

The effect of water vapour on kinetics of ethyl-*tert*-butyl ether (ETBE) and *tert*-butyl alcohol (TBA) synthesis in the gas phase on Wells–Dawson catalyst

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Abstract

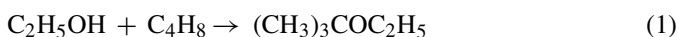
The effect of water vapour in the feed on the synthesis of ethyl-*tert*-butyl ether (ETBE) produced from isobutene and ethanol was investigated. The kinetics of gas phase etherification and accompanying formation of *tert*-butyl alcohol (TBA) by Wells–Dawson acid heteropolyacid $H_6P_2W_{18}O_{62}$ as catalyst was determined at 40 °C. Rate expression in the form of a power equation was developed to correlate the experimental data over a wide range of reactants pressures. Water presence in the catalytic reactor inhibited the formation of ETBE and was introduced into the kinetic equation as an independent additional factor. The experimental evidence of ethanol and water sorption into the bulk of catalyst was confirmed by independent gas phase sorption experiments. The results of catalytic experiments were interpreted qualitatively on the basis of the model of catalytic system containing solid heteropolyacid in which tertiary ethers are synthesized.

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Keywords: Heteropolyacid; ETBE; TBA; Wells–Dawson

1. Introduction

Oxygenates, especially methyl-*tert*-butyl ether (MTBE) and also ethyl-*tert*-butyl ether (ETBE) are introduced into gasoline as antiknocking additives. They increase gasoline octane number and simultaneously reduce the polluting carbon oxides emissions in the exhaust gases. In most cases they are obtained by electrophilic addition of alcohol to isobutene (IB) which, for example, may be shown by the following equation:



In the industry sulfonated acid resins are used as the catalysts for tertiary ethers production. However, they are not fully satisfactory because they may degrade with sulfuric acid emission, which is harmful for the environment, and hence many authors have investigated other catalysts such as acid and modified zeolites and silicalites. The catalysts which were proved to be active in this reaction are also heteropolyacids

(HPA) [1,2]. Shikata et al. [3] using unsupported Keggin-type $H_3PW_{12}O_{40}$ and also Wells–Dawson type heteropolyacid $H_6P_2W_{18}O_{62}$ (HDA) demonstrated pseudo-liquid phase synthesis and described unique dependence of MTBE synthesis on methanol partial pressure. On increasing this pressure the reaction rate at first increases but above a certain value, depending on the type of HPA, it decreases systematically. Most of the research in this field is concerned with MTBE synthesis on Keggin-type dodecaheteropolyacids, which was reviewed in Ref. [4].

Only in recent years the interest in literature has been directed towards tertiary ethers synthesis on octadecaheteropolyacids of Wells–Dawson type, in particular $H_6P_2W_{18}O_{62}$. The latter turned out to be an effective catalyst in tertiary ethers synthesis and alcohols dehydration [5]. In the liquid phase MTBE synthesis $H_6P_2W_{18}O_{62}$ as well as $H_6P_2Mo_{18}O_{62}$ [6] and in the gas phase $H_6P_2W_{18}O_{62}/SiO_2$ [5] catalysts were used. Gas phase synthesis of ETBE on $H_6P_2W_{18}O_{62}$ [7], silica supported and unsupported $H_6P_2W_{18}O_{62}$ [8] was studied.

Kinetic study of ETBE synthesis on solid $H_6P_2W_{18}O_{62}$ in gas phase carried out at the absence of water in the catalytic system published recently by the present author [9] demonstrated inhibiting effect of ethanol (EtOH) and the increase of the

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Nomenclature

EtOH	ethanol
F	velocity of isobutene flow in the feed (mol h^{-1})
$F_i(p_{\text{H}_2\text{O}})$	function of water pressure
HPA, HDA	heteropolyacid, Wells–Dawson acid
IB	isobutene
k	constant rate ($\text{mol g}^{-1} \text{h}^{-1}$)
K_i	equilibrium constant, i number of the reaction
m	mass of anhydrous catalyst (g)
p_j	experimental pressure, $j = \text{H}_2\text{O}, \text{EtOH}, \text{IB}$ (Pa)
p_j^*	standardized pressure (Pa), $p_j^* = p_j/p_0$ where $p_0 = 1.0125 \times 10^5$ Pa
r_i	reaction rate ($\text{mol g}^{-1} \text{h}^{-1}$), $i = \text{IB}, \text{ETBE}, \text{TBA}$
X_{IB}	total conversion of isobutene (%), amount of moles of isobutene consumed divided by the amount of moles of isobutene introduced
$X_{\text{ETBE}}, X_{\text{TBA}}$	conversion of isobutene to ETBE, TBA, amount of moles of isobutene transformed to ETBE, TBA divided by the amount of moles of isobutene introduced.

Greek symbols

α, β	reaction order with respect to ethanol and isobutene for anhydrous system (Table 1)
α_1, β_1	reaction order with respect to ethanol and isobutene for total conversion of isobutene
α_2, β_2	reaction order with respect to ethanol and isobutene for ETBE synthesis
β_3	reaction order with respect to isobutene for TBA synthesis
γ, η, ξ	constant value, product of the equilibrium constants: $\gamma = k_{18} K_{15}^m K_{16}^{(-n/2)} K_{17} K_{(15')}^{(-q/2)} K_{(19+16')}^{(-1/2)}$, $\eta = k_{(20a)} K_{15}^m K_{16}^{(1-n/2)} K_{17} K_{18} K_{(15')}^{(-q/2)} K_{(19+16')}^{(-1/2)}$, $\xi = k_{(17')} K_{16}^{(-n/2)} K_{17}^m K_{18} K_{19} K_{(15')}^{(-q/2)} K_{(19+16')}^{(-1/2)}$.

reaction rate with the increasing isobutene (IB) partial pressure (p_{IB}). Separate experiments have shown that ethanol is absorbed by the bulk of HPA crystallites where it is forming protonated clusters while the other reaction component, isobutene, is only adsorbed on the external surface of the crystallites. It was assumed that its adsorption is accompanied by the protonation and formation of monomeric or oligomeric carbocations. Basing on the assumption, that reaction between adsorbed carbocation and ethanol supplied from the gas phase is the reaction rate determining step, a kinetic equation was proposed satisfactorily representing the experimental results. In this reaction model the inhibiting effect of ethanol pressure (p_{EtOH}) was explained by assuming that ethanol clusters in the bulk of HPA crystallites are bonding protons of heteropolyacid and thus decreasing their availability for the carbocation formation.

Currently, in the industry ETBE is produced using fairly pure ethanol, which adds considerable costs to the final product. Thus the effect of water in the feed is interesting from the point of

view that watery ethanol use may contribute to some lowering of ETBE production costs and render it more competitive in the market.

The effect of water content ranging from 0 to 5 wt.% in alcohol on liquid phase ethers (MTBE, ETBE) synthesis was described in Ref. [10]. The authors investigated the synthesis in liquid phase on macroporous sulfonated resin K2631 and observed that the rate of ether production was strongly lowered by the initial water presence but the water presence did not affect ETBE equilibrium values; they are similar to the anhydrous system. In some cases also catalytic decomposition of MTBE on active sulfonic resins was investigated in the gas phase [11,12].

It should be observed here that the addition of water to isobutene results also in the production of some amount of *tert*-butyl alcohol (TBA):



TBA is also used as an oxygenate and antiknocking agent for automobile fuels. The mechanism and kinetics of the hydration of isobutene to TBA on the heteropolyacid catalyst ($\text{H}_4\text{SiW}_{12}\text{O}_{40}$) were tested in Ref. [13]. It was an active and selective catalyst at low temperatures of 40 °C–80 °C. The proposed model of reaction assumed the surface interaction between adsorbed molecules of isobutene and water molecules supplied from the bulk of the catalyst.

Hence the aim of the present research was to investigate the effect of water content in the feed (0.01–9.5 kPa) on the reaction rate of ETBE and parallel TBA synthesis on Wells–Dawson type solid heteropolyacid $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$. In this system water can play a dual role. It is the substrate for TBA formation, but also it penetrates (similarly as ethanol—the substrate for ETBE formation) the bulk of HPA crystallites where it gets protonated and hence changes the acidity of the catalyst.

2. Experimental

Ethyl alcohol: absolute pure (99.8 wt.%, the content of 0.07 wt.% H_2O was determined by chromatographic analysis) and ethyl alcohol ppa. (96 wt.%) (POCh Gliwice), 2-methyl propene (isobutene, *i*- C_4H_8 , p.a., Aldrich), *tert*-butyl alcohol (Aldrich) and ethyl-*tert*-butyl ether (99%, Aldrich) were used in the catalytic experiments.

$\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62} \cdot n\text{H}_2\text{O}$ was synthesized according to Refs. [5,14] and was kept at room temperature in a desiccator over a saturated solution of $\text{Mg}(\text{NO}_3)_2$. Thermal analysis (determined by TGA/SDTA 851^e Mettler-Toledo apparatus, heating rate 5 °C min^{-1}) showed that the total weight loss corresponded to 33.6 H_2O per mole of acid. The last portion of water removed above 250 °C (that is 3 moles H_2O per HDA) corresponded to the “water of constitution”. The composition of the synthesized sample was $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62} \cdot 30.6\text{H}_2\text{O}$.

A quartz constant flow differential microreactor ($\phi = 10$ mm) was used for catalytic experiments. The helium carrier gas was first saturated with absolute ethanol vapour or the ethanol–water mixture and subsequently mixed with a stream of isobutene. The composition of the reaction mixture (isobutene/ethanol molar

ratio) was kept within the range of 0.4–1.5. The catalytic reactor was connected on line with Perkin-Elmer AutoSystem XL gas chromatograph. A Porapak QS column was used for the chromatographic analyses. Samples of 0.057 g (0.034 cm^3) of $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62} \cdot 31\text{H}_2\text{O}$ ($13 \times 10^{-6} \text{ mol}$) were mixed with 0.36 g (0.37 cm^3) of quartz grains ($\phi = 0.19 \text{ mm}$) thus obtaining a catalyst layer of 0.5 cm thick. In a previous research [9] carried in the same apparatus it was stated that the conversion of isobutene to ETBE changed linearly with the increase of catalyst mass for the samples containing up to 0.15 g HDA. Hence at the use of 0.05 g HDA the effect of external mass transfer and diffusion could be neglected. Temperature was kept by temperature programmer MRT-4 (accuracy $\pm 0.1 \text{ }^\circ\text{C}$) and was controlled by a thermo-couple located in the reactor jacket close to the catalyst bed.

Catalytic experiments were carried out in the steady-state, far from the limitation by chemical equilibrium, at $40 \text{ }^\circ\text{C}$. This temperature was optimal for kinetic measurements. At temperature higher than 50 or $55 \text{ }^\circ\text{C}$ the reverse reaction, ETBE decomposition, can already influence the kinetics. At temperatures markedly lower, e.g. $20 \text{ }^\circ\text{C}$ reaction is much slower which necessitates working at conversion too low to be determined with satisfactory precision. The observed conversion was most frequently kept within the limit 5–8% and never exceeded 10%. It is generally accepted in the literature, as, e.g. in Ref. [15], that such conditions allow treating plug-flow reactor as approximately in the differential mode. However in such reactor the danger exists that at the small conversion required large errors in analysis might occur [16]. In fact this was not the case in the present research as the results of chromatographic analysis of the amounts of isobutene and ethanol appearing during catalytic experiments were determined with the precision (standard deviation) of 0.5–0.2% of the measured value. Hence the conditions in which reactor was working were not much distant from those in an ideal differential reactor. The conversions were measured free from the influence of external mass transfer and diffusion. The partial pressures of reactants in the feed were: 9–25 kPa isobutene and 13–26 kPa ethanol and W/F values (where W is the catalyst weight and F the total flow rate) were between $0.024 \text{ g h mol}^{-1}$ and $0.036 \text{ g h mol}^{-1}$. The water pressure ($p_{\text{H}_2\text{O}}$) in the gas phase (introduced into ethanol vapour) varied between 0.01 and 8.8 kPa.

Before the catalytic experiments the samples were preheated in situ in a catalytic reactor in helium flow (30 ml min^{-1} , at $220 \text{ }^\circ\text{C}$ 2 h). Such prepared catalysts were anhydrous (i.e. devoid of the water of crystallization and exhibiting the stoichiometric composition $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$) which was proved by the independent experiment in which the catalyst was activated in the catalytic reactor at the same conditions as during the catalytic tests and the change of the sample mass was controlled gravimetrically. It was proved that the temperature $220 \text{ }^\circ\text{C}$ was sufficient for the total removing of the water of crystallization but no dehydroxylation of the acid took place (no elimination of the so-called water of constitution).

Sorption of ethyl alcohol and water vapours were studied by means of a quartz spring sorption balance (sensitivity $0.6828 \text{ mm mg}^{-1}$) connected with a vacuum system. The elon-

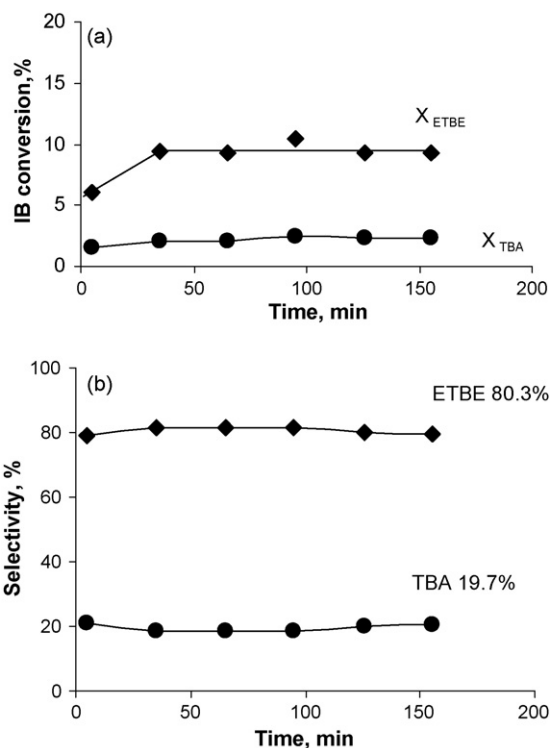


Fig. 1. Typical catalytic run: (a) isobutene conversion to ETBE and TBA, (b) selectivity to ETBE and TBA vs. time of catalytic test at 3.1 kPa water pressure ($p_{\text{EtOH}} = 17.2 \text{ kPa}$, $p_{\text{IB}} = 18.4 \text{ kPa}$, reaction temperature $40 \text{ }^\circ\text{C}$).

gation of the spring was measured with a cathetometer, the sensitivity of which was 0.01 mm.

3. Results

Wells–Dawson acid as the catalyst for ETBE synthesis was already active at temperatures as low as $35 \text{ }^\circ\text{C}$ [7,9]. Isobutene conversion passed over a maximum between 40 and $50 \text{ }^\circ\text{C}$ and then decreased reaching the values not very much distant from equilibrium values [9]. Such situation is typical of reversible exothermic reactions. On the other hand at 35 or $40 \text{ }^\circ\text{C}$ equilibrium conversion of ETBE calculated from thermodynamic data [17] reached 48.7% or 41.9%, respectively. The use of the sample 0.05 g ensured the conversion never exceeding 10% and hence the effect of the reverse reaction, ETBE decomposition, could be neglected [9]. This is why the temperature of $40 \text{ }^\circ\text{C}$ has been chosen as the temperature of all kinetic measurements.

The main products of isobutene reactions at the presence of water in the feed were ethyl-*tert*-butyl ether and *tert*-butyl alcohol appearing in different proportions. Fig. 1 shows a typical catalytic run.

In the experiments carried out at $40 \text{ }^\circ\text{C}$ the partial pressure of only one of the substrates (ethanol, isobutene or water) has been changed while the pressures of the other two were constant. The rates of isobutene consumption r_{IB} , ETBE and TBA formation r_{ETBE} and r_{TBA} , were calculated using the following equations:

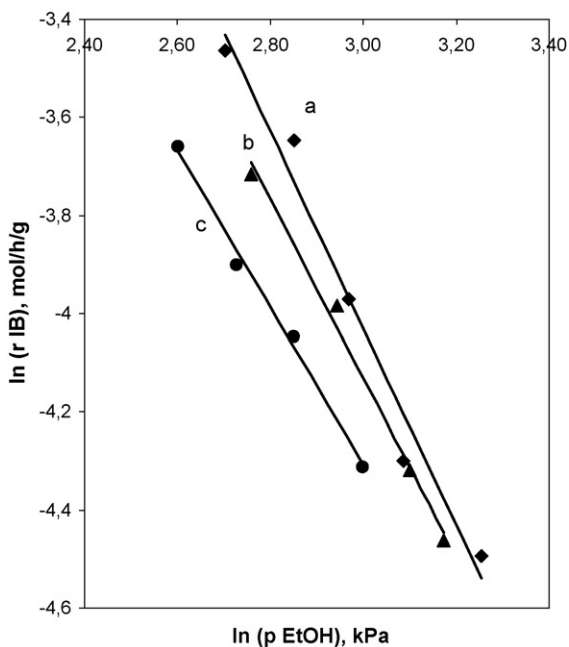


Fig. 2. $\ln(r_{IB})-\ln(p_{IB})$ plot at 40 °C at constant isobutene pressure ($p_{IB} = 10.3$ kPa) over anhydrous $H_6P_2W_{18}O_{62}$ at different water content in gas phase: (a) absolute ethanol, (b) $p_{H_2O} = 3.8$ kPa and (c) $p_{H_2O} = 5.3$ kPa.

$$r_{IB}[\text{mol g}^{-1} \text{h}^{-1}] = F \frac{X_{IB}}{m},$$

$$r_{ETBE}[\text{mol g}^{-1} \text{h}^{-1}] = F \frac{X_{ETBE}}{m},$$

$$r_{TBA}[\text{mol g}^{-1} \text{h}^{-1}] = F \frac{X_{TBA}}{m}$$

where F is the velocity of isobutene flow in the feed [mol h^{-1}], m the mass of anhydrous catalyst [g], X_{IB} the total conversion of isobutene and X_{ETBE} and X_{TBA} are the conversions of isobutene to ETBE and TBA, respectively.

The dependences of the total isobutene conversion rate, r_{IB} , the rate of ETBE synthesis, r_{ETBE} , as well as that of TBA, r_{TBA} , on the partial pressures of ethanol and isobutene are shown in Figs. 2–7 in double logarithmic plot. The plots are linear thus indicating power dependence of r_{IB} , r_{ETBE} and r_{TBA} on the partial pressures of ethanol and isobutene. No such dependence of the reaction rates on the partial pressure of water vapour was obtained. Fig. 8A shows that the rates r_{IB} and r_{ETBE} differed only slightly and monotonically decreased with the increase of p_{H_2O} . However r_{TBA} was definitely lower than r_{ETBE} and was increasing with the increase of p_{H_2O} up to $p_{H_2O} \approx 4.8$ kPa at $p_{IB} = 18.4$ kPa and $p_{EtOH} = 17.2$ kPa (Fig. 8B, curve c). At $p_{IB} = 10.3$ kPa and $p_{EtOH} = 17.2$ kPa similar maximum was reached at $p_{H_2O} \approx 3$ kPa (Fig. 8B, curve c') and then after reaching a flat maximum decreased as shown in Fig. 8B. Fig. 9A–C shows the ratio of r_{ETBE}/r_{TBA} presented as the function of p_{EtOH} , p_{IB} and p_{H_2O} .

The measurements of water vapour sorption by dehydrated catalyst were carried out at 40 °C using a spring microbalance. Sorption isotherm is shown in Fig. 10. The isotherms of

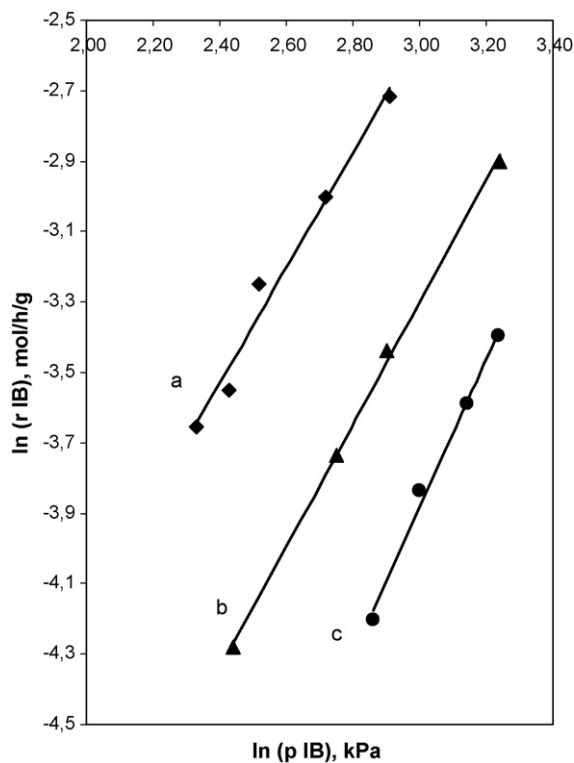


Fig. 3. $\ln(r_{IB})-\ln(p_{C4})$ plot at 40 °C at constant ethanol pressure ($p_{EtOH} = 17.2$ kPa) over anhydrous $H_6P_2W_{18}O_{62}$ at different water content in gas phase: (a) absolute ethanol, (b) $p_{H_2O} = 3.8$ kPa and (c) $p_{H_2O} = 9.5$ kPa.

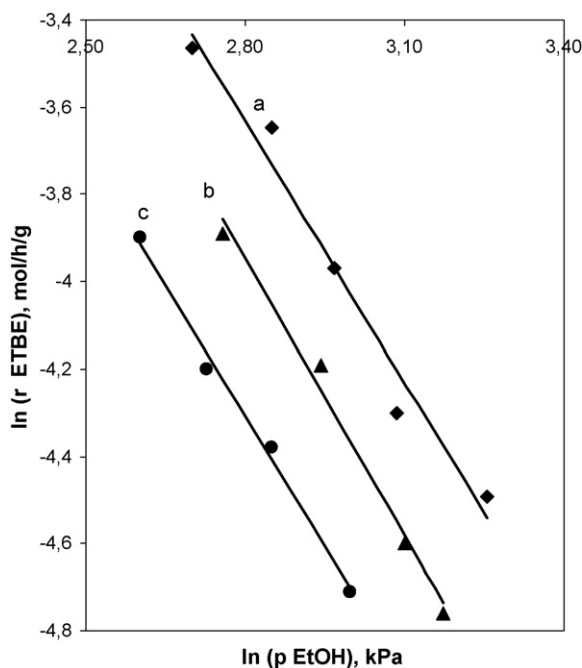


Fig. 4. $\ln(r_{ETBE})-\ln(p_{EtOH})$ plot at 40 °C at constant isobutene pressure ($p_{IB} = 10.3$ kPa) over anhydrous $H_6P_2W_{18}O_{62}$ at different water content in gas phase: (a) absolute ethanol, (b) $p_{H_2O} = 3.8$ kPa and (c) $p_{H_2O} = 5.3$ kPa.

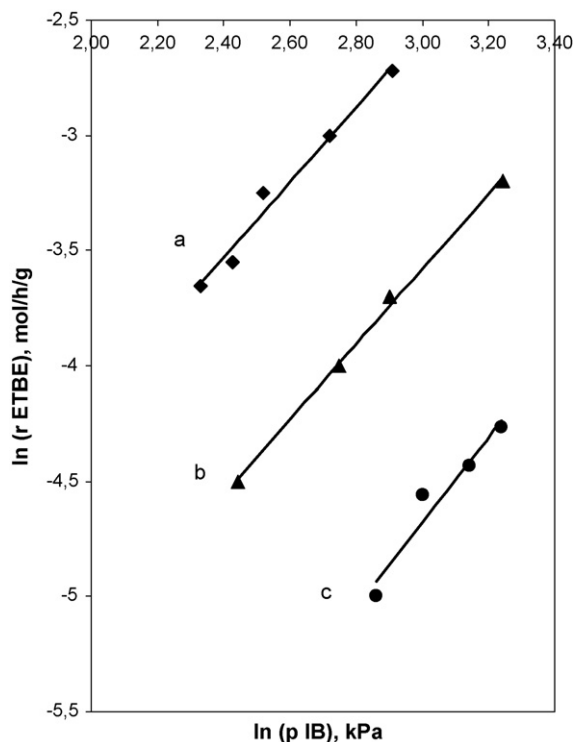


Fig. 5. $\ln(r_{ETBE})-\ln(p_{C4})$ plot at 40 °C at constant ethanol pressure ($p_{EtOH} = 17.2$ kPa) over anhydrous $H_6P_2W_{18}O_{62}$ at different water content in gas phase: (a) absolute ethanol, (b) $p_{H_2O} = 3.8$ kPa and (c) $p_{H_2O} = 9.5$ kPa.

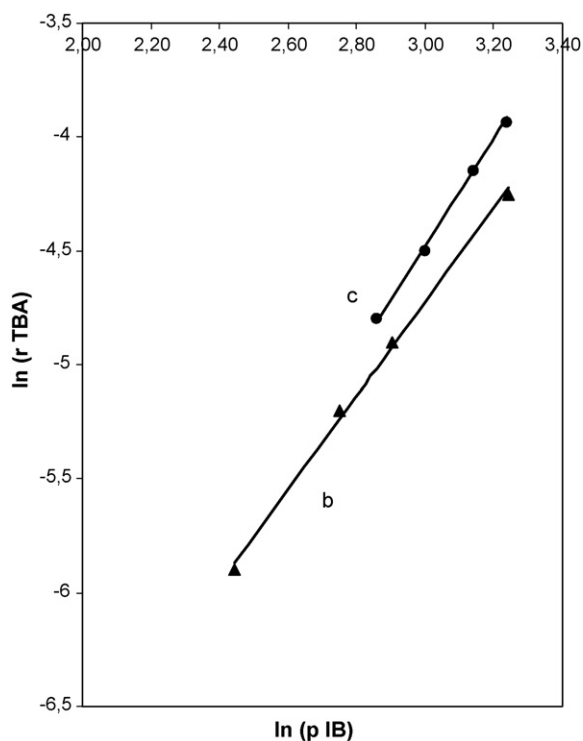


Fig. 6. $\ln(r_{TBA})-\ln(p_{C4})$ plot at 40 °C at constant ethanol pressure ($p_{EtOH} = 17.2$ kPa) over anhydrous $H_6P_2W_{18}O_{62}$ at different water content in gas phase: (b) $p_{H_2O} = 3.8$ kPa and (c) $p_{H_2O} = 9.5$ kPa.

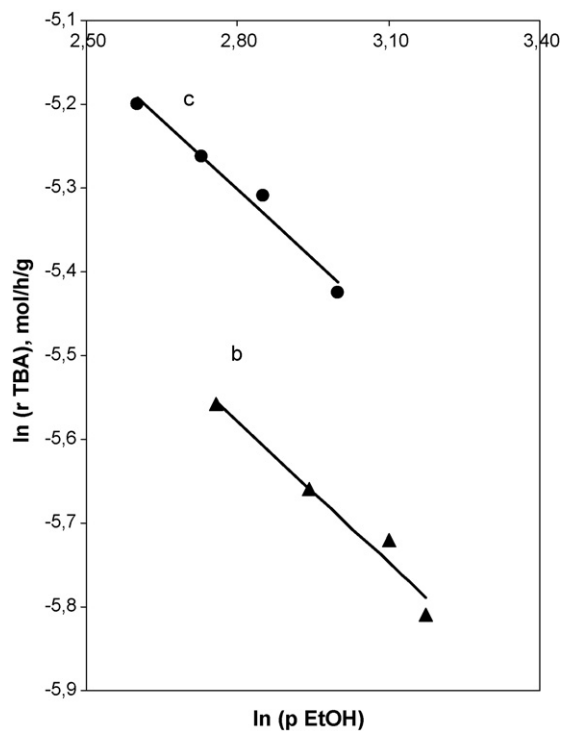


Fig. 7. $\ln(r_{TBA})-\ln(p_{EtOH})$ plot at 40 °C at constant isobutene pressure ($p_{IB} = 10.3$ kPa) over anhydrous $H_6P_2W_{18}O_{62}$ at different water content in gas phase: (b) $p_{H_2O} = 3.8$ kPa and (c) $p_{H_2O} = 5.3$ kPa.

isobutene and ethanol vapour obtained in the same apparatus were shown in the previous paper [9].

4. Discussion

As Fig. 1 shows the only products obtained in a typical run from isobutene at the presence of ethanol and water

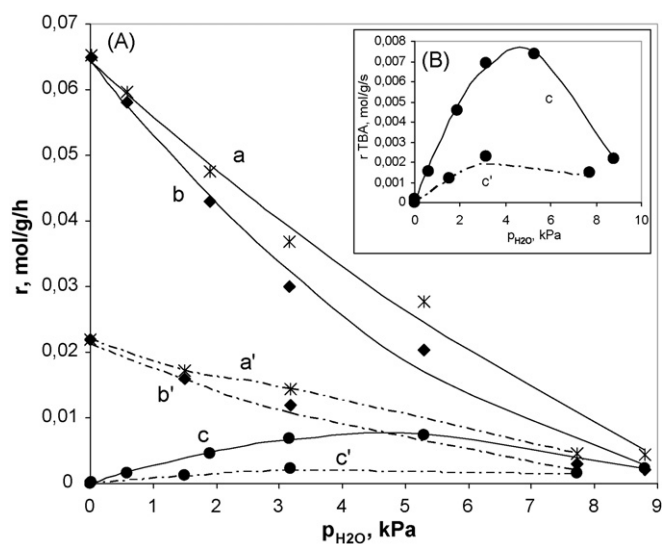


Fig. 8. (A) Rate of: total isobutene consumption – r_{IB} (curves: a, a'), ETBE formation – r_{ETBE} (curves: b, b'), TBA formation – r_{TBA} (curves: c and c') vs. water pressure at 40 °C. (B) Enlarged curves c and c'; curves a, b and c (solid lines) obtained at $p_{EtOH} = 17.2$ kPa and $p_{IB} = 18.4$ kPa, and curves a', b' and c' (dotted lines) at $p_{EtOH} = 17.2$ kPa and $p_{IB} = 10.3$ kPa.

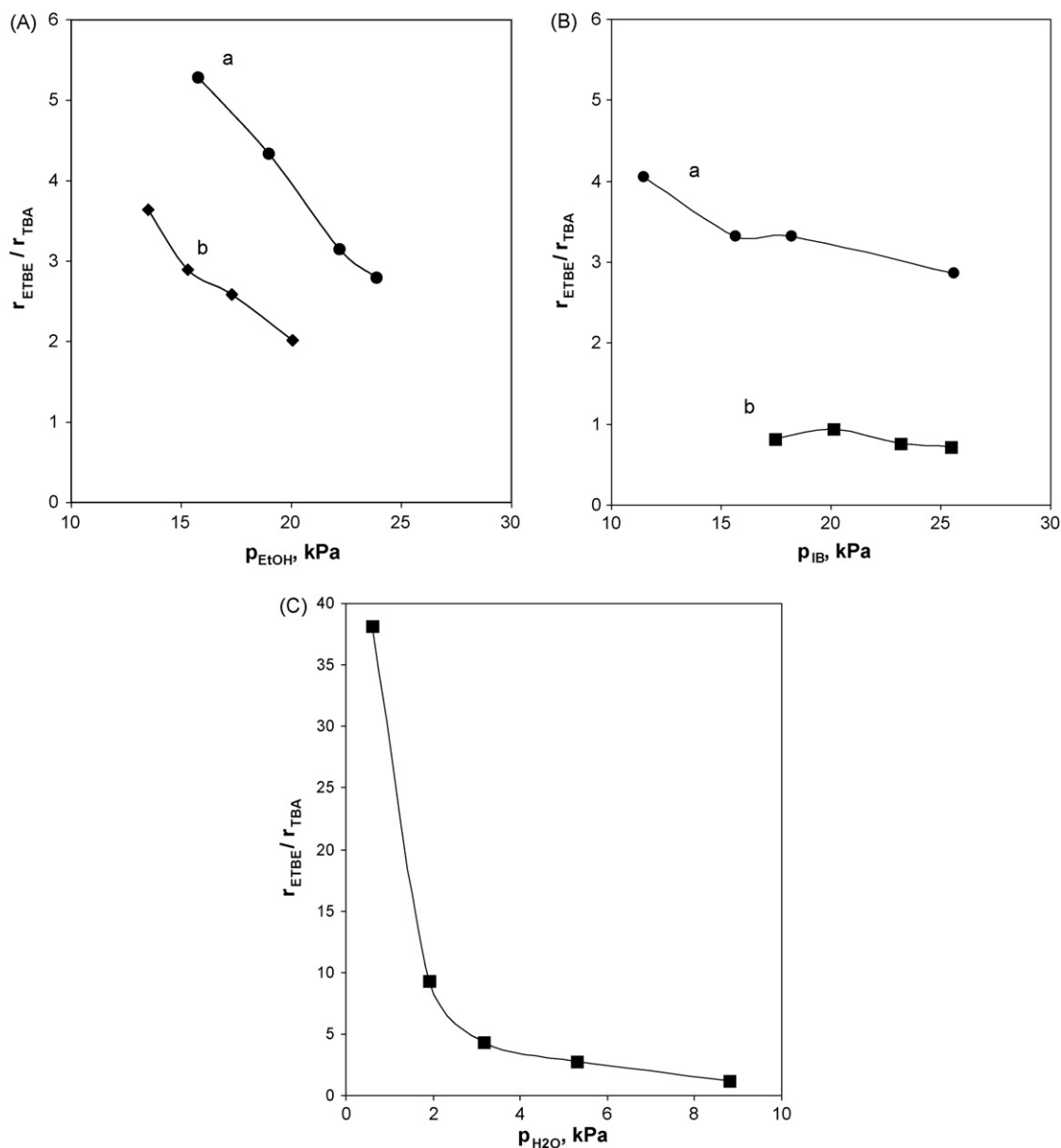


Fig. 9. (A) r_{ETBE}/r_{TBA} ratio vs. ethanol partial pressure at 40 °C at constant isobutene pressure ($p_{IB} = 10.3$ kPa) over anhydrous $H_6P_2W_{18}O_{62}$ at different water content in gas phase (a) $p_{H_2O} = 3.8$ kPa and (b) $p_{H_2O} = 5.3$ kPa. (B) r_{ETBE}/r_{TBA} ratio vs. isobutene partial pressure 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) $p_{H_2O} = 3.8$ kPa and (b) $p_{H_2O} = 9.5$ kPa. (C) r_{ETBE}/r_{TBA} ratio vs. water partial pressure at 40 °C at constant ethanol ($p_{EtOH} = 17.2$ kPa) and isobutene pressure ($p_{IB} = 18.4$ kPa) over anhydrous $H_6P_2W_{18}O_{62}$ at different water content in gas phase.

vapours are ethyl-*tert*-butyl ether and *tert*-butyl alcohol. The steady state of reaction could be reached in about 30 min or less, and the activity of the catalyst was stable over the whole runs lasting 150 min and up to 350 min in some other experiments. The only exception was the run carried out at the highest applied water vapour pressure (8.8 kPa) the initial isobutene conversion 2.5% dropped after 60 min to a stable level of 0.6%. At the conditions of the experiment presented in Fig. 1b the selectivity to ETBE was 80.3% and that to TBA 19.7%.

Figs. 2–5 show that the plots of $\ln(r_{IB})$ and $\ln(r_{ETBE})$ versus $\ln(p_{EtOH})$ and $\ln(p_{IB})$ are linear and hence the dependence of r_{IB} and r_{ETBE} on partial pressures of ethanol and isobutene can be

expressed by the power equations:

$$r_{IB} = k'_{IB}(p_{EtOH}^*)^{\alpha_1}(p_{IB}^*)^{\beta_1} \quad (3)$$

$$r_{ETBE} = k'_{ETBE}(p_{EtOH}^*)^{\alpha_2}(p_{IB}^*)^{\beta_2} \quad (4)$$

where $p_i^* = p_i/p_0$, p_i is an experimental pressure expressed in Pa and $p_0 = 1.0125 \times 10^5$ Pa. The values of the reaction orders with respect to ethanol (α_1 , α_2) and isobutene (β_1 , β_2) obtained at different partial pressures of water vapour are shown in Table 1 where also the values of reaction orders (α , β) previously obtained [9] at the absence of water vapour are given. It is seen that they practically do not depend on the water pressure. It is striking that reaction orders with respect to isobutene are posi-

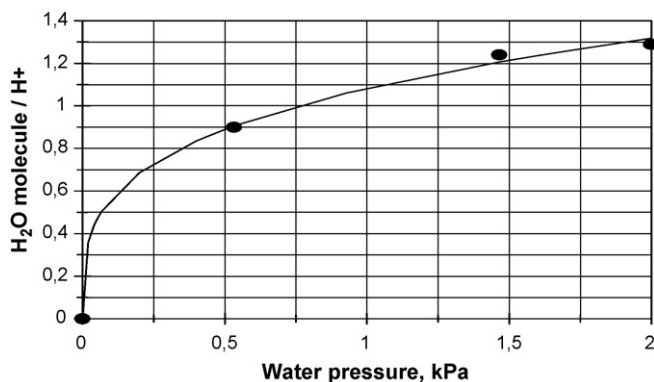


Fig. 10. Isotherm of water sorption on anhydrous Dawson acid at 40 °C (solid line is a fitted curve).

tive thus showing the increase of reaction rate with the isobutene partial pressure. On the other hand the experimental reaction orders with respect to ethanol are negative and the reaction rate decreases with the increasing ethanol partial pressure. It should also be observed that the reaction orders of r_{ETBE} with respect to isobutene and ethanol at the presence of water vapour are the same as in the case of results obtained earlier at the absence of water. This observation strongly suggests that the mechanism of ETBE formation was not changed by the introduction of water vapour into the catalytic system.

However, the reaction rates r_{IB} (Eq. (3)) and r_{ETBE} (Eq. (4)) are influenced by the presence of water and the constant rates k'_{IB} and k'_{ETBE} are the functions $f_i(p_{H_2O})$ of water:

$$k'_{IB} = k_{IB} f_0(p_{H_2O}) \quad (5)$$

$$k'_{ETBE} = k_{ETBE} f_1(p_{H_2O}) \quad (6)$$

Functions $f_i(p_{H_2O})$ have been determined on the basis of the experimental results presented in Fig. 8A:

$$f_0(p_{H_2O}) = 33.38(p_{H_2O}^*)^2 - 13.41 p_{H_2O}^* + 1 \quad (7a)$$

$$f_1(p_{H_2O}) = 84.51(p_{H_2O}^*)^2 - 18.3 p_{H_2O}^* + 1 \quad (7b)$$

Hence the values k'_{IB} and k'_{ETBE} are equalled: $k'_{IB} = k_{IB}(33.38(p_{H_2O}^*)^2 - 13.41 p_{H_2O}^* + 1)$ and $k'_{ETBE} = k_{ETBE}(84.51(p_{H_2O}^*)^2 - 18.3 p_{H_2O}^* + 1)$. The final empirical equations are obtained:

$$r_{IB} = k_{IB}(p_{EtOH}^*)^{-1.71}(p_{IB}^*)^{1.91}(33.38(p_{H_2O}^*)^2 - 13.41 p_{H_2O}^* + 1) \quad (8)$$

(correlation coefficient 0.996)

$$r_{ETBE} = k_{ETBE}(p_{EtOH}^*)^{-2.05}(p_{IB}^*)^{1.91}(84.51(p_{H_2O}^*)^2 - 18.3 p_{H_2O}^* + 1) \quad (9)$$

(correlation coefficient 0.996).

Fig. 8A shows that r_{ETBE} (curves b and b') decreased monotonically with p_{H_2O} . Within the range of experimental conditions (at $p_{EtOH} = 17.2$ kPa) the Eq. (9) takes the form:

$$r_{ETBE} = 0.0644(84.51(p_{H_2O}^*)^2 - 18.3 p_{H_2O}^* + 1) \text{ at } p_{IB} = 18.4 \text{ kPa} \quad (10a)$$

$$r_{ETBE} = 0.0213(84.51(p_{H_2O}^*)^2 - 18.3 p_{H_2O}^* + 1) \text{ at } p_{IB} = 10.3 \text{ kPa} \quad (10b)$$

Both Eqs. (10a) and (10b) are of the same shape and differ only by the pre-exponential term.

Similarly as it was calculated for the rate of ETBE synthesis the rate of TBA formation can be described by the following equation:

$$r_{TBA} = k'_{TBA} p_{IB}^{\beta_2} f(p_{H_2O}) \quad (11a)$$

According to the data given in Fig. 6 and Table 1 the rate of TBA synthesis is proportional to $(p_{IB}^*)^{2.16}$:

$$r_{TBA} = k'_{TBA}(p_{IB}^*)^{2.16} f(p_{H_2O}) \quad (11b)$$

Its dependence on water vapour pressure $f(p_{H_2O})$ is presented in Fig. 8A and B (curves c and c'). Using these experimental data the function $f(p_{H_2O})$ could be calculated:

$$f(p_{H_2O}) = 954 p_{H_2O}^* - 0.998 \times 10^4 (p_{H_2O}^*)^2 \quad (12)$$

Hence we can write:

$$r_{TBA} = k'_{TBA}(p_{IB}^*)^{2.16}(954 p_{H_2O}^* - 0.998 \times 10^4 (p_{H_2O}^*)^2) \quad (13)$$

According to Fig. 7 r_{TBA} is a power function of ethanol pressure. Hence value k'_{TBA} in Eq. (13) depends also on the partial pressure of ethanol: $k'_{TBA} = k_{TBA} f(p_{EtOH})$.

Fig. 7 shows that it is power dependence and k'_{TBA} is proportional to $(p_{EtOH}^*)^{-0.56}$. The final form of empirical equation is:

$$r_{TBA} = k_{TBA}(p_{IB}^*)^{2.16}(954 p_{H_2O}^* - 0.998 \times 10^4 (p_{H_2O}^*)^2)(p_{EtOH}^*)^{-0.56} \quad (14)$$

(correlation coefficient 0.998).

Table 1
Experimental reaction orders (correlation coefficients are in parenthesis)

Correlation	Anhydrous system	Water pressure, 3.8 kPa	Water pressure, 5.3 kPa	Average values
$\ln(r_{total}) - \ln(p_{EtOH})$ (Fig. 2)	–	$\alpha_1 = -1.81 \pm 0.12$ (0.992)	$\alpha_1 = -1.61 \pm 0.09$ (0.998)	–1.71
$\ln(r_{ETBE}) - \ln(p_{EtOH})$ (Fig. 4)	$\alpha = -2.00 \pm 0.19^*$ (0.974)	$\alpha_2 = -2.11 \pm 0.24$ (0.990)	$\alpha_2 = -1.99 \pm 0.12$ (0.990)	–2.05
$\ln(r_{TBA}) - \ln(p_{EtOH})$ (Fig. 7)	–	-0.56 ± 0.08 (0.964)	-0.55 ± 0.06 (0.977)	–0.56
$\ln(r_{total}) - \ln(p_{IB})$ (Fig. 3)	–	$\beta_1 = 1.73 \pm 0.05$ (0.998)	$\beta_1 = 2.09 \pm 0.13$ (0.992)	1.91
$\ln(r_{ETBE}) - \ln(p_{IB})$ (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
$\ln(r_{TBA}) - \ln(p_{IB})$ (Fig. 6)	–	$\beta_3 = 2.06 \pm 0.07$ (0.997)	$\beta_3 = 2.37 \pm 0.06$ (0.999)	2.16

* Data taken from the previous publication of the present author [9].

If the pressures are expressed as the standardized pressure $p^* = p/p_0$ the values of rate constants k_{IB} , k_{ETBE} and k_{TBA} are expressed as:

$$k_{IB} = 0.0805 \text{ mol}/(\text{g h}),$$

$$k_{ETBE} = 0.0443 \text{ mol}/(\text{g h}),$$

$$k_{TBA} = 0.00477 \text{ mol}/(\text{g h})$$

The above results clearly show that there exists an interconnection between the rates r_{ETBE} (Eq. (9)) and r_{TBA} (Eq. (14)). Both of them simultaneously depend on the partial pressure of ethanol and water vapour despite the fact that formally only one of the above reagents is necessary to obtain the given product by addition to isobutene.

Another way to show this interconnection is to present and discuss the effect of gas phase composition on the ratio r_{ETBE}/r_{TBA} presented in Fig. 9A–C as the function of partial pressures of ethanol, isobutene and water vapour.

It is seen that r_{ETBE}/r_{TBA} ratio at constant p_{H_2O} and p_{IB} does decrease with the increase of ethanol partial pressure (Fig. 9A). This is the result of the fact that r_{ETBE} (proportional to $p_{EtOH}^{-2.1}$) decreases with ethanol pressure more rapidly than r_{TBA} (proportional to $p_{EtOH}^{-0.56}$).

Similar argument can be proposed in order to explain the observed decrease of r_{ETBE}/r_{TBA} with the increasing p_{H_2O} (Fig. 9C). The rapid changes of r_{ETBE} and relatively small ones of r_{TBA} are clearly seen in Fig. 8 A. The fact that both r_{ETBE} and r_{TBA} exhibit similar dependences on isobutene partial pressure (proportional to $p_{IB}^{1.7 \pm 0.23}$ and $p_{IB}^{2.2 \pm 0.07}$, respectively) explains the result presented in Fig. 9B which shows that within the isobutene pressure range 1.5–25 kPa the r_{ETBE}/r_{TBA} ratio is almost constant. This constancy or very weak dependence may correspond to the situation in which both rates r_{ETBE} and r_{TBA} as related to the unit of the surface completely covered with adsorbed isobutene are approximately constant, and the changes in p_{IB} pressure change only the total coverage of the surface with this adsorbate.

When discussing the catalytic results one cannot avoid the problem of catalyst composition. Its pretreatment was done in such a way as to obtain anhydrous solid heteropolyacid $H_6P_2W_{18}O_{62}$. However, there was the possibility that on contact with water vapour introduced in the feed, it could absorb an amount of water high enough to form a definite crystallohydrate, e.g. $H_6P_2W_{18}O_{62} \cdot 6H_2O$ with a radically different “secondary” structure.

The water vapour sorption isotherm ($c_{H_2O} = 1.08 p_{H_2O}^{0.283} (\text{H}_2\text{O molecules})/\text{H}^+$) obtained at 40 °C for anhydrous $H_6P_2W_{18}O_{62}$ presented in Fig. 10. The value of c_{H_2O} obtained by extrapolation to the highest applied pressure ($p_{H_2O} = 8.8 \text{ kPa}$) is $c_{H_2O} = 1.99 (\text{H}_2\text{O molecules})/\text{H}^+$. It relates to the situation in which no any other adsorbate is present besides water vapour. Also, the isotherm of ethanol sorption on dehydrated $H_6P_2W_{18}O_{62}$ presented in the earlier paper of the present author [9] shows that at $p_{EtOH} = 8.8 \text{ kPa}$ at 40 °C about 2.4 C_2H_5OH molecules per one proton are uptaken at the absence of water vapour. However, both above isotherms

Table 2

Sorption of both ethanol and water by the catalyst during the catalytic reaction at 40 °C in the course of 100 min ($p_{EtOH} = 17.2 \text{ kPa}$ and $p_{IB} = 18.4 \text{ kPa}$)

Conditions of experiment	Sorption of ethanol molecules/DU	Sorption of water molecules/DU
$p_{H_2O} = 3.8 \text{ kPa}$	0.727	Not detected
$p_{H_2O} = 5.3 \text{ kPa}$	0.300	0.009
$p_{H_2O} = 8.8 \text{ kPa}$	0.251	0.398

do not give reliable information concerning the sorption of reagents in the course of catalytic reaction when ethanol and water supplied in the feed are mostly used for synthesis of ETBE and TBA or are passing the reactor without reaction. Hence, in the steady state of the catalytic reaction sorption of reagents, water and ethanol vapours, was expected to be much smaller than in the above independent sorption experiments.

Much more reliable information can be obtained from the mass balance carried out on the basis of chromatographic analysis, i.e. the comparison of the water and ethanol contents in the feed and in the products leaving the reactor. The sorption of both ethanol and water in the course of 100 min of the catalytic run, starting from the moment (5 min) when the sample could be taken for analysis, estimated in this way is characterized by the data presented in Table 2. It is seen that during the catalytic reaction no any appreciable sorption of water vapour was detected (within the experimental error) at $p_{H_2O} = 3.8 \text{ kPa}$. It increased to 0.01 H_2O/DU and 0.40 H_2O/DU (where DU is Dawson anion) at p_{H_2O} equal to 5.3 and 8.8 kPa, respectively. The formation of crystallohydrate phase could not occur and the deviation of the composition of the catalyst was not essential in any of these cases.

It should be observed that at $p_{H_2O} = 3.8 \text{ kPa}$ and 5.3 kPa sorption of ethanol was predominant and only at the highest water content in the feed, 8.8 kPa, sorption of water became higher than that of ethanol.

Let us now compare the above-presented results with the model of the catalytic system in which electrophilic addition of an alcohol to isobutene occurs on a solid heteropolyacid. It was developed for MTBE formation in Ref. [18] and for ETBE in Ref. [9]. It can be now enlarged by including into consideration besides alcohol (in the present case ethanol), also water introduced together with ethanol into the feed, both as the vapours in helium carrier gas. Hence in a parallel reaction two products, ETBE and TBA, are forming.

The present reaction system can be described as follows:

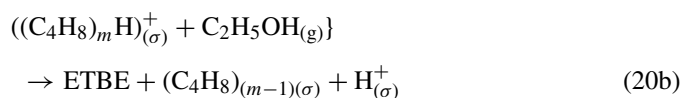
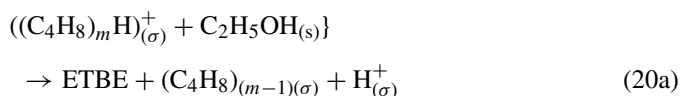
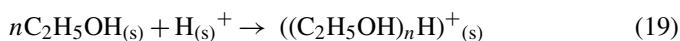
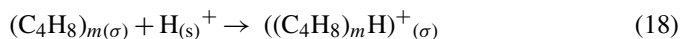
1. The electrophilic addition of ethanol and/or water to isobutene occurs – as it is accepted in organic chemistry – with the formation of carbocation as an intermediate.
2. As it has been shown in Refs. [7] and [9] the non-polar isobutene does not penetrate the bulk of HPA crystallites and remains adsorbed at the surface. It is assumed that it is forming the protonated monomers or oligomers using loosely bonded protons supplied from the bulk of the catalyst.
3. As the earlier experiments show ethanol [19] and water [20] penetrate easily the bulk of HPA crystallites and are forming

the protonated clusters. The formation of protonated ethanol and water molecules has been confirmed by FTIR investigations as, e.g. in Ref. [19].

- In the catalytic system protons contained in the solid HPA are partly forming hydrogen bonds (detected by FTIR investigations [19]) between HPA anions and partly bonded in protonated ethanol and water clusters. Protonation enthalpy of methanol coming from the gas phase in $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ to $\text{CH}_3\text{OH}_{2(\text{s})}^+$ was determined as $-58.9 \text{ kJ mol}^{-1}$ [21]. Similar values can be expected for the formation of protonated ethanol $\text{C}_2\text{H}_5\text{OH}_{2(\text{s})}^+$ in the bulk of $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$.
- As already said protons loosely bonded in the interanionic hydrogen bonds are also used for the formation of carbocations, which are intermediate species in the catalytic reaction. Hence such loosely bonded protons are playing the role of catalytically active centers.
- The catalytic reaction occurs between isobutene carbocations and ethanol and/or water molecules supplied from the bulk (or possibly from the gas phase).

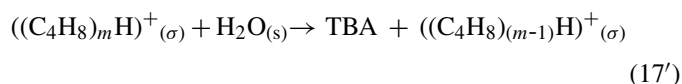
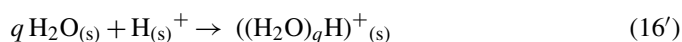
Considering the fact that sorption of ethanol and water on dehydrated heteropolyacid is definitely fast it may be assumed that in the bulk the equilibrium is established between different proton containing species, protons in hydrogen bonds, protonated ethanol and water clusters as well as non-protonated $\text{C}_2\text{H}_5\text{OH}$ and H_2O molecules. The latter are assumed to react with surface carbocations. Hence the role of $\text{C}_2\text{H}_5\text{OH}$ and H_2O molecules absorbed in the bulk appears to be double: when protonated they decrease the concentration of loosely bonded protons, catalytically active, and hence decrease the reaction rate which is reflected in the negative reaction order (ethanol in empirical rate equation for r_{ETBE} , Table 1). On the other hand as non-protonated species they are assumed to be the substrate for ETBE and TBA formation. At concentrations of absorbed water at the pressures lower than 5.3 kPa this effect controlled the rate of TBA formation, r_{TBA} increased with the increase of $p_{\text{H}_2\text{O}}$. At $p_{\text{H}_2\text{O}} > 5.3 \text{ kPa}$ we can expect an increased participation of absorbed water in bonding the protons involved in the formation of interanionic hydrogen bonds. At this situation the retardation of r_{TBA} with the increase $p_{\text{H}_2\text{O}}$ is observed.

In the previous publication [9] in which synthesis of ETBE on $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ catalyst was investigated at the absence of water vapour in the feed and also in the solid HDA in the form of crystal water the following sequence of reactions in catalytic process has been discussed:



where g and s are the molecules in the gas or solid phase, σ the molecule adsorbed at the surface, m the number of isobutene molecules in the surface oligomer and n is the number of ethanol molecules in protonated cluster.

In the present catalytic reaction system one additional substrate, water vapour, and one additional product, TBA, appear and hence, the reactions:



(q is the number of water molecules in protonated cluster) should be taken into account.

In an attempt to deduce theoretical rate equations two possibilities of proposing the rate determining step were chosen. The first one was the same as it was proposed for the system devoid of water: the formation of carbocation reaction (18). Assuming:

$$r_{\text{IB}} = k_{18}[(\text{C}_4\text{H}_8)_m(\sigma)][\text{H}_{(\text{s})}^+] \quad (21)$$

using the virtual equilibrium of reactions (17) and (18) as well as (15') and (16') the equation:

$$r_{\text{IB}} = \gamma p_{\text{IB}}^m p_{\text{EtOH}}^{(-n/2)} p_{\text{H}_2\text{O}}^{(-q/2)} [(C_2H_5OH)_n H_{(\text{s})}^+][(\text{H}_2\text{O})_q H_{(\text{s})}^+]^{1/2} \quad (22)$$

where $\gamma = k_{18} K_{15}^m K_{16}^{(-n/2)} K_{17} K_{(15')}^{(-q/2)} K_{(19+16')}^{(-1/2)}$ was obtained.

As the other possibility as the rate determining step the reaction of carbocation with polar molecules (ethanol and water) supplied from the solid was taken. In such case:

$$r_{\text{IB}} = r_{\text{ETBE}} + r_{\text{TBA}} \quad (23)$$

The values r_{ETBE} and r_{TBA} , reactions (20a) and (17') were calculated starting from the equations:

$$r_{\text{ETBE}} = k_{(20a)} [((\text{C}_4\text{H}_8)_m\text{H}^+(\sigma))][\text{C}_2\text{H}_5\text{OH}_{(\text{s})}] \quad (24)$$

$$r_{\text{TBA}} = k_{(17')} [(\text{C}_4\text{H}_8)_m\text{H}^+(\sigma)][\text{H}_2\text{O}_{(\text{s})}] \quad (25)$$

Assuming the virtual equilibrium of reactions (15)–(19) and (15') and (16') the following kinetic equations were obtained:

$$\begin{aligned} r_{\text{ETBE}} &= \eta p_{\text{IB}}^m p_{\text{EtOH}}^{(1-n/2)} p_{\text{H}_2\text{O}}^{(-q/2)} [(C_2H_5OH)_n H_{(\text{s})}^+][(\text{H}_2\text{O})_q H_{(\text{s})}^+]^{1/2} \\ & \end{aligned} \quad (26)$$

$$\begin{aligned} r_{\text{TBA}} &= \xi p_{\text{IB}}^m p_{\text{EtOH}}^{(-n/2)} p_{\text{H}_2\text{O}}^{(1-q/2)} [(C_2H_5OH)_n H_{(\text{s})}^+][(\text{H}_2\text{O})_q H_{(\text{s})}^+]^{1/2} \\ & \end{aligned} \quad (27)$$

$$\eta = k_{(20a)} K_{15}^m K_{16}^{(1-n/2)} K_{17} K_{18} K_{(15')}^{(-q/2)} K_{(19+16')}^{(-1/2)} \quad \text{and}$$

$$\xi = k_{(17')} K_{16}^{(-n/2)} K_{17}^m K_{18} K_{19} K_{(15')}^{(-q/2)} K_{(19+16')}^{(-1/2)}.$$

In the case of the catalytic system devoid of water previously investigated it could be assumed that $[(C_2H_5OH)_n H^+]_{(s)}$ value was proportional to the total content of ethanol in the solid c_{EtOH} expressed by the Freundlich isotherm of sorption:

$$[(C_2H_5OH)_n H^+]_{(s)} \sim c_{EtOH} = 1.2 p_{EtOH}^{0.3} \quad (28)$$

The above discussion concerning the content of H_2O and C_2H_5OH in the catalyst during the catalytic reaction indicates that similar substitution cannot be done and hence such comparison of the above results with the experimental results is at present not possible. Also the effect of the term $([(C_2H_5OH)_n H^+]_{(s)} [(H_2O)_q H^+]_{(s)})^{1/2}$ in which $[(C_2H_5OH)_n H^+]_{(s)}$ and $[(H_2O)_q H^+]_{(s)}$ values depend on the partial pressure of ethanol and water cannot be estimated based on the present results.

It should be observed that in the case of an analogous reaction, formation of MTBE by methanol addition to isobutene on an acid resin [15] the Langmuir–Hinshelwood–Hougen–Watson approach was applied and this enabled to calculate reaction parameters. However, the application of this latter approach to the interpretation of the present results would be only strictly formal as LHHW approach assumes that adsorption of the reactants obeys Langmuir adsorption isotherm which concerns only with the surface sorption and does not take into account the possibility of simultaneous surface and volume sorption, the fact well-confirmed by the presented experimental results.

5. Conclusions

1. At the presence of water vapour in the feed, *tert*-butyl alcohol (TBA) is forming besides ethyl-*tert*-butyl ether (ETBE), which, up to $p_{H_2O} = 8.8$ kPa, is the main product. The rate of ETBE formation, r_{ETBE} , depends not only of the partial pressures of isobutene and ethanol but also on that of water vapour, which formally does not participate in ETBE formation. Similarly the rate of TBA formation, r_{TBA} depends not only on the partial pressures of isobutene but also that of ethanol.
2. Empirical rate equations were formulated in which both r_{ETBE} and r_{TBA} exhibit exponential dependence on isobutene and ethanol partial pressures. However, while the reaction rates with respect to isobutene are positive and the rates increase with p_{C_4} , reaction orders with respect to ethanol are negative and the rates decrease with the increase of p_{EtOH} . The dependence of the rates on water vapour content is complicated and cannot be represented by a simple function.
3. The experimental results can be explained qualitatively based on the model of the catalytic system in which protonated isobutene molecules, intermediate species of catalytic reaction, remain at the surface of heteropolyacid crystallites and react with C_2H_5OH and/or H_2O molecules supplied from

the bulk or from the gas phase. Polar ethanol and water molecules penetrate the bulk of the solid and get partially protonated by the protons loosely bonded in the interanionic hydrogen bonds. In the bulk an equilibrium is established between protons in the hydrogen bonds and protonated as well as not protonated C_2H_5OH and H_2O molecules. This equilibrium determines the concentration of loosely bonded protons considered to be catalytically active centers.

4. An attempt to obtain theoretical rate equations similar to those obtained previously and adequately representing experimental results has not been successful, owing to the complicated dependence of the simultaneous sorption of ethanol and water vapour by the catalyst on the composition of the gas phase.

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