutron diffraction. In their investigation, hexahydrate  $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 6\text{H}_2\text{O}$  was described. According to them, water is present in the investigated acid in the form of  $\text{H}_5\text{O}_2^+$  ions. Each  $\text{H}_5\text{O}_2^+$  ion is linking four  $(\text{PW}_{12}\text{O}_{40})^{3-}$  anions, forming with them hydrogen bonds involving terminal  $\text{O}_d$  atoms, as it was suggested later by Ganapathy et al. [32]. This was also shown by the following Scheme 2 taken from the paper by Kozhevnikov et al. [33].

The presence of  $\text{H}_5\text{O}_2^+$  ion in hexahydrated  $\text{H}_4\text{SiW}_{12}\text{O}_{40}$  and  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  was also confirmed by Kearly et al. by the inelastic neutron scattering method [34].

Brown et al. [30] calculated interatomic distances in  $(\text{PW}_{12}\text{O}_{40})^{3-}$  anion and on the basis of the  $(\text{H}_5\text{O}_2^+)_3(\text{PW}_{12}\text{O}_{40}^{3-})$  structure postulated the composition of other Keggin-type hexahydrated HPAs containing  $(\text{H}_5\text{O}_2^+)$  anions:  $(\text{H}_5\text{O}_2^+)_3(\text{HSiW}_{12}\text{O}_{40})^{3-}$  and  $(\text{H}_5\text{O}_2^+)_3(\text{H}_2\text{BW}_{12}\text{O}_{40})^{3-}$ .

Neutron diffraction method was used by Noe-Spirlet and Busing [29] for the study of the structure of  $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 21\text{H}_2\text{O}$ . They showed that in highly hydrated heteropolyacid anions water and water molecules are forming parallel layers. Due to the hydrogen bonds a variety of coordination arrangements is present inside the layers.

The X-ray diffraction studies of the anion structure in the salts of Wells–Dawson heteropolyacids were published in [35,36]. On the other hand, the studies in which X-ray and neutron diffraction



Scheme 2.

were carried out on HPAs other than Keggin type [31], enabling the localization of water molecules, is missing.

Sambeth et al. [11] using semi-empirical extended Hückel method studied theoretically the relative energies of the particular steps of the formation of the Wells–Dawson acid secondary structure. Formation of the secondary structure of the acid was divided into two stages. In the first one, the energy of addition of each of the six protons to the  $(P_2W_{18}O_{62})^{6-}$  anion was calculated ( $-215$  eV) and neutral  $P_2W_{18}O_{62}H_6$  was formed. In the second step, the energy of addition of each of six water molecules to the previous structure was calculated ( $-225$  eV). Authors finally concluded that in the hydrated solid acid three different water species can exist:

- water molecules interacting with terminal oxygen of the anion,
- water molecules hydrogen bonded to anion's OH group,
- water molecules forming  $H_5O_2^+$  protonated clusters.

### 2.3. Protons and water molecules in the structure of hydrated and non-hydrated heteropolyacids

As it was said in the preceding chapter, the position of water molecules in the crystal lattice of hexahydrated  $H_3PW_{12}O_{40}$  could be determined by the inelastic neutron scattering compared with the XRD data [28–30]. The most valuable information concerning the behaviour of water molecules and protons in solid heteropolyacids, hydrated and not hydrated, may be also obtained from IR studies. The earliest investigations of this kind belong to Furuta [22] and Highfield and Moffat [37], studying the behaviour of  $H_3PW_{12}O_{40} \cdot nH_2O$ . In most papers the samples were prepared for the transmission studies by the evaporation of HPA solutions on silicon wafers. Dehydration of  $H_4SiW_{12}O_{40} \cdot nH_2O$  heteropolyacid by IR and thermogravimetric measurements was presented by Bielański et al. [38]. Figs. 2 and 3 present the changes, observed during step-wise dehydration of the HPA in two spectral regions, characteristic of hydroxyl and water vibrations ( $3700$ – $1000$   $cm^{-1}$ ) and structure vibrations  $1030$ – $555$   $cm^{-1}$  of HPA anion. On the right sides of both figures the approximate content of crystallization water in the heteropolyacid is given. This latter has been determined in a separate, parallel series of experiments carried out in a sorption balance.

Fig. 2a shows the spectrum of the sample equilibrated at room temperature with atmospheric humidity and containing about four water molecules per one proton ( $H_4SiW_{12}O_{40} \cdot 15H_2O$ ). In the spectral region characteristic for OH groups involved in hydrogen bond a strong, broad band with two submaxima  $3445$  and  $3550$   $cm^{-1}$  is present. The band at  $1702$   $cm^{-1}$  is ascribed to the bending O–H vibration in oxonium ion  $H_3O^+$  or more probably in dioxonium  $H_5O_2^+$  one [39]. The shoulder at  $1616$   $cm^{-1}$  indicates the presence of non-protonated water molecules. On evacuation at room temperature (Fig. 2b) the band around  $3500$   $cm^{-1}$  is vanishing and a new band at  $3106$   $cm^{-1}$  appears, the best seen on the difference spectrum (Fig. 2d). Simultaneously the band at  $1616$   $cm^{-1}$  vanishes. The negative band on spectrum d, visible as a positive maximum also on the spectrum of the hydrated acid (Fig. 2a), are characteristic of the most loosely bonded, not protonated “zeolitic” water molecules. Fig. 2c shows the spectrum of the sample evacuated at  $100^\circ C$ . The absence of both  $1616$  and  $1702$   $cm^{-1}$  bands points at the complete departure of water from the sample. The existence of the latter in  $H_3PW_{12}O_{40} \cdot 6H_2O$  was proved in [28–30]. The remaining band at  $3106$   $cm^{-1}$  has to be assigned to hydrogen bonds O–H...O forming between neighbouring anions as it was proposed in Ref. [30] with the participation of the acid protons of anhydrous heteropolyacids.

Fig. 3 shows the spectra of the structural vibrations in the HPA polyanion. No distinct changes of the latter ones were observed on evacuation the sample at r.t. except of a small bathochromic shift of the  $\nu(W-O_c-W)$  band. Upon the evacuation at  $100^\circ C$ , accompanied by the departure of the water of crystallization in form of

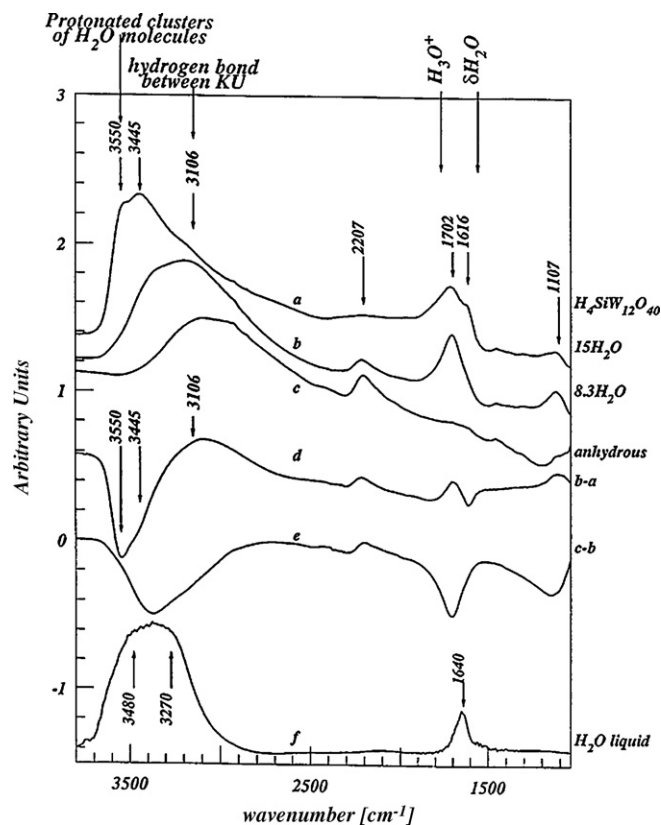


Fig. 2. The IR spectra of dodecatungstosilicic acid in the range  $3800$ – $950$   $cm^{-1}$ , (a) spectrum of hydrated sample, (b) spectrum after 30 s evacuation, (c) spectrum of dehydrated sample (evacuation at  $100^\circ C$ ), (d) difference spectrum (spectrum b minus spectrum a), (e) difference spectrum (spectrum c minus spectrum b), and (f) spectrum of liquid water [38].

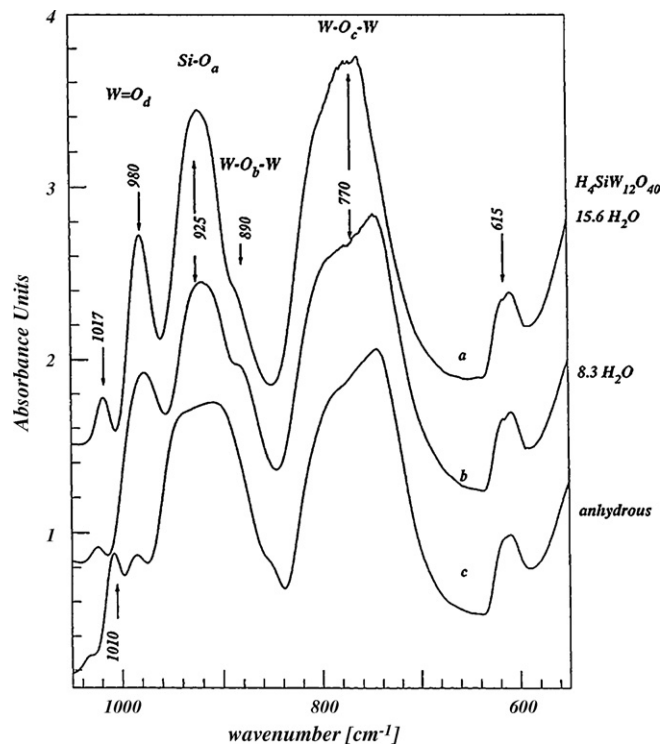


Fig. 3. The IR spectra of dodecatungstosilicic acid in the range  $1030$ – $555$   $cm^{-1}$ , (a) spectrum of hydrated sample, (b) spectrum after 30 s evacuation, and (c) spectrum of dehydrated sample (evacuation at  $100^\circ C$ ) [38].

**Table 3**  
Experimental reaction orders  $\alpha_i$  (correlation coefficients are in the brackets) [93].

Correlation	Anhydrous system	Water pressure 3.8 kPa	Water pressure 5.3 kPa	Average values of reaction order
$\ln r_{\text{ETBE}} - \ln p_{\text{C}_4\text{H}_8}$ (Fig. 5)	$\beta = 1.64 \pm 0.14$ (0.980)	$\beta_2 = 1.64 \pm 0.05$ (0.990)	$\beta_2 = 1.84 \pm 0.34$ (0.940)	1.74
$\ln r_{\text{ETBE}} - \ln p_{\text{EtOH}}$ (Fig. 6)	$\alpha = -2.00 \pm 0.19$ (0.974)	$\alpha_2 = -2.11 \pm 0.24$ (0.990)	$\alpha_2 = -1.99 \pm 0.12$ (0.990)	-2.05

$\text{H}_5\text{O}_2^+$  clusters, the band at  $980\text{ cm}^{-1}$  split into two bands: a band at  $987\text{ cm}^{-1}$  assigned to  $\text{W}=\text{O}_d$  groups the oxygen of which participates in the postulated  $\text{O}_d-\text{H}^+-\text{O}_c$  hydrogen bond, and a band at  $1010\text{ cm}^{-1}$  assigned to  $\text{W}=\text{O}_d$ , not participating in the hydrogen bond formation. Similar splitting of  $\nu(\text{W}=\text{O}_d)$  mode was also observed in Ref. [40] for  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  and  $\text{H}_6\text{PMo}_9\text{V}_3\text{O}_{40}$ .

Generally, the results obtained for hydrated and dehydrated heteropolyacids in Refs. [41] for  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  and [42] for both  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  and  $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$  show very much similar sequence of IR spectra (Table 3) suggesting following interpretation:

1. departure of loosely bonded water molecules (“zeolitic”) from highly hydrated HPAs indicated the band at  $1600\text{ cm}^{-1}$   $\delta(\text{H}_2\text{O})$  and decrease of a broad band characteristic of hydrogen bonded species ( $3500\text{--}3600\text{ cm}^{-1}$ ),
2. departure of water present in the form of protonated clusters  $\text{H}_3\text{O}^+$  and/or  $\text{H}_5\text{O}_2^+$  accompanied by vanishing of a band at about  $1700\text{ cm}^{-1}$ ,
3. remaining hydrogen bonded OH is shifted to  $3200\text{--}3100\text{ cm}^{-1}$  and is assigned to non-hydrated OH groups, linking neighbouring HPA anions:  $\text{O}-\text{H}^+-\text{O}$ .

The problem of location of acidic protons in anhydrous and hydrated heteropolyacids was tackled by several authors using MAS NMR measurements and theoretical calculations applied either simultaneously or separately. Unfortunately, the results given in the literature are not always consistent which may be due to some differences in the preparation of the samples as well as influenced by the models and methods of theoretical calculations.

Ganapathy et al. [32] using Rotational Double Resonance (REDOR) NMR and DFT calculations concluded that in dehydrated  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  acid protons are localized in the bridging oxygen positions while in dehydrated  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  in terminal ones. In the recent, Janik et al. [43] on the basis on in situ FTIR spectroscopy, water sorption and DFT quantum chemical calculations showed that the proton affinities of bridging  $\text{O}_c$  and terminal  $\text{O}_d$  oxygen atoms are similar and hence protons reside with the same probability on both types of sites of Keggin unit. Somewhat later Yang et al. [44] when using  $^{13}\text{C}$  NMR spectroscopy investigating dehydrated  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ , partially covered with acetone, proved that there are two kinds of protons differing by acid strength and the acid protons are localized both on bridging and terminal oxygen atoms.

The possibility of the location of acid proton on the terminal oxygen atoms in the HPA anions in  $\text{PW}_{12}\text{O}_{40}^{3-}$ ,  $\text{PMo}_{12}\text{O}_{40}^{3-}$  and  $\text{SiW}_{12}\text{O}_{40}^{4-}$  was indicated by Moffat as early as in 1984 [45] on the basis his theoretical calculations in which semiempirical extended Hückel method was used. The location of acid protons on terminal oxygen atoms  $\text{O}_d$  was also confirmed by Kozhevnikov et al. [33] by  $^{17}\text{O}$  NMR in anhydrous HPW. On the other hand Lee et al. [46] when comparing IR spectra of  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  and  $\text{D}_3\text{PW}_{12}\text{O}_{40}$  found that during the dehydration of the hexahydrates, the protons which had been hydrogen bonded to the oxygen atoms of water molecules, in the form of  $\text{H}_5\text{O}_2^+$ , migrated onto the bridging oxygen of  $[\text{PW}_{12}\text{O}_{40}]^{3-}$ .

However, it should be observed that DFT calculations carried out by Bardin et al. [47] revealed the most energetically favorable site of the acidic proton are bridging oxygen atoms in the anhydrous Keggin type heteropolyacid. Calculations on structurally

optimized small metal oxide clusters, as well as the complete Keggin unit, were used to determine the protons affinities by the DFT method.

The number of papers in which the authors investigated hydrated heteropolyacids using NMR measurements is much smaller than that, pertaining anhydrous ones. Kanda et al. [48] registered  $^{31}\text{P}$  NMR spectra in  $\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$  sample at the different stages of its dehydration. The chemical shifts were:  $-15.1$  to  $-15.6$  ppm for  $n=6$  and  $-11.1$  to  $-10.5$  ppm for  $n=0$ . The authors explained as follows: in the former  $\text{H}(\text{H}_2\text{O})_2^+$  is connected with the heteropolyanion and in the latter, protons are directly attached to the heteropolyacid's oxygen.

A more detailed study of the partially dehydrated  $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$  ( $0 \leq n \leq 6$ ) was undertaken by Uchida et al. [49] who were using  $^1\text{H}$ ,  $^{31}\text{P}$  and  $^{17}\text{O}$  MAS NMR and carried out the measurements at  $173\text{--}298\text{ K}$ .  $^1\text{H}$  MAS NMR spectra, recorded for the anhydrous ( $n=0$ ) sample, exhibited a narrow peak at 9 ppm assigned to the acidic protons directly attached to the polyanion of  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ . For hexahydrate  $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 6\text{H}_2\text{O}$ , a very broad peak centred at about 9 ppm was obtained. Considering that all protons and water in hexahydrate are present in form of  $\text{H}_5\text{O}_2^+$  [30] the broad signal has been ascribed to this protonated water cluster.  $^{31}\text{P}$  MAS NMR measurements for partially dehydrated sample ( $0 < n < 3$ ) at  $173\text{ K}$  has shown several peaks. For example,  $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 2.1\text{H}_2\text{O}$  exhibited the peaks at  $-10.6$ ,  $-11.9$ ,  $-13.5$  and  $-14.9$  ppm assigned to polyanions having different numbers of protons (3, 2, 1 and 0) directly attached to the polyanions, i.e. protons assumed to be acidic. In the latter case, the number of water molecules is not high enough for the formation  $\text{H}_5\text{O}_2^+$  as the only protonated water clusters and the presence of  $\text{H}_3\text{O}^+$  monomer has to be assumed. In fact, the existence of such ions has been confirmed by neutron diffraction [50]. According to Uchida, the relative concentration of  $\text{H}_5\text{O}_2^+$  does increase monotonically with the water content (the  $n$  value) but that of  $\text{H}_3\text{O}^+$  reaches maximum for the trihydrated heteropolyacid  $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 3\text{H}_2\text{O}$ .

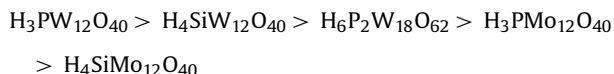
The above mentioned papers, in which MAS NMR spectroscopy was used to establish the positions of protons in hydrated and totally or partly dehydrated heteropolyacids, concerned Keggin type HPAs. However, there are only few papers concerning Wells–Dawson heteropolyacids.

Baronetti et al. [10] carried out  $^1\text{H}$  and  $^{31}\text{P}$  MAS NMR measurements to characterize catalysts containing  $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$  on a silica support. In Ref. [11],  $^1\text{H}$  MAS NMR measurements were carried out on  $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62} \cdot n\text{H}_2\text{O}$  after heat treatment at different temperatures. For pristine sample at room temperature two peaks were registered: main one at 7.3 ppm, assigned to the large protonated clusters  $\text{H}^+(\text{H}_2\text{O})_n$  and the other at 5.9 ppm, assigned to the residual not protonated water in the structure. Dehydration at  $100^\circ\text{C}$  resulted in the appearing of only one peak at 8.8 ppm which was attributed to  $\text{H}_3\text{O}^+$  species. For the sample dehydrated at  $330^\circ\text{C}$  the chemical shift value decreased to 7.6 ppm. The authors assigned the latter peak to the  $\text{H}^+(\text{H}_2\text{O})_2$  species.

Parallel to the NMR measurements, a theoretical study of the proton location in  $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$  was undertaken using extended Hückel method. It was showed that three different water species associated to Wells–Dawson HPA structure  $\text{H}_2\text{O}_5^+$ ,  $\text{H}_3\text{O}^+$  and  $\text{H}_2\text{O}$  may exist and the species  $\text{H}_5\text{O}_2^+$  is the most stable in the acid structure [30,45,47,49].

#### 2.4. Acidity of solid hydrated and dehydrated heteropolyacids

Relatively small negative charge of heteropolyacid anion smeared over large number of the external oxygen atoms (20–60) in heteropolyacids results in their very high Brønsted acid strength, comparable to that of the so-called superacids [51]. Acid strength and the number of proton acid centres were measured using different methods: colours changes of Hammett indicators [24], titration with *n*-butylamine in the presence of Hammett indicators [52], thermometric titration [53,54], thermoprogrammed desorption of ammonia [7,19,55] as well as NH<sub>3</sub> calorimetry [56–58]. All these techniques enabled to obtain the following sequence of acid strength of anhydrous heteropolyacids:



As it was previously mentioned both acid strength and the number of proton centres in heteropolyacids depend on the water content. Acid strength of H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> and H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub> measured by the titration with *n*-butylamine at the presence of Hammett indicators strongly decreased with the extent of hydration [24]. The use of Hammett sorption indicators has shown that *H*<sub>0</sub> changes from *H*<sub>0</sub> = –8.2 for anhydrous H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, through *H*<sub>0</sub> = –5.6 for H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>·5H<sub>2</sub>O to *H*<sub>0</sub> = –3.0 for H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>·24H<sub>2</sub>O. In the case of dehydrated H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub> the value *H*<sub>0</sub> = –5.6 was obtained and *H*<sub>0</sub> = –3.0 for the highly hydrated H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub>·22.5H<sub>2</sub>O. The concentration of strong acid centres (*H*<sub>0</sub> ≤ –5.6) and weak acid centres (*H*<sub>0</sub> ≤ 6.8) in H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> and H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub> increases with the activation temperature up to 400 °C and on further heating suddenly decreases practically to zero which can be explained by heteropolyacids deprotonation [52].

Jozefowicz et al. [19] studied ammonia sorption heat on a series of Keggin type solid heteropolyacids using the samples activated at 150 and 250 °C. In the case of H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, the sample activated at 150 °C the curve presenting differential heats of ammonia sorption exhibited a vast plateau corresponding to about 170 kJ per one mole of ammonia. However, the total sorption corresponded to ~1.4 NH<sub>3</sub>/KU. On the other hand, differential sorption heat measured for the sample activated at 250 °C was only 150 kJ mol<sup>–1</sup> but the total sorption of ammonia increased to the stoichiometric amount 3 NH<sub>3</sub>/KU. The lower sorption capacity of the sample activated at 150 °C was explained by blockage of protons by the residual water molecules while the higher sorption heat could be attributed to an inductive effect of the same residual water molecules.

In Ref. [13] the authors using TPD desorption of pyridine with mass spectrometer studied the acidity of H<sub>3+x</sub>PV<sub>n</sub>Mo<sub>12–n</sub>O<sub>40</sub>. Authors pointed at the extreme sensitivity of the HPAs to the degree of hydration. The comparison of the desorption profiles for H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> sample pretreated at 300 and 200 °C showed that the sample which was outgassed at the lower temperature and therefore retained more water, contained a significant amount of strong acidic centres, in contrast to the sample pretreated in more drastic conditions.

### 3. The effect of water in the catalytic processes on solid heteropolyacid catalysts

As it was shown in the preceding section, water in the catalytic systems based on heteropolyacids may be present in different forms: in protonated or non-protonated monomers and clusters participating in the formation of heteropolyacid secondary structure. The other possible form is so-called “water of constitution”, when water is in fact present in the form of acidic hydroxyl groups.

Water molecules participate frequently in the catalytic reactions:

1. as a reaction product,
2. as a reaction substrate,
3. as a factor, influencing the secondary and primary heteropolyacid structures without actual participation of water in the reaction.

In the next chapter, the exemplary reactions will be presented, explaining the role of water in some catalytic processes. The most typical example of the catalytic reaction with water, being its product (point 1) is dehydrogenation of alcohols, while hydration of olefins to alcohol can be used as the reaction proceeding with water used as a substrate (point 2). As the example of reactions mentioned in the (point 3) the formation of tertiary ethers on heteropolyacid catalyst will be presented.

#### 3.1. Catalytic dehydration of alcohols on heteropolyacid catalysts

Catalytic conversion of alcohols belongs to the most frequently studied catalytic reactions on the solid heteropolyacids. In fact when studying catalytic dehydration of ethanol Misono et al. developed and proved their conception of catalytic reaction occurring in the pseudo-liquid phase [59]. In a later paper Okuhara et al. [60] have shown that in the dehydration of ethanol over H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, ethylene, the main product of ethanol dehydration, was yielded predominantly from ethanol absorbed in the bulk of the catalyst. Diethyl ether (DEE), the second product, was then considered to be produced on the surface. The pseudo-liquid phase mechanism (the mechanism with the participation of pseudo-liquid phase) of isopropanol dehydration on the same catalyst was confirmed [61]. The most complete research on ethanol dehydration on heteropolyacids was described in Refs. [62,63]. A variety of methods: solid-state NMR combined with IR spectroscopy, TPD and transient-response catalytic measurements was used. The authors confirmed absorption of large amounts of ethanol in the dehydrated H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> under the conditions of catalytic reaction and the formation of the protonated ethanol clusters such as C<sub>2</sub>H<sub>5</sub>OH<sub>2</sub><sup>+</sup> or (C<sub>2</sub>H<sub>5</sub>OH)<sub>2</sub>H<sup>+</sup> in the bulk, which were assumed to be the intermediates in the formation of ethylene and diethyl ether, respectively. The transient-response experiments provided the proof that at the steady-state the sorption and desorption of ethanol from the bulk of HPA crystallites is much faster than the rate of catalytic reaction. However, no such sorption–desorption of DEE was observed which may indicate its formation mainly at the surface. When investigating the dependence of reaction rate on the ethanol vapour pressure in the feed the authors discovered an unusual effect: the rate of ethanol conversion at the given experimental conditions increased up to the pressure of about 15 kPa and then decreased with the increasing ethanol partial pressure. The decrease of the reaction rate was accompanied by the distinct growth of ethanol absorption in the bulk. The most plausible explanation of the observed unusual correlation assumed that in the region of higher ethanol pressure, ethanol was absorbed in the bulk in the form of protonated clusters containing more than two C<sub>2</sub>H<sub>5</sub>OH molecules. These complexes were thought to be catalytically not active in contrast to the protonated monomer and dimers present at the low ethanol partial pressures.

In most of the mentioned papers the effect of water appearing as one of the ethanol conversion products was not discussed. The only paper tackling this problem, known to the present author, was published by Varisli et al. [64]. When investigating reaction proceeding on anhydrous phosphotungstic, silicotungstic and phosphomolybdic heteropolyacids they observed “some reduction in ethanol conversion” when small amount of water ((H<sub>2</sub>O/C<sub>2</sub>H<sub>5</sub>OH) = 0.1 (volume/volume)) was introduced into the feed.

Conversion of methanol on solid heteropolyacids and their salts appears more complicated than that of ethanol. Among its

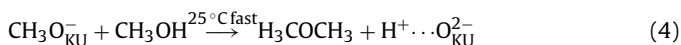
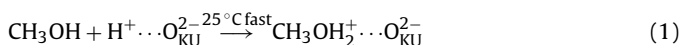
products water, methane, dimethyl ether (DME) and hydrocarbons are present, some of them forming the predominant products. The composition of the products depends on the kind of heteropolyacid and counter cations in the salts, the pretreatment of the catalyst and catalytic reaction conditions. This is why methanol conversion has been used as the test reaction characterizing the catalysts.

The product of methanol conversion at 350 °C on the solid HPMo, HSiW, HPW, HP2W [24] were dimethyl ether, carbon monoxide, carbon dioxide and C<sub>1</sub>–C<sub>3</sub> hydrocarbons. The authors did not observe inhibiting effect of water on the catalytic activity of any of the heteropolyacids.

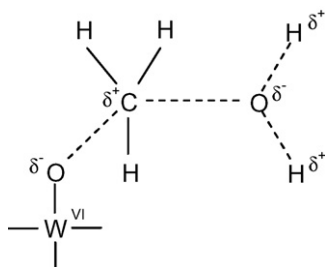
Methanol dehydration at 100–400 °C [65] on phosphomolybdic acid and salts with sodium, calcium, magnesium and zinc, reduced in a flow of hydrogen led to the production of dimethyl ether and methanol. The activation temperature of the salts influenced alcohol conversion markedly: the samples activated at lower temperatures exhibited higher activity. Ammonium salt was found to have considerably higher activity for the conversion of methanol to hydrocarbons than any other of heteropoly compounds [66]. The methanol conversion mechanism proposed by the authors did not assume the bulk sorption. According to them, two surface neighboring alkoxide groups reacted with the formation of ether while the formation of methane needed interaction of surface alkoxides and carbenium ion. Kinetics of both reactions was interpreted using Langmuir–Hinshelwood formalism; the formation of ether was assumed to be the reaction of the second and methane of the first order. Dehydrated Wells–Dawson acid did not show catalytic activity for methanol dehydration [9] but after the exposure to the stream of air saturated with water the catalyst became active.

In a series of papers concerning the conversion of methanol to hydrocarbons on heteropolyacids (12-molybdophosphoric acid, 12-tungstophosphoric acid, dimeric 9-tungstophosphoric acid [24]) and metal salts of 12-tungstophosphoric acid [66,67] Hayashi did not observe the decrease of catalytic activity due to the presence of water vapour being the product of alcohol conversion.

According to the Highfield and Moffat's conclusions [68] the first step in methanol conversion on solid heteropolyacids is the protonation of CH<sub>3</sub>OH molecule which becomes hydrogen bonded to the Keggin unit oxygen atom O<sub>KU</sub> (step 1 in the reaction scheme):



The dissociation of CH<sub>3</sub>OH<sub>2</sub><sup>+</sup> (step 2) was identified as the rate determining step in the dehydration reaction requiring temperatures over 50 °C. Although (2) and (3) have been written as consecutive steps the authors accept also a parallel process with a protonated complex:



The cleavage of the C–O bond would lead to fast detachment of water molecule, therefore methoxy species at the surface may react with a physisorbed CH<sub>3</sub>OH (also fast) producing DME molecule. In this mechanism water molecule is desorbed in a fast process, congruently with the experimental observation that water produced in the course of catalytic reaction does not restrain the whole process.

The reaction mechanism proposed by Moffat does not consider the problem of the participation of the “pseudo-liquid” phase in the methanol dehydration process. In the reaction scheme proposed in Ref. [68] the oxygen atom O<sub>KU</sub> participating in reaction, may be situated either in the bulk or at the surface of HPA crystallites.

The behaviour of methanol molecules in contact with solid dehydrated H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> was investigated by Hirano et al. [69]. On the basis of the high resolution <sup>13</sup>C, <sup>1</sup>H and <sup>31</sup>P MAS NMR results they proved that CH<sub>3</sub>OH molecules easily penetrate the bulk of HPA crystallites. If the number of CH<sub>3</sub>OH adsorbed was less than 3 molecules per one anion, part of protons still was remained directly bonded to the heteropolyanion and the rest was connected to methanol. In turn when ratio (CH<sub>3</sub>OH/heteropolyanion) ≥ 3 all protons were transferred from anions to methanol, forming CH<sub>3</sub>OH<sub>2</sub><sup>+</sup> or (CH<sub>3</sub>OH)<sub>2</sub>H<sup>+</sup>.

Dehydration of i-propanol or propan-2-ol was frequently used for the characterization of different acid catalysts, among them supported heteropolyacids and their salts. Vazquez et al. [70] studied alumina, silica, titania and carbon supported H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> and Aranzabe et al. [71] studied the same acid supported on SiO<sub>2</sub>. Okuhara et al. [72] investigated influence of acidity of copper salt of H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> on this reaction. An interesting study on the mechanism of isopropanol dehydration over H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> was given by Okuhara et al. [61]. In this case isotopically labelled isopropanol was used for the transient-response experiments carried out at the reaction stationary state. It was found that sorption–desorption process of isopropanol was about 50 times faster than its dehydration. The authors compared also the results of isopropanol dehydration on H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> supported on SiO<sub>2</sub>. From the decay curve of adsorbed isopropanol its concentration in the bulk was estimated to be 7 isopropanol molecules per one HPA anion, indicating that the “pseudo-liquid phase” model may be applied also to this catalytic system. This conclusion was confirmed also by the experiments with isopropanol dehydration on H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, the surface area of which was increased by supporting it on SiO<sub>2</sub>. The activity of HPA for dehydration increased only 4 times, comparing to non-supported H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>. Simultaneously, the isomerization of butane (adsorbed only at the surface and not penetrating the bulk) increased 10 times, at supported sample compared with the non-supported one.

### 3.2. Gas-phase hydration of olefins on solid heteropolyacids

Not only are heteropolyacids good catalysts for dehydration of alcohols they can be successfully used in the reverse reaction: hydration of olefins to alcohols. In fact, hydration of propene in a liquid phase on such catalysts was realized industrially in 1972, hydration of isobutene in 1984 and that of n-butene in 1985 in liquid phase as well [73]. The mechanism of the liquid phase propene hydration was studied by Izumi et al. [74,75]. More recently, several catalytic systems based on heteropolyacids for the gas phase olefin hydration were patented [76–79]. One of the most interesting is ethylene and propylene hydration to ethanol and isopropanol on niobia supported heteropolyacids [76]. The reaction occurs at temperatures 100–350 °C at 1–2.5 MPa. The specific surface area of niobia was over 100 m<sup>2</sup> g<sup>−1</sup>. The hydration of olefins on the catalysts in the form of pellets or extrudates containing heteropolyacids on siliceous support [77–79] was investigated.

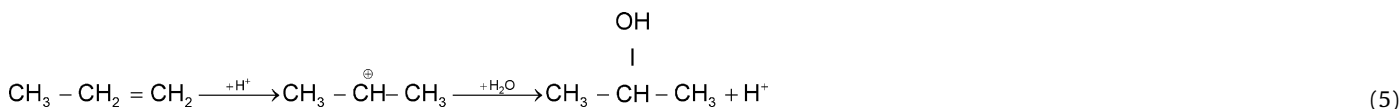


The most recent patent [80] concerns the hydration of olefin on mono- or di-potassium salts of tungstosilicic or tungstophosphoric acids.

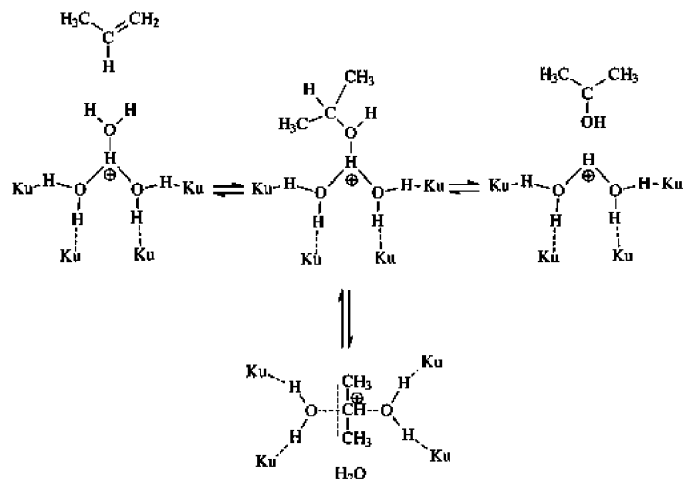
In contrast to the numerous patents, the number of scientific publications in this field is relatively small. Baba and Ono [81] studied the gas phase hydration of 2-methyl propene to 2-methyl propanol on the different solid acid catalysts, among them heteropolyacids:  $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ ,  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ ,  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  and their salts, supported on sulfonated resin—Amberlyst-15. The side product of the hydration reaction was 2-methyl propene dimer. Catalyst  $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ /Amberlyst-15 was twice as active as the acid support itself. Among the heteropolyacid salts (with  $\text{Al}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ag}^+$ ) on Amberlyst-15 support the highest activity exhibited the catalyst  $\text{Al}_4(\text{SiW}_{12}\text{O}_{40})_3$ . Catalytic activity of this material was stable over the whole test, lasting 5–6 h.

The isobutene hydration over unsupported crystalline  $\text{H}_4\text{SiW}_{12}\text{O}_{40}$  was studied in the gas phase at 40–80 °C [14]. The formation of olefin dimer besides the main product *tert*-butyl alcohol (TBA) was observed. Presumably, also small amount of  $\text{C}_2\text{H}_4$  oligomer was formed. Selectivity to TBA was 40–80%. On the basis of the gravimetric investigations water and isobutene sorption experiments were carried out on  $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ . Sorption of water molecules was fast into the bulk of heteropolyacid crystallites. The second reagent, isobutene, did not penetrate the bulk of the crystallites, and remained adsorbed at the external surface. The mechanism of TBA formation assumed that isobutene adsorbed at the catalyst's surface reacted with a proton from heteropolyacid thus forming carbocation  $\text{C}_4\text{H}_9^+$ . Subsequently, the latter reacted with water, supplied from the bulk of the catalyst eventually forming TBA.

Catalytic properties of non-supported and supported tungstophosphoric acid (10%  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$  and 70%  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$ ) were compared with the catalytic properties of acidic zeolite HZSM-5, using propene hydration as a test reaction [82]. Zeolite HZSM-5 exhibited much lower activity than the catalyst containing  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ . The most active was the catalyst of the composition 70%  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$ . The investigation of the effect of propene pressure over  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  has shown the first order of reaction with respect to propene. On the other hand, the dependence of reaction rate on the partial pressure of water was complicated. For low water vapour pressure, the rate of propanol formation increased in parallel to the increase of water pressure, and then it reached a maximum and finally decreased. Inhibiting effect of water was more distinct for 10%  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$  than 70%  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$ . Similar effect was observed in Ref. [37] when unsupported crystalline  $\text{H}_4\text{SiW}_{12}\text{O}_{40}$  was used as the catalyst. On unsupported  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  the negative reaction order, showing inhibiting effect of water was observed in the whole investigated region of water pressures. Classical mechanism for the reaction on acidic zeolites assumes the formation of propyl carbenium ion as an intermediate species, following the reaction:



According to Ivanov et al. [82], the hydration of propene on heteropolyacids has a different course. The mechanism of olefin hydration on the basis of the kinetic and spectroscopic investigations was proposed [82]. According to the authors the role of active centres is played by the hydroxonium ion  $\text{H}_3\text{O}^+$  formed in the bulk of the heteropolyacid in 70 wt.%  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$ . The reaction occurs between propene from the gas phase and oxonium ions situated between Keggin anions, resulting in the formation of the intermediate product of the composition  $\text{C}_3\text{H}_7\text{OH}_2^+$ , according to the scheme:



### 3.3. Catalytic tertiary ethers (MTBE, ETBE) formation on solid heteropolyacids

Tertiary ethers: methyl-*tert*-butyl (MTBE) and ethyl-*tert*-butyl (ETBE) are important additives to the automotive fuel. In the industry, they are obtained by the electrophilic addition of methanol or ethanol to isobutene in liquid phase, using acid resins as the catalysts. The first information, in which the possibility of MTBE formation on heteropolyacids both in gas and in liquid phase was enounced, was given by Igarashi et al. [83] and also USA patent registered by Guttman and Graselli [84]. Ono and Baba [85] applied this process as a gas phase test reaction in their study of catalytic properties of heteropolyacids:  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ ,  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  and  $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ .

#### 3.3.1. Water in a gas phase

In the case of tertiary ethers synthesis usually carried out in the alcohol–isobutene system, water may easily be introduced together with hydrophilic alcohol. In the industry, the use of absolute alcohol would increase the costs of the ether production. The use of alcohol which contains water needs a previous study of the effect of water presence.

The studies of tertiary ethers: MTBE and ETBE in liquid phase [86] with the use of commercial sulfonated resin K2631 showed that water content in alcohol up to 5 wt.% slowed down the rate of ether formation. However, the equilibrium constants determined for both ethers remained unchanged [87,88]. The use of wet ethanol (4 wt.% of water) resulted in a decrease of isobutene conversion and ether product purity because of the formation of some amounts of *tert*-butyl alcohol [89].

Gas phase synthesis of tertiary ethers on solid heteropolyacids represents a case in which one of the reaction substrate: alcohol

penetrates the bulk of HPA crystallites, while the other substrate, isobutene, remains adsorbed on their external surface. The mechanism of such reaction is not included into the classification of catalytic reactions on solid heteropolyacids given by Misono [90]. The latter includes: (1) surface type reaction (reaction occurring at the surface without any participation of the catalyst's bulk), (2) bulk "type I" reaction (only one reactant, which penetrates the bulk where is chemically transformed) and (3) bulk "type II" reaction (reactant remains at the surface and exchanges some charged par-

ticles, e.g. electrons or protons, with the bulk). The formation of tertiary ethers might be introduced in it as the bulk “type III” reaction, defined as reaction between reagent on the catalytic surface and reactant supplied from the bulk of the catalyst.

The possibility of methyl-*tert*-butyl ether synthesis (MTBE) on heteropolyacids was first indicated by Igarashi et al. [83]. A systematic study of the MTBE formation was undertaken by Shikata et al. [6] who investigated unsupported Keggin type HPAs:  $H_nXW_{12}O_{40}$  ( $X=P, Si, Ge, B$  and  $Co$ ) and Wells–Dawson heteropolyacid  $H_6P_2W_{18}O_{62}$ . In this research, a unique dependence of the reaction rate on methanol vapour pressure in the feed was observed. On increasing  $p_{CH_3OH}$ , the reaction rate at first increased but above the certain value of pressure, depending on the kind of heteropolyacid, decreased systematically. Such behaviour was interpreted as being due to the fact that at higher pressures methanol penetrating the bulk of the catalyst is forming protonated clusters  $[(CH_3OH)_nH^+]$  which in contrast to the protonated monomers and dimers are assumed not to be active in the catalytic reaction.

More extensive studies on the influence of water on the catalytic formation of ethyl-*tert*-butyl ether (ETBE) was undertaken by the present author in a series of papers [91–93]. The first of them concerned kinetics and mechanism of the reaction in a case of water absence in the gas phase and the second one presented the changes in kinetics and reaction mechanism due to the introduction of water vapour into the feed. In both investigations solid, anhydrous  $H_6P_2W_{18}O_{62}$  Wells–Dawson heteropolyacid was used. Dehydration was performed by heating at 220 °C in a stream of helium gas. Catalytic experiments were preceded by the independent investigation of sorption of reactants, ethanol and isobutene, on the solid  $H_6P_2W_{18}O_{62}$  heteropolyacid [91]. It was proved that ethanol easily penetrates the bulk of HPA crystallites where as it was showed by FTIR investigation [42] gets protonated with the formation of ethoxonium ions  $C_2H_5OH_2^+$ . At ethanol pressure equal to 6.3 kPa and the temperature 40 °C the amount of uptaken alcohol corresponded to about 20 monolayers ( $2C_2H_5OH$  molecules per one proton present in the sample). On the other hand, the amount of adsorbed isobutene corresponding to about 2.6 monolayers (or the uptake of 0.22  $C_4H_8$  molecule per one proton) was much lower than that of ethanol. Such behaviour is characteristic for non-polar hydrocarbons which do not penetrate the bulk of HPA crystallites. The formation of oligomers, e.g. dimers was not excluded. Considering high proton affinity of olefins one has to expect the formation of a tertiary carbocation on the surface on which proton is supplied from the bulk of heteropolyacid.

Isobutene conversion on  $H_6P_2W_{18}O_{62}$  was observed at temperature as low as 35 °C. On further heating, catalyst activity increases up to a maximum at about 40–50 °C and then decreases. Such behaviour is typical of the reversible exothermic catalytic reactions and the descending branch of the conversion–temperature plot corresponds to the situation in which the observed conversion approaches the equilibrium conversion and the reverse reaction, the decomposition of ETBE, must be taken into account (Fig. 4).

This is why the kinetic measurements were carried out at 40 °C, the temperature at which equilibrium conversion of isobutene reaches 41.9% [92]. In the experimental conditions it was kept within the limit 5–8% and never exceeded 10%. Simultaneously, the selectivity of the catalytic reaction carried out at the absence of water vapour in the feed was higher than 90%.

Fig. 5a shows the plot of  $\ln(r_{ETBE})$  versus  $\ln(p_{C_4H_8})$  (where  $r_{ETBE}$  - rate of ETBE formation,  $p_{C_4H_8}$  - partial pressure of isobutene in the feed) and Fig. 6a presents plot of  $\ln(r_{ETBE})$  versus  $\ln(p_{EtOH})$  ( $p_{EtOH}$  - partial pressure of ethanol in the feed). In both cases the experiments were carried out at the absence of water vapour in the feed. The first diagram (Fig. 5a) shows the increase of the reaction rate with the increase of isobutene pressure and hence a positive reac-

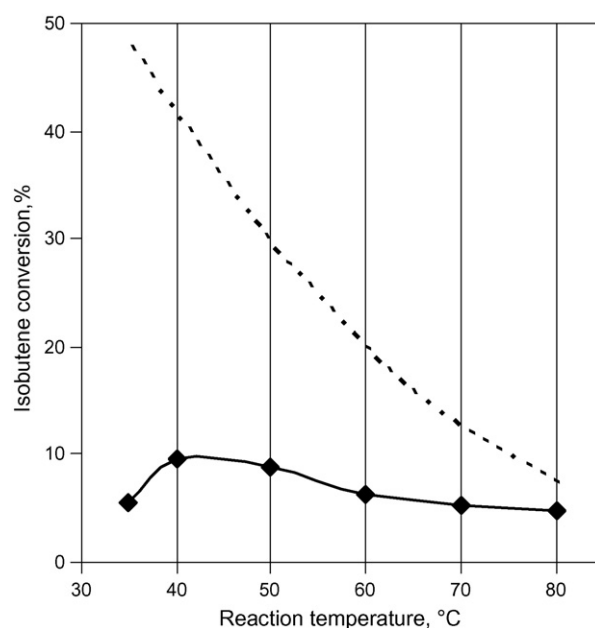


Fig. 4. Dependence of isobutene conversion as a function of the reaction temperature at  $p_{EtOH} = 17.7$  kPa and  $p_{C_4} = 14.6$  kPa [91]. Dotted line presents the equilibrium conversion of ETBE calculated using the equilibrium constants determined by Iborra [92].

tion order with respect to isobutene. The second diagram (Fig. 6a), on the other hand, shows the decrease of the reaction rate with increasing ethanol pressure and the negative reaction order with respect to ethanol (Table 3).

On the basis of all these experimental results, the following qualitative model of the reaction system could be proposed for anhydrous system:

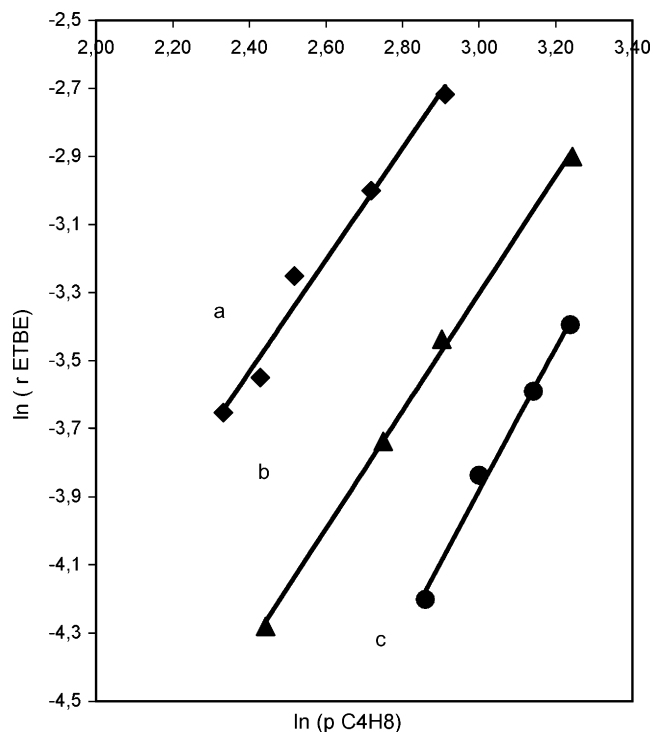
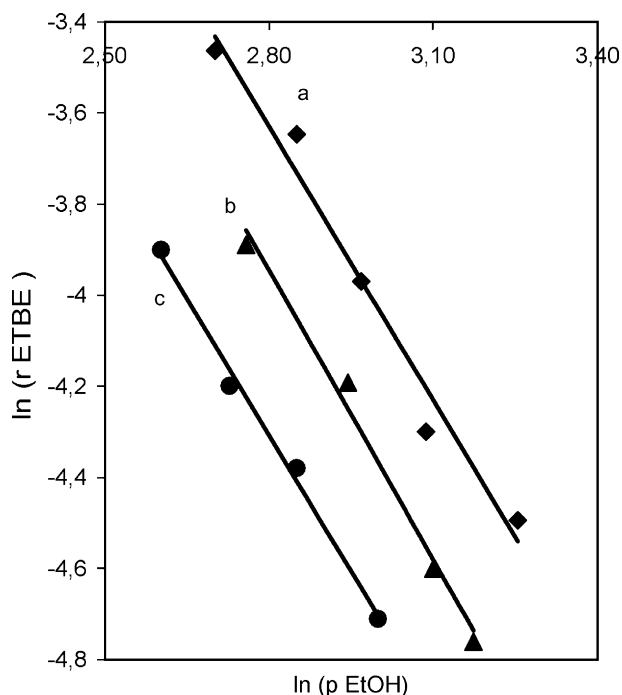
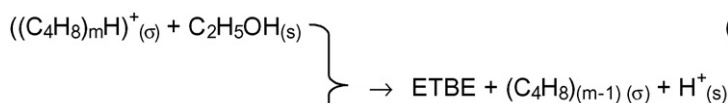
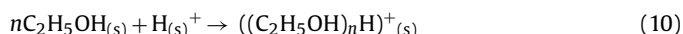
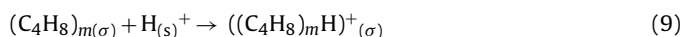


Fig. 5.  $\ln(r_{ETBE}) - \ln(p_{C_4H_8})$  plot at 40 °C at constant ethanol pressure ( $p_{EtOH} = 17.2$  kPa) over anhydrous  $H_6P_2W_{18}O_{62}$  at different water content in gas phase (a) absolute ethanol, (b)  $p_{H_2O} = 3.8$  kPa, and (c)  $p_{H_2O} = 9.5$  kPa [93].



**Fig. 6.**  $\ln(r_{\text{ETBE}}) - \ln(p_{\text{EtOH}})$  plot at 40 °C at constant isobutene pressure ( $p_{\text{C}_4\text{H}_8} = 10.3$  kPa) over anhydrous  $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$  at different water content in gas phase (a) absolute ethanol, (b)  $p_{\text{H}_2\text{O}} = 3.8$  kPa, and (c)  $p_{\text{H}_2\text{O}} = 5.3$  kPa [93].

- ethanol is absorbed into the bulk of heteropolyacid crystallites where it becomes protonated, forming also protonated monomers  $(\text{C}_2\text{H}_5\text{OH})\text{H}^+$  or clusters,
- isobutene is adsorbed exclusively on the external surface of the catalyst and gets protonated by the protons supplied from the bulk of heteropolyacid crystallites. The formation of its oligomers on the surface is not excluded,
- the catalytic reaction occurs at the surface, between carbocation  $\text{C}_4\text{H}_9^+$  or  $(\text{C}_4\text{H}_8)_n\text{H}^+$  and ethanol supplied from the bulk (or from the gas phase),
- In such system the following reaction steps should be taken into account:



(g and s, molecules in the gas or solid phase;  $\sigma$ , molecule adsorbed at the surface;  $m$ , number of isobutene molecules in oligomer;  $n$ , number of ethanol molecules in protonated cluster;  $m, n = 1, 2, 3, \dots$ ).

Each of the enumerated steps may comprise several elementary reactions. For example Eq. (10) consists in fact of a series of equations for different integral values of  $n$ .

Let us now assume – as it is usually done in organic chemistry – that the formation of carbocation is the slowest step [95] and hence reaction (9) is the rate determining step. Reaction rate would be

then defined by

$$r = k_9 [(\text{C}_4\text{H}_8)_{m(\sigma)}][\text{H}_{(\text{s})}^+] \quad (12)$$

where  $k_9$  is the rate constant of reaction (9).

Assuming the virtual sorption equilibria between ethanol in gas and solid phase, between isobutene in gas phase and at the surface and also assuming that the reaction (9) is the rate determining step, the rate Eq. (13) may be obtained:

$$r = k_4 K_1^m K_2^{(-n)} K_3 K_5^{-1} p_{\text{C}_4\text{H}_8}^m p_{\text{EtOH}}^{(-n)} [(\text{C}_2\text{H}_5\text{OH})_n\text{H}_{(\text{s})}^+] \quad (13)$$

where  $K$  are the equilibrium constants of reactions (6)–(8) and (10). The last term in this equation could be eliminated assuming that the value of  $(\text{C}_2\text{H}_5\text{OH})_n\text{H}_{(\text{s})}^+$  is not significantly different than the total concentration of  $\text{C}_2\text{H}_5\text{OH}$  in the bulk. The latter, according to the separate experiments, could be expressed by the experimentally determined Freundlich isotherm:  $[(\text{C}_2\text{H}_5\text{OH})_n\text{H}_{(\text{s})}^+] \approx c = 1.2 p_{\text{EtOH}}^{0.3}$ . Therefore, the final form of rate equation is

$$r = \xi p_{\text{C}_4\text{H}_8}^m p_{\text{EtOH}}^{(0.3-n)} \quad (14)$$

where  $\xi = 1.2 k_9 K_1^m K_2^{(-n)} K_3 K_5^{-1}$

Positive value of theoretical reaction order  $m$  with respect to isobutene pressure can be compared with the experimental one (+1.64) suggesting the formation of both isobutene monomers and dimers. Kinetic equation indicates also that at  $n > 0.3$  the reaction rate order becomes negative. The experiments show that the theoretical order of the reaction  $0.3 - n$  is equal to  $-1.93$  therefore the value of  $n$  should be equal to 1.96 which, in turn, indicates the predominance of ethanol dimers in the solid heteropolyacid.

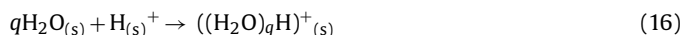
Let us now discuss the case in which water vapour is introduced into the feed [93]. As independent experiments have shown, water vapour is absorbed by the bulk of dehydrated  $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$  crystallites and its content in the solid can be expressed at 40 °C by a Freundlich sorption isotherm  $c_{\text{H}_2\text{O}} = 1.08 p_{\text{H}_2\text{O}}^{0.283} [\text{H}_2\text{O molecules}/\text{H}^+]$ . Absorbed water plays a dual role: when protonated, is bonding “free” protons and simultaneously, may react with isobutene forming tert-butyl alcohol (TBA). The selectivity to ETBE was 80.3% and that to TBA 19.7% at  $p_{\text{EtOH}} = 17.2$  kPa,  $p_{\text{C}_4\text{H}_8} = 18.4$  kPa and  $p_{\text{H}_2\text{O}} = 3.1$  kPa. The effect of water vapour in the feed is shown in Fig. 5 (curves b and c). At constant  $p_{\text{EtOH}}$  the plots of  $\ln(r_{\text{ETBE}})$  versus  $\ln(p_{\text{C}_4\text{H}_8})$  are linear. The plots a, b and c corresponding to: the anhydrous system (a), containing water vapour pressure at  $p_{\text{H}_2\text{O}} = 3.8$  kPa (b) or at  $p_{\text{H}_2\text{O}} = 9.5$  kPa (c) respectively, show that the reaction rate  $r_{\text{ETBE}}$  in all cases increases with isobutene pressure (positive reaction order with respect to  $\text{C}_4\text{H}_8$ ) but the reaction rate is decreased by the presence of water vapour.

The analogous plots in Fig. 6 (curves b and c) shows that the rate of ethanol consumption decreases with the increasing  $p_{\text{EtOH}}$



(negative order of reaction with respect to ethanol). Water vapour in the feed decreases the rate of catalytic reaction (see Figs. 5 and 6).

The presence of water vapour in the feed and the formation of some amounts of TBA have to be taken into account in the already discussed list of expected reactions in the catalytic system:



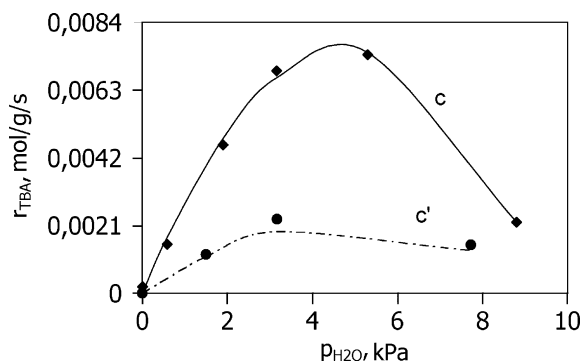
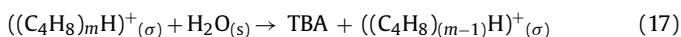


Fig. 7. Rate of TBA formation— $r_{TBA}$  versus water pressure at 40 °C, curve c at  $p_{EtOH} = 17.2$  kPa and  $p_{C_4H_8} = 18.4$  kPa, and c' (dotted line) at  $p_{EtOH} = 17.2$  kPa and  $p_{C_4H_8} = 10.3$  kPa [93].



Two parallel reactions are occurring with the participation of the same substrate, the addition of ethanol to isobutene and the addition of water to isobutene.

The dependence of the rate of isobutene conversion to TBA ( $r_{TBA}$ ) on the water vapour pressure is complicated and no linear dependence in logarithmic scale can be obtained (Fig. 7) in contrast to the effect of ethanol vapour and isobutene pressure presented in Figs. 5 and 6. At the lowest  $p_{H_2O}$  (below 3 kPa) the reaction rate increases with  $p_{H_2O}$  and after reaching maximum between 3 and 5 kPa, systematically decreases. Dual effect of water vapour pressure in the feed suggests that at the lowest  $p_{H_2O}$  the reaction (16) is the rate determining step. On the other hand, most probably, the rate determining step at  $p_{H_2O} \geq 5$  kPa is reaction (9), involving the formation of carbocation. The increasing bulk concentration of water molecules results in additional decrease of “free” protons content, apart of the “free” protons bonding by ethanol absorbed in the bulk of HPA crystallites.

The experimental correlations (Figs. 5–7) allowed fitting the empirical equation for the rate of ETBE formation:

$$r_{ETBE} = k_{ETBE} (p_{EtOH}^*)^{-2.05} (p_{C_4H_8}^*)^{1.91} (84.51 (p_{H_2O}^*)^2 - 18.3 p_{H_2O}^* + 1) \quad (18)$$

where  $k_{ETBE} = 0.0443$  mol/(g h).

Taking into account the reactions (6–11b) and (15, 16) and assuming that the formation of carbocation (reaction (9)) was the rate determining step the author obtained a complicated theoretical kinetic equation:

$$r_{ETBE} = \eta p_{C_4H_8}^m p_{EtOH}^{(1-n/2)} p_{H_2O}^{(-q/2)} ([(C_2H_5OH)_n H^+]_{(s)} [(H_2O)_q H^+]_{(s)})^{1/2} \quad (19)$$

However, in order to compare it with the experimental one it would be necessary to know the bulk concentrations of ethanol and water (term  $[(C_2H_5OH)_n H^+]_{(s)} [(H_2O)_q H^+]_{(s)}$  in Eq. (19)) at the conditions of parallel sorption of both reagents. Unfortunately, this could not be estimated from the data obtained in the research [92].

The rate of ETBE formation depends not only on the pressures of isobutene and ethanol but also on that of water vapour, which formally does not participate in ETBE formation. The correlation between the rate of ether synthesis and the pressure of water is complicated and cannot be represented by a simple function.

### 3.3.2. Water in the form of crystallization water in heteropolyacids structure

Water is frequently present in the heteropolyacids in the form of water of crystallization as it was described in the chapter 2. The

content of crystallization water can be regulated by the temperature and conditions of sample pretreatment.

Distinct differences of MTBE yield at 50 °C between Keggin  $H_3PW_{12}O_{40}$  and Wells–Dawson  $H_6P_2W_{18}O_{62}$  heteropolyacids were observed [96] for the samples activated at different temperatures, i.e. with the different content of crystallization water. Both heteropolyacids in the first 10 min of the catalytic test exhibited the increase of the MTBE yield. After this period, high activity of  $H_6P_2W_{18}O_{62}$  remained constant (about 20%) and independent of activation temperature (150 and 250 °C). On the other hand, in the case of Keggin type sample, the acidity decreased with time and depended on catalyst's activation temperature. The MTBE yield over the sample activated at 150 °C was lower than over the sample activated at 250 °C.

Baronetti et al. [9] investigated the MTBE synthesis at 100 °C on  $H_6P_2W_{18}O_{62}$  with different content of crystallization water. Catalyst was activated within large temperature range (100–400 °C). Conversion of isobutene for the samples activated at 100–200 °C, i.e. the composition below  $2H_2O/anion$  ( $0.33H_2O/H^+$ ) was constant. The increase of activation temperature above 200 °C resulted in a drastic decrease of isobutene conversion. This decrease was explained by trapping of the proton between anions, due to the departure of water. Such protons are considered to be catalytically not active. The sample activated at 400 °C was completely inactive, which according to Ref. [9] is congruent with the FTIR investigations [6] indicating that after activation at 300 °C the primary structure of Wells–Dawson heteropolyacid collapses. The present author suggests that the observed decrease in activity may also be interpreted as the result of sample dehydroxylation (departure of the so-called water of constitution).

The investigations of selectivity and yield of the ETBE synthesis on  $H_6P_2W_{18}O_{62}$  in a larger activation temperature range (80–300 °C) were also carried out at 40 °C [12]. In the case of the  $H_6P_2W_{18}O_{62} \cdot nH_2O$  where  $n = 5.4$ –8.6 (activation temperature 150–128 °C) reaction yield is about 20% higher than for  $H_6P_2W_{18}O_{62} \cdot nH_2O$  where  $n < 5.4$ . The most active sample contained 8–9 molecules of crystallization water per mole of HPA. The authors explain such high activity of octa-hydrate by its much higher (separately investigated) sorption capacity of ethanol in comparison with the much less active three-hydrated sample ( $H_6P_2W_{18}O_{62} \cdot 3H_2O$ ).

Ethanol sorption capacity was also compared in a series of experiments in which  $H_3PW_{12}O_{40} \cdot nH_2O$  and  $H_6P_2W_{18}O_{62} \cdot mH_2O$ , initially hydrated, were activated at 40–300 °C [94].

In the case of samples with the content of crystallization water  $[H_2O]/[H^+] < 0.8$  the catalytic activity  $r_m$  related to mass unit of  $H_6P_2W_{18}O_{62}$  was higher than that of  $H_3PW_{12}O_{40}$  in accordance with the orders of proton concentration in catalyst's mass

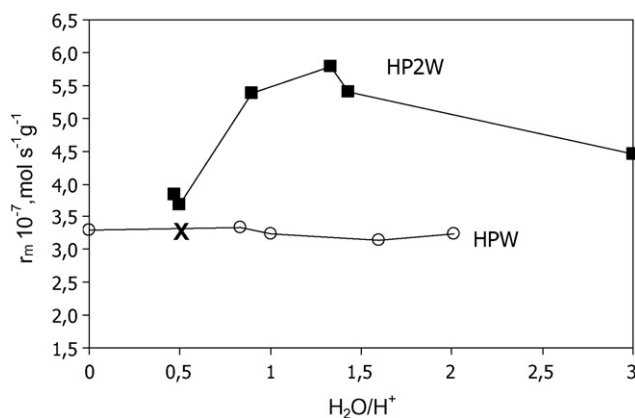


Fig. 8. Catalytic activity  $r_m$  related to mass of catalyst as a function of proton hydration: (■) HP2W, (○) HPW, and (×) HPW interpolated value [94].

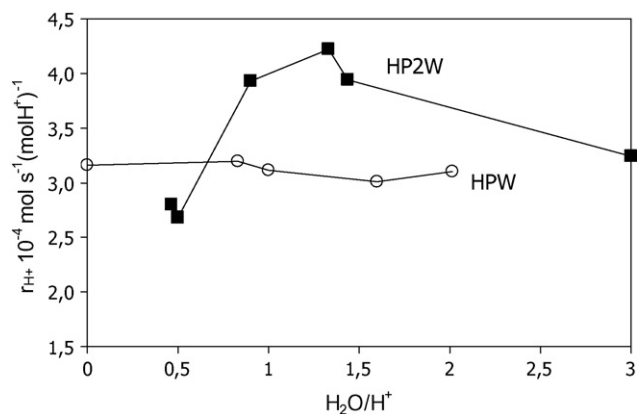


Fig. 9. Catalytic activity  $r_{H^+}$ , related to one mole of protons as the function of proton hydration [94].

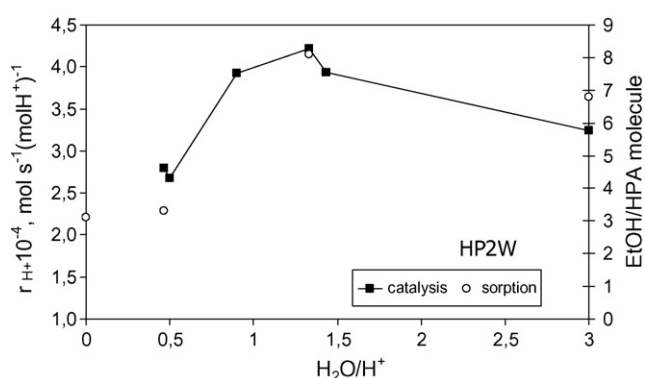


Fig. 10. Catalytic activity  $r_{H^+}$ , related to one mole of protons as a function of proton hydration compared with the ethanol sorption capacity of HP2W: (■) catalytic activity and (○) sorption capacity [94].

unit (Fig. 8). On the other hand, the activity  $r_{H^+}$  related to one mole of protons in the sample (Fig. 9) indicated higher activity in  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  than in  $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$  in accordance with the order of acid strength (see Section 2.4). In the series of samples with  $[\text{H}_2\text{O}]/[\text{H}^+] > 0.8$  the activity was much higher in the case of  $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$  than that of  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ . Maximum of catalytic activity observed for  $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$  was accompanied by a maximum of ethanol sorption capacity (Fig. 10, hollow squares). Both maxima corresponded to the  $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$  containing 8–9  $\text{H}_2\text{O}/\text{anion}$ , i.e. the ratio  $[\text{H}_2\text{O}]/[\text{H}^+] \approx 1.3$ . The observed parallelism suggests that it is the bulk concentration of ethanol which may be the dominant factor determining the differences between activities observed for the particular series of heteropolyacids, Keggin or Wells–Dawson type. The differences of sorption capacities appearing at the same  $[\text{H}_2\text{O}]/[\text{H}^+]$  indicate the difference in the secondary structures of both solid catalysts.

#### 4. Summary

In heteropolyacids, water may be present in different forms. Heteropolyacids obtained by crystallization from water solution may contain up to above 30  $\text{H}_2\text{O}$  molecules of water of crystallization per one HPA's anion. A part of crystallization water desorbs in a stream of dry helium or nitrogen, starting from the room temperature. The rest of the crystallization water is bonded in the form of  $\text{H}_3\text{O}^+$  or  $\text{H}_5\text{O}_2^+$  ions and is given off at 150–200 °C. Anhydrous of heteropolyacid loses its water of constitution (dehydroxylation) at 350–500 °C.

The primary structure (heteropolyanion) of heteropolyacid is rather stable but the secondary structure (heteropolyanion together with protons) is rather mobile due to the interaction with polar molecules, water among them, which are absorbed into the bulk of crystallites of heteropolyacids and forms the protonated clusters. Water participates in a number of acid–base reactions catalyzed by HPAs, such as dehydration of alcohols, hydration of olefins, where water is either the substrate or product of the catalytic reaction. Sometimes only the presence of water, without the direct participation in the reaction, as it was observed in the etherification, is enough to modify the mechanism of reaction by influencing the secondary structure of heteropolyacids. The rate of acid–base reactions depends on the concentration of non-solvated free protons, forming hydrogen bonds between the anions of HPAs. The presence of water in the catalytic system influences the physicochemical properties of HPAs such as acidity and the sorption capacity. Dehydration of heteropolyacids influences the acid strength, while the decrease of sorption capacity of alcohol decreases the rate of etherification reaction. These two parameters decide on the catalytic activity of HPAs. Moreover, water competes with other polar molecules in the interception of free protons. Hence, the knowledge of heteropolyacid's secondary structure is important for the understanding the catalysis on heteropolyacids. Summarizing, water plays the important and sometimes unorthodox role in many reactions with participation of heteropolyacids as the catalysts.

#### List of symbols

HPA, HDA	heteropolyacid, Wells–Dawson heteropolyacid
HPW, HP2W, HPMo, HSiW	$\text{H}_3\text{PW}_{12}\text{O}_{40}$ , $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ , $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ , $\text{H}_4\text{SiW}_{12}\text{O}_{40}$
EtOH	ethanol
KU, DU	Keggin, Wells–Dawson unit (anion)
$\text{O}_{\text{ku}}^{2-}$	oxygen ion
K	constant rate ( $\text{mol g}^{-1} \text{h}^{-1}$ )
$K_i$	equilibrium constant, $i$ —number of reaction
$r_i$	reaction rate ( $\text{mol g}^{-1} \text{h}^{-1}$ ), $i$ = ETBE, TBA

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