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Review

# Polyoxometalates as the catalysts for tertiary ethers MTBE and ETBE synthesis

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## Abstract

Heteropolyacids (HPA) are polyoxometalates exhibiting high activity in the acid–base type of catalytic reaction. This review paper discusses the role of the primary and secondary structure of solid HPAs in the catalytic synthesis of tertiary ethers, MTBE and ETBE, on $H_4SiW_{12}O_{40}$ and $H_6P_2W_{18}O_{62}$ catalysts.

*Keywords:* Heteropolyacids; MTBE; ETBE synthesis

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## 1. Introduction

Polyoxometalates are compounds of elements of groups 5 and 6 of the periodic table, mostly molybdenum, tungsten and vanadium, in their highest degree of oxidation. They are characterized by complex anions, the composition of which can be schematically expressed as $[X_xM_mO_y]^{n-}$ ($M = Mo, W, V$; $m > x$). In the case of $x = 0$ we deal with isopolymetalates and $x > 0$ with heteropolymetalates. The role of heteroatoms X can be played by almost all elements but mostly by P or Si [1,2]. Although the history of polyoxometalates can be traced back as early as 1826 (Berzelius, synthesis of ammonium phospho- and arseno-molybdates), and numerous compounds of this group were already synthesized and described in the XIX century, modern X-ray structural studies of their structure were initiated by Keggin as late as 1933. However, further progress in structural research was slow until the seventies and eighties of XX century, when new developments in X-ray crystallographic hardware and software were introduced. The detection of new, complex, but fascinating structures resulted in the renaissance of studies in the field of polyoxometalate chemistry. New syntheses were realised and studies on the link between the structure and the physico-chemical properties undertaken, based on such modern methods as NMR, EPR, Raman and FTIR spectroscopy, etc. Interest has also been directed towards potential applications of polyoxometalates. Amongst other discoveries during this period, it was shown that some polyoxometalates exhibited interesting catalytic properties as catalysts for both redox and/or acid–base type reactions

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in industrial applications [3,4]. The subject of the present paper is the case of heteropoly compounds in acid–base type catalysis.

Examples of acid–base type catalysis are: cracking and alkylation of hydrocarbons, dehydration of alcohols and electrophilic addition of alcohols to olefins. Heteropolyacids (HPA), both solid and in solution, belong to the strongest mineral acids exhibiting an acid strength higher than $H_2SO_4$ or $HClO_4$, comparable to that of the so-called superacids [5]. Until now, most of fundamental investigations and all practical applications used molybdenum or tungsten dodecaheteropolyacids, with the general formula of anion $[XM_{12}O_{40}]^{z-}$. The structure of dodecaheteropolyanion, the so-called Keggin structure, is shown in Fig. 1a.

In recent times, interest in octadecaheteropolyacids has grown, especially in diphosphooctadecatungstic acid $H_6P_2W_{18}O_{62}$. Its structure, known as the Wells–Dawson structure, is shown in Fig. 1b. In both Keggin and Wells–Dawson structures, the polyatoms M exhibit coordination number 6 in $[MO_6]$ octahedra. Such octahedra, joined by common edges, form the $[M_3O_{13}]$ subunits. The latter, joined by common vertices form structures of $T_d$ (Keggin) or $D_{3h}$ (Wells–Dawson, α-$H_6P_2W_{18}O_{62}$) symmetry. The heteropolyatom occupies in Keggin anion a tetrahedral position and is coordinated by $\mu_3O$ atoms belonging to four different $[M_3O_{13}]$ subunits. In Wells–Dawson structure heteropolyatom is coordinated only to three $O_a$ atoms. There are four different positions of oxygen in both structures: $O_a$ atom in the P–O bonds, $O_b$ atoms joining $[M_3O_{13}]$ subunits, $O_c$ atoms in $[M_3O_{13}]$ subunits and $O_d$ terminal atoms in M=O double bond.

As mentioned above, HPAs exhibit a very high acid strength. In fact, in aqueous solutions, they are completely dissociated. The $pK_1$ values determined in anhydrous acetic acid solution: 4.39 for $H_6P_2W_{18}O_{62}$, 4.68 for $H_3PMo_{12}O_{40}$ and 4.87 for $H_4SiW_{12}O_{40}$, are comparable only to $HClO_4$ (4.87), but are definitely lower than the values obtained for HBr (5.60), $H_2SO_4$ (7.00) and HCl (8.40) [6]. Also calorimetric studies of ammonia bulk sorption confirm the high acid strength of crystalline heteropolyacids although in somewhat different sequence. For $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$ and $H_6P_2W_{18}O_{62}$ the following values were obtained: 196 kJ mol$^{-1}$ for $H_3PW_{12}O_{40}$, 185 kJ mol$^{-1}$ for $H_4SiW_{12}O_{40}$ and 156 kJ mol$^{-1}$ for $H_6P_2W_{18}O_{62}$ [7]. The simplest explanation for this unusually high acid strength is the fact, that the negative charge of the anion is smeared over the numerous (36 in Keggin and 56 in Wells–Dawson structure) external oxygen atoms and the attraction of protons is very much weaker than, for example, in the case of sulphuric acid. Jolivet [8] observed, also, that this effect can be enhanced by the fact that the $[MO_6]$ octahedra, each of which possesses one terminal oxygen $O_d$ atom, are strongly distorted. The M=$O_d$ double bond is particularly short (1.70 Å in $[VO_6]$), while the trans M–$O_a$ bond is long (2.26 Å). Hence, the cation is shifted towards the exterior of the anion. The shift of the cation results in the formation of a layer of oxygen atoms, strongly polarized (due to dπ–pπ interactions) towards the inside of the polyanion. Such polarized oxygen atoms are weakly basic and weakly attract protons.

Approximate calculations of the partial changes in the oxygen and hydrogen carried out on the basis of Sanderson's Electronegativity Equalization Principle [9] also indicate the decrease of negative charge $\delta_O$ on the oxygen atoms and the increase of positive charge $\delta_H$ on the hydrogen atoms in the heteropolyacids, as compared with typical mineral acids (Table 1). In fact, the higher positive charge on hydrogen atom indicates higher acid strength of HPA molecules and lower absolute value of negative charge of oxygen atoms indicates lower basicity of HPA anions.

Due to their high acid strength, dehydrated solid HPAs exhibit specific sorption properties. Polar molecules such as $H_2O$, $NH_3$, amines and alcohols are not only adsorbed on the external surface of the HPA crystallites, which is usually of the order of several m$^2$ g$^{-1}$, but also penetrate the bulk, where they interact with the loosely bonded protons, thus forming protonated monomers or protonated clusters. Generally, such sorption and desorption processes are fast, indicating that at least a fraction of the absorbed molecules exhibits mobility, remembering to some extent the mobility of solute molecules in concentrated liquid solution. Such behaviour has been called "pseudoliquid behaviour". The values of the diffusion coefficient of alcohols and amines in the lattice of dehydrated dodecaheteropolyacids are of the order $10^{-14}$ to $10^{-15}$ cm$^2$ s$^{-1}$ [10,11], and are very similar to the diffusion coefficient in micropores in ZSM-5 zeolite, estimated as 0.42–1.80 × $10^{-14}$ cm$^2$ s$^{-1}$ [12].

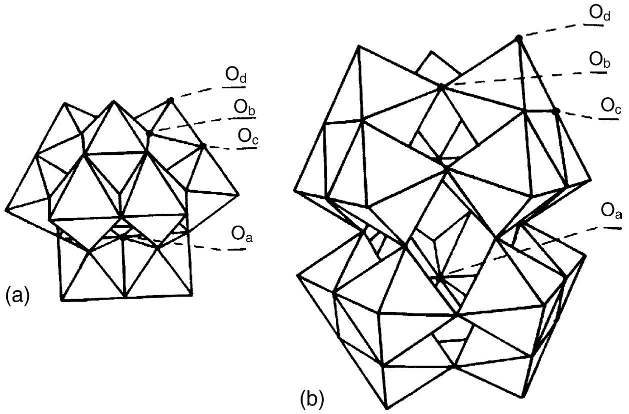

Fig. 1. Keggin (a) and Wells–Dawson (b) structures [14].

Table 1
Partial charges $\delta_i$ of the atoms in some mineral acids (elementary charge)

| Acid | $\delta_H$ | $\delta_O$ | $\delta_X$ | $\delta_W$ |
|---|---|---|---|---|
| $H_3BO_3$ | 0.254 | −0.354 | 0.300 | – |
| $H_3PO_4$ | 0.311 | −0.311 | 0.305 | – |
| $H_4SiW_{12}O_{40}$ | 0.366 | −0.267 | 0.366 | 0.718 |
| $H_6P_2W_{18}O_{62}$ | 0.375 | −0.260 | 0.369 | 0.729 |
| $H_3PW_{12}O_{40}$ | 0.378 | −0.257 | 0.372 | 0.731 |

$\delta_X$, partial charge on B, P or Si atom.

In solid anhydrous HPAs, the cohesion between Keggin and Wells–Dawson type anions is realized by an array of hydrogen bonds between them. They are signalled by a broad IR band at about 3200–3000 cm$^{-1}$ [13,14]. In hydrated or generally, solvated HPAs the link between anions is realized mostly by the intermediation of protonated solvate molecules or clusters, forming interanionic bridges. A new system of hydrogen bonds is then observed in the IR spectra [15].

The complicated structure of crystalline HPAs is best described on three levels, as proposed by Misono [16,17]. HPA anions form the primary structure, characterized by IR spectra in the spectral region 1100–400 cm$^{-1}$, are suffering only minor changes on hydration–dehydration. The secondary structure comprises anions, protons and cations (if present), as well as solvating molecules. Frequently the number of solvating molecules corresponds to the integral multiple of the number of protons in the acid molecule. The tertiary structure comprises the HPA crystallites, differing by their shape, dimensions, porosity, etc.

All these levels of molecular and supramolecular structure should be taken into account when the catalytic properties of HPA are discussed. Misono [3] classified the catalytic reactions occurring on solid HPAs into three groups:

- *Surface reactions* in which no penetration of the reagents into the bulk of HPA crystallites takes place. In an ideal case, the adsorbed molecules interact only with the surface atoms and no interactions with the bulk occur. Cracking of nonpolar cumene with nonpolar products may be cited as an example [18].
- *Bulk type I reactions* in which the polar molecules of the substrate penetrate the bulk of HPA crystallites, where their transformation occurs and the products are given off to the external liquid or gas phase. In this case, diffusion and reaction in the bulk are faster than the reaction occurring on the external surface. A classic example of such a reaction taking place in the pseudoliquid phase is dehydration of ethanol [19].
- *Bulk type II reactions* in which the nonpolar reagent remaining at the surface reacts with some species supplied from the bulk, e.g., electrons or protons.

The above classification becomes more complicated when there are two substrates of catalytic reaction: one polar, penetrating the bulk of HPA crystallites and one nonpolar, not penetrating the bulk, as in the case of the formation of tertiary ethers by the addition of a polar alcohol to a nonpolar olefin. This case has been chosen for the present paper as a presentation of the authors' work in the field of acid–base catalysis on solid HPAs. In comparison with the earlier review published by them [20a] it presents a more fundamental approach and includes new results illustrating the role of secondary structure of HPAs. Two examples will be discussed in some details: the formation of methyl-*tert*-butyl ether (MTBE) on the Keggin type dodecatungstosilicic acid $H_4SiW_{12}O_{40}$, and the synthesis of ethyl-*tert*-butyl ether (ETBE) on the Wells–Dawson octadecatungstophosphoric acid $H_6P_2W_{18}O_{62}$. In the former case, dehydrated HPA samples were used in the course of the catalytic reaction and the secondary structure was built of HPA anions, protons and protonated monomers, or clusters of methanol. In the latter case, both dehydrated and hydrated samples were used and, in some of the catalytic experiments, the secondary structure was not only built of anions, protons and protonated ethanol molecules, but also of water molecules, which formally do not participate in catalytic processes. However, as will be shown later, from the point of view of catalysis, their presence is not neutral.

Until now, methyl-*tert*-butyl ether was the most frequently used octane booster added to automotive fuels. Its use, in large part, has made possible the elimination of poisonous tetra-ethyl lead as the anti-knocking component of gasoline. However, in recent years suggestions, that it can contaminate soils and waters resulted in restraints in its use in some States of the USA and in Canada. The problems connected with its use and production were recently reviewed in [20b]. Ethyl-*tert*-butyl ether obtained from the renewable substrate, ethanol, is now recommended as a substitute for MTBE. The synthesis of both ethers needs catalysts with Brönsted centres of high acidity. In industry, ion exchanged sulphonic resins in liquid phase are used for this purpose, at a pressure in the order of 1.5 MPa and at temperatures between 90 and 100 °C [21,22]. Under these conditions, the sulphonic resins are not stable enough and gradually evolve sulphuric acid, thus decreasing activity and creating the possibility of environmental damage. This is why many laboratories are searching for more convenient catalysts. As acid catalysts zeolites, modified zeolites and silicates were investigated [23,24]. The investigations of heteropolyacids as catalysts for MTBE and ETBE synthesis described in this paper belong also to this group.

## 2. MTBE synthesis on $H_4SiW_{12}O_{40}$

The first information, in which the possibility of MTBE formation on heteropolyacids both in gas and liquid phase was enounced, was given in a paper by Igarasi et al. [25] and also USA patent registered by Guttmann and Graselli [26]. Ono and Baba [27] applied this process as a test reaction in their study of catalytic properties of heteropolyacids: $H_3PW_{12}O_{40}$, $H_3PMo_{12}O_{40}$ and $H_4SiW_{12}O_{40}$.

A systematic study of MTBE formation in the gas phase on Keggin and Wells–Dawson type HPAs was undertaken by Shikata et al. [28]. In their paper, a unique dependence of the reaction rate on methanol vapour pressure was observed. On increasing partial pressure of the methanol, the reaction rate at first increased, but above a certain value, depending on the kind of HPA studied, it systematically decreased. An analogous effect was observed earlier by Lee et al. [19], who studied the dehydration of ethanol on solid $H_3PW_{12}O_{40}$. In this case, the reaction occurred in the pseudoliquid phase and it was assumed that the protonated monomeric or dimeric clusters in the bulk were active in the catalytic reaction, while the higher clusters predominating at high ethanol partial pressure were not active. The same model was used by Shikata et al. [28] in order to explain their results concerning MTBE. They observed, namely, that at temperatures below 50–60 °C the MTBE yield on $H_6P_2W_{18}O_{62}$ catalyst is much higher than over $H_3PW_{12}O_{40}$. However, considering the fact that both the acid strength and the BET specific surface area of $H_6P_2W_{18}O_{62}$ are lower than those determined for $H_3PW_{12}O_{40}$, one might expect lower activity of Wells–Dawson heteropolyacid. In order to explain this contradiction Shikata et al. assumed that reaction between methanol and isobutene occurs in the "pseudoliquid" state (bulk type I reaction), it is in the bulk of HPA crystallites. They proposed that, although isobutene is not absorbed by pure dehydrated $H_6P_2W_{18}O_{62}$, its sorption might be enhanced by the presorption of methanol, expanding the crystal lattice of HPA.

In the study of the gas phase, MTBE synthesis on heteropoly catalysts the present authors concentrated on the problems of the mechanism of the catalytic reaction. The investigation, for which dodecatungstosilicic acid $H_4SiW_{12}O_{40}$ was chosen, comprised kinetic studies of the reaction and also a parallel study of the interaction of particular reagents with the catalyst.

The composition of the catalyst "as obtained" corresponded to the formula $H_4SiW_{12}O_{40}\cdot 24.8H_2O$. As the TG and DTA analyses show, most of the crystallization water was removed on heating below 100 °C. The remaining tetrahydrate was stable up to about 190 °C and above this temperature decomposed into anhydrous acid. The slow release of the so-called "water of constitution" (dehydroxylation process) began at above 400 °C [29]. All experiments described in this section were carried out using anhydrous $H_4SiW_{12}O_{40}$ preheated at 200 °C.

Fig. 2 shows the sorption and desorption of methanol on $H_4SiW_{12}O_{40}$ at constant temperatures and under different partial pressure of $CH_3OH$. Both processes are very fast. On sorption, the saturation depends on the partial pressure and temperature of the methanol and corresponds to the formation of stable secondary structures. The number of $CH_3OH$ molecules per anion are approximate integral number of protons 4, 8, 12 and 16. This suggests the formation of protonated methanol clusters, with one type of cluster predominating [30,31]. Using data corresponding to the equilibrium pressure at 40 °C, the following empirical sorption isotherm was obtained

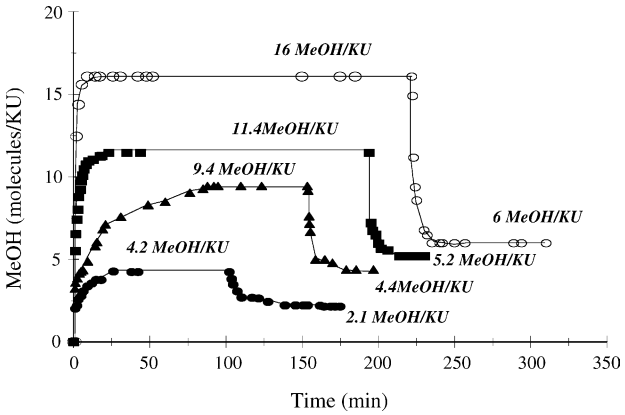

Fig. 2. Sorption and desorption of methanol by $H_4SiW_{12}O_{40}$ carried out at different methanol pressures: (●) 40 °C, 8.5 kPa; (▲) 40 °C, 11.1 kPa; (■) 40 °C 14.9 kPa; (○) 19 °C, 8.5 kPa [31].

$$c_{CH_3OH} = 0.109 p_{CH_3OH}^{1.76} \tag{1}$$

where $c_{CH_3OH}$ is the concentration of methanol in the solid expressed as the number of $CH_3OH$ molecules per anion. This equation will be used in the discussion of the catalytic results.

Sorption of methanol on dehydrated $H_4SiW_{12}O_{40}$ using IR spectroscopy was studied in [30]. In the FTIR spectrum of dehydrated $H_4SiW_{12}O_{40}$ in the spectral region 4000–2500 cm$^{-1}$ a broad band at ~3100 cm$^{-1}$ was present. It was ascribed to the hydrogen bonds linking Keggin anions. On contact with the methanol vapour this band gradually vanished, and simultaneously, a new band at 3420 cm$^{-1}$ grew, which was ascribed to the hydrogen bonds in the system composed of the protonated methanol clusters and the HPA anions. It is similar to the 3445 cm$^{-1}$ band observed in hydrated $H_4SiW_{12}O_{40}$, ascribed to the protonated water cluster in the secondary structure [32]. The presence of the protonated methanol species $CH_3OH_2{}^+$ was also confirmed by the 1550 cm$^{-1}$ band, observed when methanol was sorbed on HZSM-5 zeolite [33] and $H_3PW_{12}O_{40}$ [34].

Sorption and desorption of methanol result only in minor changes [30] in the spectral region of structural vibrations of Keggin anion 1100–600 cm$^{-1}$, which will not be discussed here.

All the experiments with the sorption of methanol (and water vapour) on dehydrated heteropolyacids indicate that the penetration of polar molecules into the bulk of HPA crystallites is connected with the transfer of the loosely bonded protons from the hydrogen bonds between Keggin anions to the sorbate molecules thus forming protonated clusters. In the case of methanol sorption, it was also possible to gain some data on the enthalpy of such processes. The enthalpy was determined [30] by means of thermometric titration, in which a suspension of dehydrated $H_4SiW_{12}O_{40}$ in toluene was titrated with the solution of methanol in toluene. The application of the thermochemical cycle, to the results obtained in this way, made possible the calculation of the values of the enthalpy of methanol sorption from the gas phase. The enthalpy of the formation of the protonated monomer $CH_3OH_2{}^+$ in the bulk thus obtained was $\Delta H_1 = -58.9$ kJ mol$^{-1}$, and the enthalpy of adding the second $CH_3OH$ molecule to the monomer with the formation of $(CH_3OH)_2H^+$ cluster was $\Delta H_2 = -53.5$ kJ mol$^{-1}$. These relatively high values are comparable to the enthalpy of neutralization of $H_3O^+ + OH^-$ in aqueous solutions and explain the thermal stability of both protonated monomer and dimer.

In contrast with the sorption of methanol, the sorption of nonpolar isobutene, the second substrate of the catalytic reaction, was definitely weak. At room temperature and $p_{C_4H_8} = 8.53$ kPa only 0.34 $C_4H_8$ molecules per anion were taken up. After the evacuation 0.17 $C_4H_8$ molecules remained. These values corresponded to 0.15 and 0.07 of the isobutene monolayer, thus indicating adsorption only on the external surface of the catalyst. There were suggestions in the literature [28] that in the case of Wells–Dawson type HPA, the sorption of isobutene on $H_6P_2W_{18}O_{62}$ may be enhanced by presorption of methanol. In order to verify this suggestion, in the case of Keggin type HPA $H_4SiW_{12}O_{40}$, an experiment was carried out in which methanol was first sorbed at $p_{CH_3OH} = 8.5$ kPa up to 16 $CH_3OH$ molecules per HPA anion. Then the sample was evacuated and 6.3 $CH_3OH$ molecules remained irreversibly absorbed. The subsequent take-up of isobutene 0.4 $C_4H_8$ molecules per anion was the same as in the experiments without methanol pre-adsorption within the range of experimental error.

The main product of the gas phase catalytic reaction was methyl-*tert*-butyl ether. Small amounts of isobutene dimer $C_8H_{16}$ (0.2–0.3%) were detected at a temperature as high as 80 °C. No dimethyl ether (DME) was detected under the conditions of experiments.

Fig. 3 shows an example of a typical catalytic run. After an initial period lasting about 1 h, the isobutene conversion stabilized at a constant level about 10% and the selectivity of MTBE formation from isobutene was almost 90%. The mass balance calculated from particular chromatographic analyses indicated a certain deficit of both methanol and isobutene. As Fig. 3b shows, the deficit of methanol was highest at the beginning of the run and then strongly decreased. Initially, it was higher than that of isobutene. This is due to the fact that polar $CH_3OH$ molecules penetrate the bulk of the HPA crystallites, while isobutene does not and remains only on their external surface becoming protonated there and forming carbocation $C_4H_9^+$ or protonated oligomers. After some 2 h the deficits of both, isobutene and methanol, become equal within the limits of experimental error. It suggests that deficits of both substrates are mainly due to the accumulation of MTBE in the bulk. The initial deficit of methanol was about 4.4% and that of isobutene about 3.0%, while in the reaction steady state they both were about 1%.

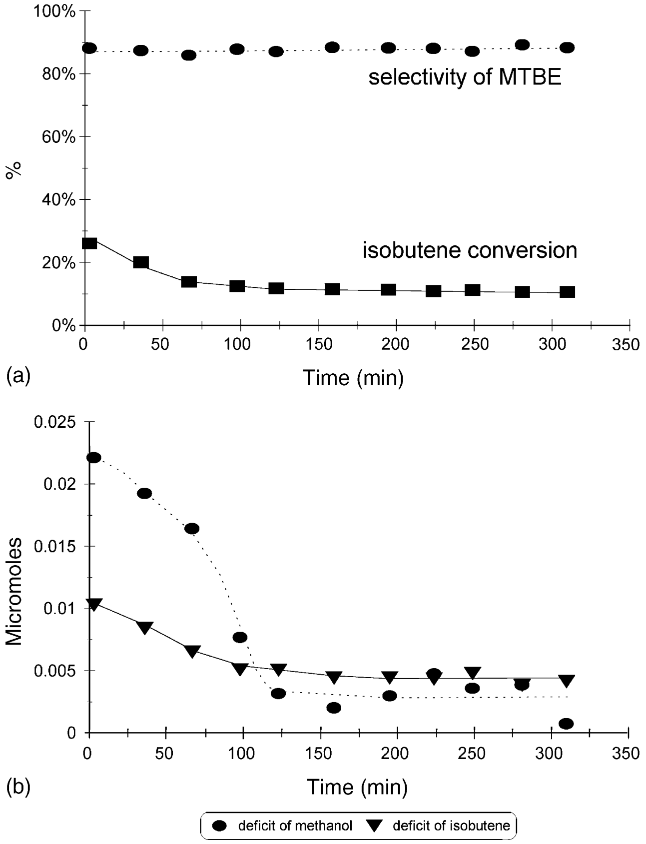

Fig. 3. Typical run on $H_4SiW_{12}O_{40}$ at 50 °C (0.2 g, pretreated in helium at 200 °C, 1/2 h, $i$-$C_4$/MeOH = 0.65). (a) Isobutene conversion and selectivity of MTBE formation and (b) temporary deficits of methanol and isobutene during the test.

Fig. 4 shows the temperature dependence of the isobutene conversion. At 40 °C, i.e., at close to ambient temperature, the heteropolyacid is already active as the catalyst. The conversion at 40 °C is much lower than that corresponding to the conversion of the expected equilibrium represented by the dotted line. The conversion reaches a maximum at 60 °C and decreases with the further increase of the reaction temperature. The descending branch of the curve reaches values not much different from equilibrium. Such behaviour is typical of catalytic endothermic reactions. At temperatures below 60 °C, the rate of MTBE decomposition into isobutene and methanol (the reverse reaction to MTBE formation) is low, obviously due to the low MTBE concentration in gas phase. At temperatures higher than 60 °C, the rate of the reverse reaction becomes similar or equal to that of MTBE formation and the yield of the MTBE becomes similar or equal to the equilibrium yield.

The simplest and most interesting aspect of kinetic studies is the region of low temperature when the kinetics of MTBE formation is almost undisturbed by the reverse process.

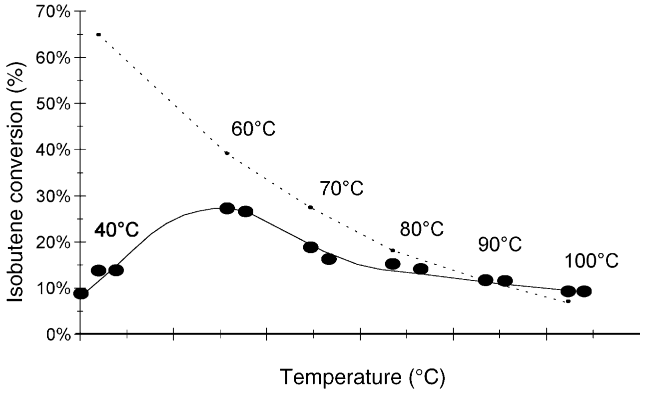

Fig. 4. Gas phase MTBE synthesis on $H_4SiW_{12}O_{40}$ (0.2 g, pretreated in helium at 200 °C, 1h, $i$-$C_4$/MeOH = 0.91); isobutene conversion in polythermic test, dotted line represents equilibrium yield.

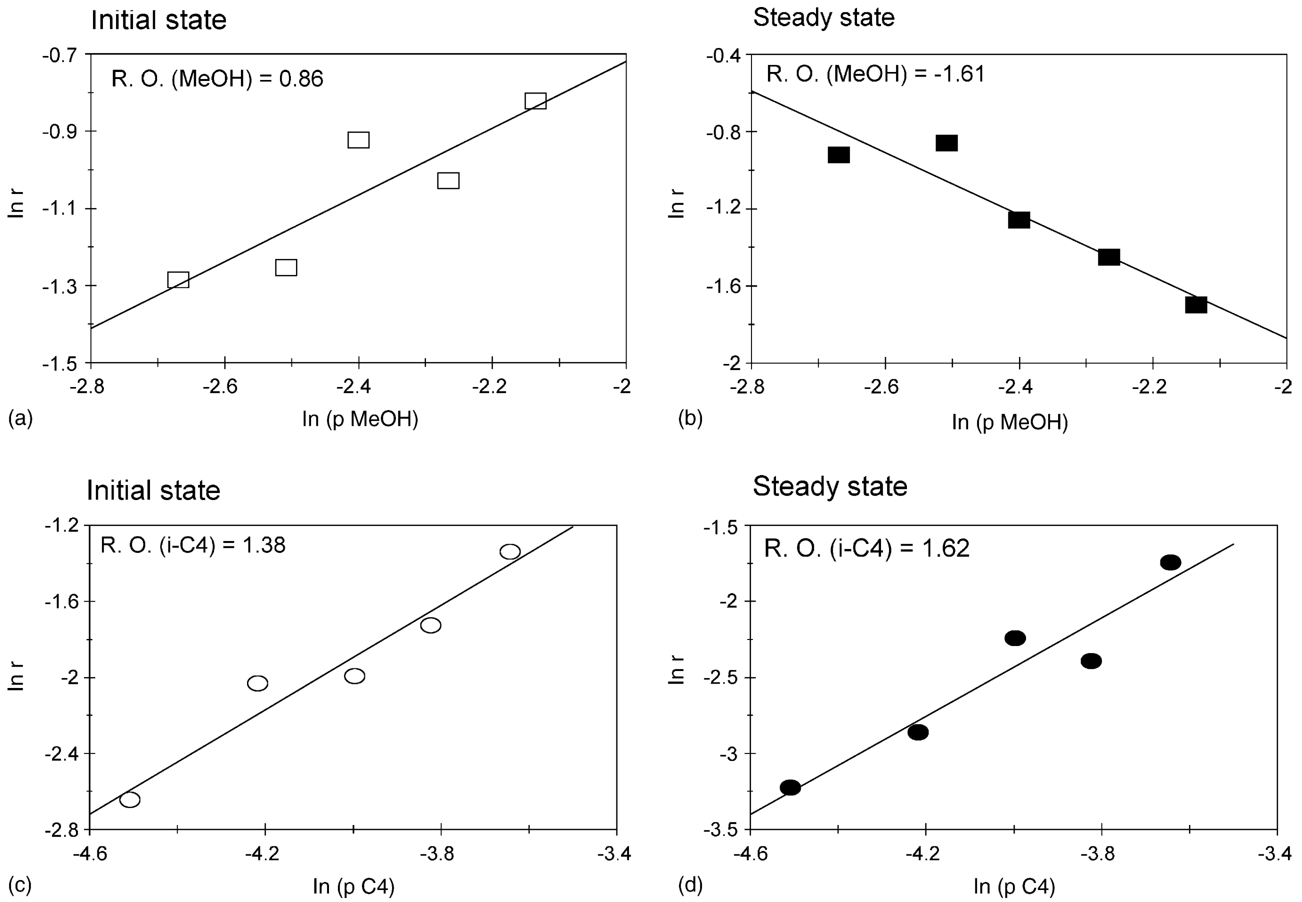

Fig. 5. Reaction orders (R.O.) at 40 °C. (a and b) With respect to methanol ($p_{CH_3OH} = 7-12$ kPa, $p_{C_4H_8} = 5.2$ kPa). (c and d) With respect to isobutene ($p_{C_4H_8} = 1.1$–$2.6$ kPa, $p_{CH_3OH} = 12.7$ kPa,); at the initial state (a and c) and at the steady state (b and d). Catalyst weight $W = 0.1$ g, space velocity of feed $F = 1.8$ l/h [31].

Therefore, this paper presents only the results corresponding to the low temperature region. The information concerning the kinetics at higher temperatures is given in [31].

Fig. 5 shows in double logarithmic scale the dependence of reaction rate on the partial pressures of methanol and isobutene both at the initial and steady state of the catalytic reaction. From the slopes of the linear plots the reaction orders (R.O.) were calculated.

One can see that the reaction order in respect to isobutene, calculated both from the initial rate of reaction and the steady state of reaction, was positive. On the other hand, the reaction order in respect to methanol was positive (0.86) only if the calculation was based on the initial rate, and negative (−1.61) in the case of steady state reaction, thus showing the non typical "unique behaviour" observed earlier by Shikata et al. [28]. At the beginning of the catalytic test, the reaction occurs on the catalyst, devoid of $CH_3OH$ molecules, and its secondary structure is comprised only of HPA anions and protons neutralizing them. The penetration of methanol into the bulk soon begins, thus changing the properties of the solid and also its secondary structure. After some 30 min, a new constant rate of catalytic process is established, indicating that a kind of dynamic equilibrium exists between methanol in the gas phase and methanol in the surface layer of the solid. Continuous slow sorption of methanol (methanol deficit) suggests a slow diffusion from this equilibrated layer to the bulk of crystallites.

In the search for a reasonable explanation for these observations, we have to propose a model of the catalytic system, in which, depending on the conditions, the order of reaction in respect to methanol will change from positive to negative [31]. As already said, Shikata et al. [28] assumed that nonpolar isobutene could penetrate the bulk of $H_6P_2W_{18}O_{62}$ crystallites saturated with methanol and catalytic reaction occurs in the pseudoliquid phase. According to him, the decrease of the rate of reaction with the increased partial pressure of the methanol is due to the formation of inactive protonated clusters $(CH_3OH)_nH^+$ ($n > 3$) in the bulk. However, the application of this model seems inappropriate in our case, since it has been experimentally confirmed that isobutene is not absorbed by the bulk of $H_4SiW_{12}O_{40}$ crystallites, even when they are saturated with methanol. Hence, we have assumed an alternative model in which the isobutene molecules, protonated with protons supplied from the bulk, remain at the external surface of the HPA crystals and react with methanol molecules supplied from the next-to-surface layer of the catalyst. In order to obtain a reasonable kinetic equation for such a model it has been assumed that, in the steady state of the catalytic reaction, equilibrium was established between methanol in the gas phase and methanol in the next-to-surface layer. The latter can be either neutral or protonated in the form of monomer $CH_3OH_2{}^+$ or clusters $(CH_3OH)_nH^+$. Protons for the methanol protonation are supplied from the interanionic hydrogen bonds. The high enthalpy of methanol protonation indicates that protons in interanionic hydrogen bonds are more loosely bonded than those involved in methanol protonation. We have called such protons the “free protons”.

In organic chemistry, the addition of alcohol to a tertiary olefin is classified as an electrophilic addition. Generally, it is accepted that a carbocation forming on a Brönsted acid site is involved in the rate-determining step of the reaction.

It is logical, therefore, to propose for such catalytic system the reaction scheme comprising, at least, the following steps [31]:

$$C_4H_{8(g)} + H^+_{(s)} \rightarrow C_4H^+_{9(\sigma)} \tag{2}$$

$$CH_3OH_{(g)} \rightarrow CH_3OH_{(s)} \tag{3}$$

$$C_4H^+_{9(\sigma)} + CH_3OH_{(s)} \rightarrow C_4H_9OCH_{3(g)} + H^+_{(s)} \tag{4}$$

$$nCH_3OH_{(s)} + H^+_{(s)} \rightleftarrows (CH_3OH_n)_n + H^+_{(s)} \tag{5}$$

where g and s indicate molecules in the gas or solid phase and $\sigma$ molecules adsorbed at the surface.

Assuming that reaction (4) is now the rate-determining step, reaction rate $r$ can be expressed by the equation:

$$r = k_4[C_4H^+_{9(\sigma)}][CH_3OH_{(s)}] \tag{6}$$

Assuming the virtual equilibria of the reactions (2) and (3) with the equilibrium constants $K_2$ and $K_3$ the following equation was obtained:

$$r = k_4K_2K_3[H^+_{(s)}]p_{C_4H_8}p_{CH_3OH} \tag{7}$$

where $p_{C_4H_8}$ and $p_{CH_3OH}$ are the partial pressures of isobutene and methanol in the gas phase and $[H^+]$ is the concentration of “free” protons forming hydrogen bonds between HPA anions and available for the protonation of $CH_3OH$ molecules in the bulk and $C_4H_8$ at the surface. At the initial state of the reaction, when the concentration of methanol absorbed by the solid is small, as compared to the concentration of free protons, the latter can be assumed as constant and equal to the initial one $[H^+]_o$. Equation (7) transforms to:

$$r = \alpha p_{C_4H_8}p_{CH_3OH} \quad \text{where } \alpha = k_4K_2K_3[H^+_{(s)}]_o \tag{8}$$

In this latter equation, the order of reaction in respect of the methanol is positive and equal to 1. Its experimental value 0.87 is near to this expected value. On the other hand, the reaction order in respect to the isobutene 1.29, indicates deviation from the proposed model, suggesting the parallel occurrence of a bimolecular reaction. This is most probably the formation of isobutene dimer 2,5-dimethyl-3-hexane, which on further reaction with methanol would produce one molecule of MTBE and regenerate one molecule of isobutene.

At the steady state of the catalytic reaction, the concentration of free protons markedly decreases, owing to the formation of protonated clusters in the bulk. Their concentration can be now calculated from the equation:

$$K_5 = \frac{[(CH_3OH)_nH^+_{(s)}]}{[CH_3OH_{(s)}]^n[H^+_{(s)}]} \tag{9}$$

expressing the equilibrium of the reaction (5). The integral value of $n$ approximates the state in which a protonated cluster with $n$ methanol molecules predominates. A fractional value of $n$ indicates the predominance of two clusters differing in $n$ by unity and present in comparable concentrations.

Combining Equations (7) and (9) one can obtain:

$$r = \frac{k_4K_2}{K_3^{n-1}K_5}p_{C_4H_8}p_{CH_3OH}^{(1-n)}[(CH_3OH)_nH^+_{(s)}] \tag{10}$$

The concentration of the predominant cluster can be approximated by the equation $[(CH_3OH)_nH^+_{(s)}] \approx c_{CH_3OH}$, where $c_{CH_3OH}$ is the total concentration of methanol in the next-to-surface layer (both concentrations expressed as the number of molecules per HPA anion).

As already mentioned, at 40 °C, the dependence of $c_{CH_3OH}$ on $p_{CH_3OH}$ has been experimentally determined within the pressures of the methanol 8.53–14.9 kPa (overlapping with the $p_{CH_3OH}$ range in which determination of the reaction order with respect to the methanol was carried out). It has the form of a Freundlich isotherm:

$$[(CH_3OH)_nH^+_{(s)}] \approx c_{CH_3OH} = 0.109p_{CH_3OH}^{1.76} \tag{11}$$

Inserting this into Equation (10) gives:

$$r = \beta p_{C_4H_8}p_{CH_3OH}^{2.76-n} \quad \text{where } \beta = \frac{0.109k_4K_2}{K_3^{(n-1)}K_5} \tag{12}$$

Hence, at $n > 2.76$, a negative order of reaction should be obtained. In fact, the reaction order in respect to the methanol at 40 °C and the steady state of the reaction was equal to −1.61, corresponding to $n \approx 4$. This suggests that tetrameric protonated clusters predominate in the next-to-surface layer during the catalytic reaction.

The other reaction, which involves isobutene carbocation is reaction (2). Hence, the kinetic equation, which assumes it as the rate-determining step should also be taken into account. In this case the reaction rate is expressed as:

$$r = k_2p_{C_4H_8}[H^+_{(s)}] \tag{13}$$

Applying a similar procedure of calculations to that used previously, the general equation is obtained:

$$r = \frac{0.109k_2}{K_5K_3^n}p_{C_4H_8}p_{CH_3OH}^{(1.76-n)} = \gamma\ p_{C_4H_8}\ p_{CH_3OH}^{1.76-n} \tag{14}$$

It has an analogous form to Equation (12). However, it leads to a somewhat lower value of $n$ (=3) and differs by the values of constants, which cannot be determined without further experiments. One can only conclude, that both Equations (12) and (14) qualitatively explain the negative order of reaction in respect of methanol, observed at the steady state of reaction at 40 °C.

## 3. ETBE synthesis on $H_6P_2W_{18}O_{62}$ catalyst

In the case of MTBE synthesis on dehydrated $H_4SiW_{12}O_{40}$ in the course of the catalytic reaction, the secondary structure of HPA consisted of anions, protons and molecules of methanol participating in the catalytic reaction. Baronetti et al. [35,36], when studying MTBE formation on the Dawson type HPA $H_6P_2W_{18}O_{62}$ catalyst, stated that its activity had been influenced by the presence of water, i.e., the substance that formally does not participate in the catalytic process but may enter into the secondary structure. A fuller study of this effect was undertaken recently by the present authors [37]. They studied it on the example of the formation of ethyl-*tert*-butyl ether by the addition of ethanol to isobutene, using as a catalyst, $H_6P_2W_{18}O_{62}$ samples with varying content of water of crystallization. Parallel to the catalytic experiments, the sorption of reaction substrates on the catalyst samples was studied [37].

Thermal analysis of the hydrated $H_6P_2W_{18}O_{62}$ (aq) sample showed that its decomposition comprised two main stages. In the first, between room temperature and 200 °C, weight loss corresponded to the departure of 28.8 mole $H_2O$ per mole of acid. Between 200 and 250 °C, a plateau appeared on the TG curve. Above this temperature, the second decomposition stage was characterized by an endothermic DTA peak at 300 °C and a parallel DTG peak at the same temperature. The weight loss of 3.01 $H_2O$ per anion corresponded to the departure of the so-called "water of constitution" (dehydroxylation). Above 400 °C, no other changes in weight were registered. It should be noted here that, although in the first stage of decomposition, the weight decreased monotonically, the TG curve showed several inflexion points to which local maxima or minima of sample decomposition corresponded. The analysis of these effects enabled us to suppose an enhanced stability of the hydrates $H_6P_2W_{18}O_{62}\cdot 12H_2O$ and $H_6P_2W_{18}O_{62}\cdot 6H_2O$ containing dioxonium $H_5O_2^+$ or, respectively, oxonium $H_3O^+$ ions.

In the case of ETBE catalytic synthesis, the catalyst samples with varying content of crystallization water were used. This was achieved by preheating the original $H_6P_2W_{18}O_{62}\cdot 28.8H_2O$ for a fixed period in the catalytic reactor between 80 and 300 °C. Subsequently, the catalytic tests have been carried out at 40 °C. In separate experiments, the composition of the samples after analogous pretreatment was determined. Considering the fact that for catalytic experiments ethanol of azeotropic composition (4.4 wt.% of $H_2O$) was used as the substrate, possible changes in the composition of the catalysts were controlled by comparing the contents of the water vapour in the feed with that in the gas leaving the layer of the catalyst.

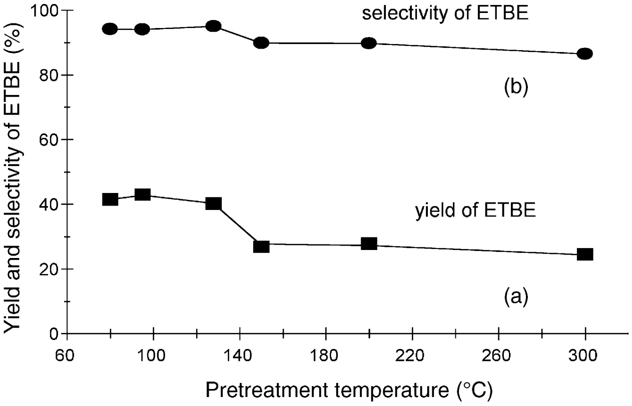

Fig. 6. The catalytic activity of $H_6P_2W_{18}O_{62}$ vs. pretreatment temperature. (a) Yield of ETBE and (b) selectivity of ETBE formation [37].

The effect of pretreatment temperature on the ETBE yield and the selectivity is illustrated in Fig. 6 [37], where two levels of ETBE yield are shown. The higher of them, about 40%, corresponds to the samples preheated at 80, 95 and 128 °C exhibiting the content of crystallization water of 8.6, 8.0 and 5.4 $H_2O$ molecules per anion, respectively. The lower level, about 27%, corresponds to the catalysts preheated at 150 and 200 °C, which contained 3.0 and 2.8 $H_2O$ molecules per anion. Similar, but somewhat lower, yield was also exhibited by the anhydrous sample calcined at 300 °C. In all cases, selectivity of ETBE was high and amounted to 90–95%. The shape of the curve in Fig. 6 exhibiting two different levels of catalytic activity can be understood if we compare it with the results of the ethanol and water sorption experiments.

They are represented in Fig. 7a, where sorption and desorption on anhydrous $H_6P_2W_{18}O_{62}$ is shown, and Fig. 7b presenting the sorption on $H_6P_2W_{18}O_{62}\cdot 8H_2O$ [37]. The sorption of water and ethanol vapours on anhydrous and also trihydrated $H_6P_2W_{18}O_{62}$ is fast at 40 °C, and after some 20–30 min reaches a constant level. The amounts of $H_2O$ and $C_2H_5OH$ taken up at equilibrium correspond to the coverage of the sample with 11 and 18 monolayers, respectively. Considering the low relative pressure of both adsorbates ($p/p_0$ about 0.3), no such surface coverage can be expected, and the bulk sorption has to be assumed. It is quite striking, that although the final increase in weight is different for $H_2O$ and $C_2H_5OH$, the number of molecules per anion are the same. In both cases, 3 moles of adsorbate are taken up for mole of $H_6P_2W_{18}O_{62}$. Fig. 7b shows also that, in the case of octahydrated $H_6P_2W_{18}O_{62}$, the sorption of water and ethanol is stoichiometrically identical (8 moles of adsorbate per mole $H_6P_2W_{18}O_{62}$). However, an unexpected observation was that higher amounts were sorbed, than in the previous case, and a further 8 molecules of adsorbate were added to the $8H_2O$ molecules per anion, which were initially present in the sample. This difference in the capacity of sorption can

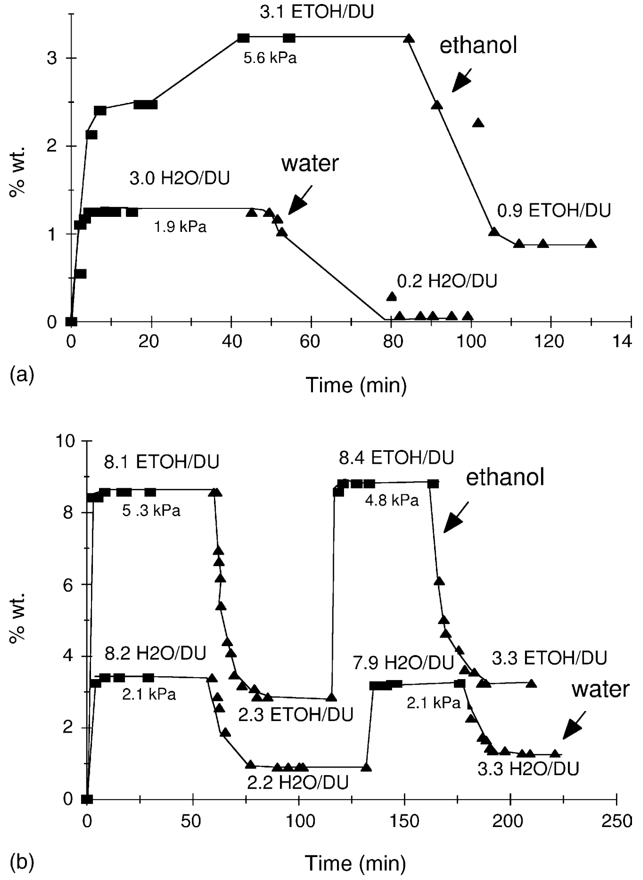

Fig. 7. Sorption and desorption of ethanol and water at 40 °C on (a) anhydrous $H_6P_2W_{18}O_{62}$ and (b) octahydrated $H_6P_2W_{18}O_{62}$. ETOH/DU and $H_2O$/DU express the number of $C_2H_5OH$ or $H_2O$ molecules respectively per Dawson anion.

be explained by the differences in the secondary structure. In fact, the secondary structure of fully hydrated Wells–Dawson HPA ($H_6P_2W_{18}O_{62}\cdot 24H_2O$) proposed recently by Sambeth at al. [38] presents a loose structure, joined by bridges formed by protonated clusters. It seems that the loose secondary structure of highly hydrated $H_6P_2W_{18}O_{62}$ can accommodate more sorbate molecules than the more compact structure of non-hydrated or only weakly hydrated ones. In the case of the latter samples, no sorption of isobutene was observed. On the other hand, if isobutene was contacted with octahydrated $H_6P_2W_{18}O_{62}$, at first, it absorbed up to about seven molecules per anion, but after some 5–10 min, the weight of the sample began to decrease to the value of a few tenth of *i*-$C_4H_8$ per mole HPA. This indicated a reaction between isobutene and crystallization water, leading to the formation of *tert*-butyl alcohol (TBA) removed to the gas phase.

The above results show that the catalytic experiments presented in Fig. 6 were carried out on samples differing by their secondary structure. Samples with an initial content of about $8H_2O$ per anion, exhibiting higher sorption capacity, are more active than those of low capacity.

## 4. Conclusions

1. Solid heteropolyacids due to their high acid strength are effective catalysts of acid–base type reactions. Solid HPAs represent supramolecular systems in which large anions (forming the so-called “primary” structure) interbonded by hydrogen bonds are the host system, into which polar molecules such as $H_2O$, alcohols or amines (guest) easily penetrate thus forming the “secondary” structure.
2. Methyl-*tert*-butyl ether formation in gas phase has been studied on dehydrated $H_4SiW_{12}O_{40}$ using both sorption and catalytic experiments. The secondary structure consists in this case of HPA anions and methanol molecules penetrating the bulk of crystallites. According to the proposed model the catalytic reaction occurs at the surface between adsorbed protonated isobutene molecules and methanol molecules supplied from the bulk.
3. Ethyl-t*ert* butyl ether has been studied on octa-hydrated as well as on non-hydrated or tri-hydrated solid $H_6P_2W_{18}O_{62}$. In this case, the secondary structure of pristine catalyst has been composed of HPA anions and $H_2O$ molecules, which formally are not participating in the ethanol to isobutene addition. Different content of crystallization water resulted in the secondary structure of different $C_2H_5OH$ sorption capacity. The $C_2H_5OH$ sorption was higher in the case of octa-hydrated catalysts, which also were catalytically more active thus showing the role of the secondary structure in the catalytic process.

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