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Gas phase synthesis of MTBE on dodecatungstosilicic acid as the catalyst

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Abstract

Catalytic synthesis of methyl-*tert*-butyl ether (MTBE) in gas phase on solid $H_4SiW_{12}O_{40}$ was studied at 40 and 80°C using differential constant flow reactor. Independently sorption of substrates, methanol and isobutene, as well as the product MTBE was studied using sorption balance. From the fact that methanol was easily sorbed by the whole volume of the solid (depending on pressure its uptake at 40°C reached up to 12 CH_3OH molecules per 1 Keggin unit (KU)) while isobutene remained only adsorbed at the surface of heteropolyacid both pristine and saturated with methanol it was concluded that catalytic reaction occurs at the surface of $H_4SiW_{12}O_{40}$ and reaction scheme has been proposed including the formation of *tert*-butyl carbenium ion with the participation of protons supplied by the catalyst. The assumption that reaction of this carbocation with methanol supplied also from the bulk or next-to-surface layer is the rate determining step led to the kinetic equations enabling to interpret the observed negative reaction order with respect to methanol at the steady state at 40°C but about one at initial period of the run. Reaction was characterised by the apparent activation energy as low as 25 kJ mol^{-1}. At 80°C reaction order with respect to isobutene was one but that with respect to methanol decreased to about 0.5 indicating that reaction was diffusion controlled. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Heteropolyacids; Methyl-*tert*-butyl ether; MTBE

1. Introduction

Methyl-*tert*-butyl ether (MTBE) is widely used as octane booster in automotive fuel enabling to reduce the use of tetraethyl lead which is a well known environment poison. It is obtained commercially by the reaction of 2-methylpropene (isobutene) with methanol in the liquid phase at 90–100°C under the pressure about 1.5 MPa. As the catalyst macroreticular cation-

exchanged sulfonic resin of the type of Amberlyst-15 is used. However, this catalyst becomes unstable above 90°C and releases sulfonic and sulfuric acids inducing corrosion of industrial installation.

These circumstances stimulate research aiming to obtain new less troublesome catalysts for MTBE synthesis. As the typical acid catalysts necessary for this reaction zeolites [1–3], modified zeolites [4–6] as well as silicalites [7] were investigated as the catalysts acting in the gas phase reaction. The catalytic properties of Ag,

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Cu and Al salts of heteropolyacids (HPA) were studied in Ref. [8]. The Ag and Cu salts initially only weakly active became after pretreatment in hydrogen at 573 K, nearly as active as their parent acids $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$. The same authors have shown that the activity of the same heteropolyacids is markedly enhanced if they are supported on Amberlyst-15 resin [9]. MTBE formation of isobutene and methanol in the liquid phase using heteropolyacids of different composition and structure was described in Ref. [10]. The highest activity per one proton was exhibited by heteropolyacids of Dawson structure $H_6P_2W_{18}O_{62}$ and $H_6P_2Mo_{18}O_{62}$ which appeared to be more effective than dodeca-heteropolyacids of Keggin structure. The superiority of $H_6P_2W_{18}O_{62}$ over $H_nXW_{12}O_{40}$ (X = P, Si, Ge, B and Co) in the case of gas phase catalytic reaction was confirmed in Ref. [11]. In this paper, a unique pressure dependence of reaction rate on the methanol vapour pressure was observed. On increasing this pressure the reaction rate at first increases but above a certain value depending on the kind of HPA it decreases systematically. This behaviour was interpreted as being due to the fact that at higher pressures methanol penetrating the bulk of HPA crystallites is forming protonated oligomers $(CH_3OH)_nH^+$ ($n > 3$) which—in contrast to the protonated monomers $CH_3OH_2^+$—are non-active in the catalytic reaction. The authors suggest that at the presence of methanol in the bulk of HPA crystallites the non-polar isobutene molecules may also penetrate the bulk and the formation of MTBE occurs in the so called pseudo-liquid phase.

The aim of the present research was to study MTBE formation from isobutene and methanol in the gas phase on the example of $H_4SiW_{12}O_{40}$ catalyst and to compare the catalytic results with those of the separate measurements of the sorption of isobutene, methanol and methyl-*tert*-butyl ether by anhydrous heteropolyacid. It was also expected that further information concerning the sorption of reagents in the course of catalytic reaction will be obtained by calculating

the mass balance. In the present paper an attempt to formulate a model of catalytic reaction will also be undertaken. The effects of contact time and the isobutene/methanol molar ratio in the feed will be presented and discussed in the next publication.

2. Experimental

2.1. Materials

Powdered crystalline dodecatungstosilicic acid ($H_4SiW_{12}O_{40} \cdot 24.8$ H_2O, p.a. Fluka) dehydrated in situ in the catalytic reactor at 200°C for 30 min in a current of helium gas was used as the catalyst. It has been shown previously [12] that after the departure of the water of crystallisation no dehydroxylation occurs at this temperature. BET surface area of the dehydrated product was 8 m^2 g^{-1}. The photographs taken in electron scanning microscope (magnification 5000 ×) have shown its high porosity. The hydrated heteropolyacid on loosing water molecules disintegrates into small blocks of the order of some tens of μm separated by crevasses the width of which is of the order of several tenth of μm. The micrograph also shows that the blocks are porous the width of the crevasses being at least 1 order of magnitude lower. The surface area of the patches corresponding to the pores in the micrograph is about 6–7% of the total surface of the sample visible on a given picture. Methyl alcohol (CH_3OH) (p.a.) and 2-methylpropene (isobutene, C_4H_8) (p.a. Aldrich) were used as reaction substrates.

2.2. Apparatus

Constant flow quartz microreactor was used for the catalytic experiments. Helium carrier gas was at first saturated with methanol vapours and subsequently mixed with a current of 2-methyl-propene taken from the steel cylinder through the pressure regulator. The composition of the

reaction mixture was fixed at the isobutene/methanol molar ratio R 0.03–2.54 by changing the temperature of saturator filled with methanol and/or changing the intensity of isobutene flow. Catalytic reactor was connected on line with Hewlett-Packard 6980 Ser. II A gas chromatograph. Porapak QS filled column was used for chromatographic analyses. The experiments with 0.1 g sample were carried out at 40°C and 80°C.

Independent sorption experiments of the substrates and product were carried out using a quartz spring sorption balance (sensitivity 0.7 mm/1 mg) and 50-mg sample. Prior to the sorption experiments catalyst samples were dehydrated at 240°C at constant pumping the system and then cooled to temperature at which subsequently sorption experiments were carried out.

3. Results

The main product of the catalytic reaction at 40°C and 80°C was methyl-*tert*-butyl ether (MTBE). At 80°C, small amounts of isobutene dimer could be detected. Conversion of isobutene to dimer never exceeded 0.5% although in most cases it was 0.2–0.3%. At higher temperature and excess of methanol the formation of dimethyl ether (DME) should also be taken into account. Owing to very much similar retention times of DME and methanol it was not possible to detect chromatographically DME in our conditions. However at 80°C and C_4H_8/CH_3OH ratio equal to 0.6 or higher the small increase of the peak signalling the presence of traces of water in the substrates was observed and this could be interpreted as product of methanol dehydration to DME. It should
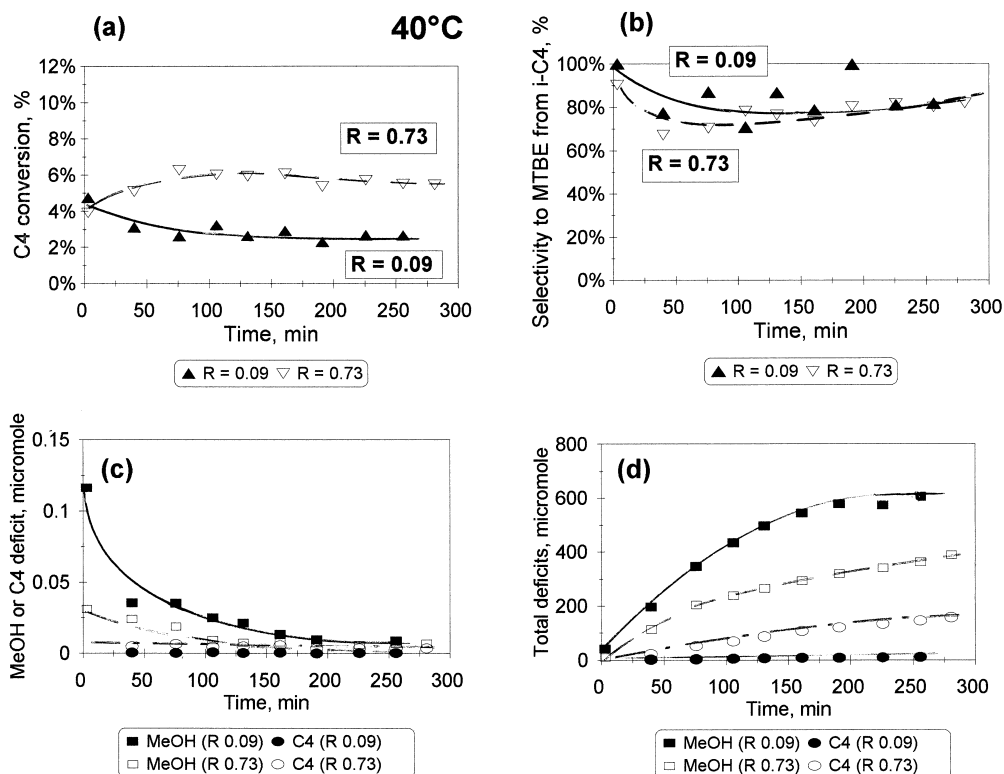

Fig. 1. Typical examples of catalytic runs at 40°C: (a) isobutene conversion, (b) selectivity, (c) deficit of methanol (squares) and isobutene (ovals) and (d) accumulated deficit of methanol (squares) and isobutene (ovals). (Run 53, $R = p_{C_4H_8}/p_{CH_3OH} = 0.09$; run 44, $R = 0.73$).

be mentioned here that Highfield and Moffat [13], observed slow formation of DME over $H_3PW_{12}O_{40}$ in a batch reactor. At 60°C, the methanol conversion to DME was 2% after 60 min. At 80°C it was 7% in 15 min. Considering the much shorter contact time in our constant flow reactor, only the formation of minor quantities of DME in our conditions was possible. This has been confirmed by mass-spectroscopic analysis of the effluent gases in one experiment carried out by us at 80°C. No quantitative analysis has been done but considering the ratio of DME and unreacted methanol one could conclude that the content of DME was lower than 0.4%.

Figs. 1 and 2 show some examples of the catalytic runs at 40 and 80°C. It is seen that three types of conversion vs. time curves were obtained. Most frequently conversion of isobutene was the highest initially and in the

course of 40–100 min reached a new lower level which was constant during the rest of the catalytic run usually lasting 6 h (Fig. 1a, $R = 0.09$). The initial decrease of the activity was much more pronounced at 40°C than at 80°C. The second type of the conversion vs. time curves characterised by increasing activity in the initial period of the run (Fig. 1a, $R = 0.73$) was observed at 40°C when in a series of experiments in which partial pressure of isobutene was kept constant (8.00 kPa) and that of methanol increased in consecutive runs. The initial increase in the activity was observed only at 40°C in the runs in which R was 0.64 and 0.73 at p_{CH_3OH} equal to 5.22 kPa (no experiments were carried out with higher R value and the same methanol partial pressure). The third type of conversion vs. time curves with practically constant activity was observed only at 80°C at R between 0.6 and 1.14 (at $p_{C_4H_8}$
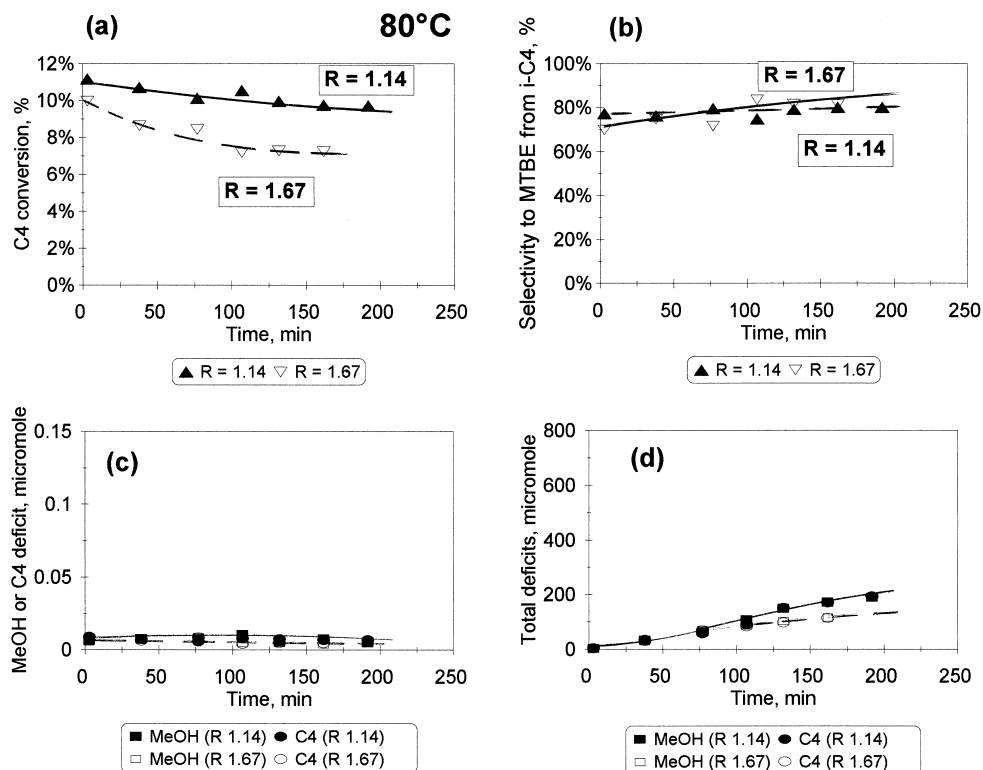

Fig. 2. Typical examples of catalytic runs at 80°C: (a) isobutene conversion, (b) selectivity, (c) deficit of methanol (squares) and isobutene (ovals) and (d) accumulated deficit of methanol (squares) and isobutene (ovals). (Run 38, $R = p_{C_4H_8}/p_{CH_3OH} = 1.14$; run 41, $R = 1.67$).

constant and equal to 5.1 kPa) (Fig. 2a, $R =$ 1.14).

The initial selectivity of MTBE formation from isobutene was close to 100% at 40°C but in the steady state of catalytic activity it decreased to 60–85%. At 80°C it was somewhat higher, between 75 and 90%, and practically the same all over the run.

Mass balance calculated from particular chromatographic analyses indicated a certain deficit of both methanol and isobutene. As Figs. 1 and 2 show the deficit of methanol as calculated for one portion of gas taken for the chromatographic analysis (0.25 ml) was the highest at the beginning of the run and then strongly decreased. Most frequently it was higher than that of isobutene evidently due to the fact that polar molecules of methanol can penetrate the bulk of HPA crystallites while not polar isobutene may only be adsorbed on their external surface. The value of deficit determined from one portion of effluent gases taken for the chromatographic analysis divided by the time needed by this volume of gases to pass catalyst bed gives the rate of the deficit production (similarly the rate of MTBE formation may be obtained). By the numerical integration of the curve expressing

this rate as the function of the time the total amount of methanol (or isobutene) remaining at the catalyst can be calculated. It will be named the accumulated deficit (AD). Examples of the graphs showing the increase of the accumulated deficit with time of run are shown in Figs. 1 and 2.

Considering the fact that no other products than the already mentioned were detected one has to assume that the observed deficit is due to the accumulation of substrates or products at the surface or in the bulk of HPA crystallites. This is why in separate experiments the interaction of methanol, isobutene and MTBE with the catalyst was studied using spring sorption balance.

Sorption of methanol by crystalline dodecatungstosilicic acid was investigated at 22, 40 and 80°C. For each run a fresh sample of 50 mg has been taken and dehydrated in situ at 240°C at constant pumping the apparatus. Sorption has been carried out at constant pressure of methanol vapour and after it completely ceased reaching an equilibrium the desorption run has been started by pumping off the system without changing the temperature. The examples of the runs carried out at 40°C are shown in Fig. 3 and the results obtained at different temperatures are
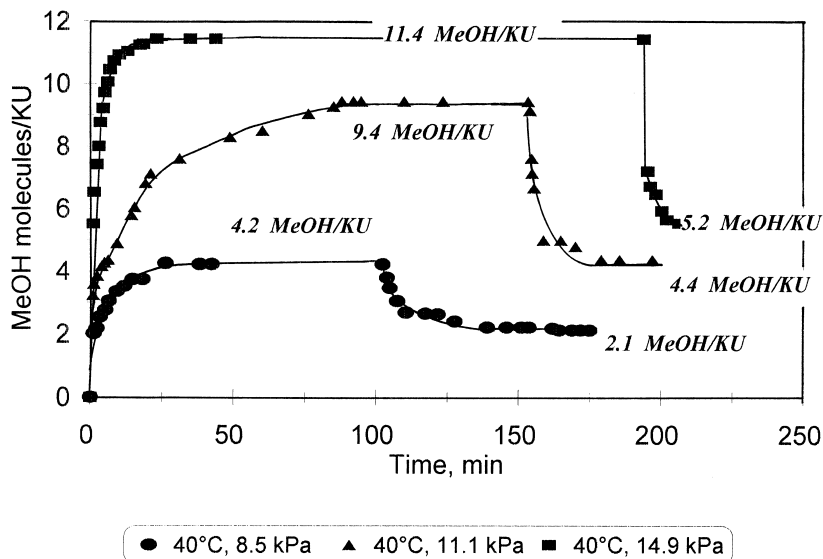

Fig. 3. Sorption and desorption of methanol by $H_4SiW_{12}O_{40}$ at 40°C carried out at different methanol pressures.

Table 1
Sorption of methanol by dehydrated $H_4SiW_{12}O_{40}$

Temperature (°C)	CH_3OH vapour pressure (kPa)	Composition of the sample			
		After sorption		After desorption	
		CH_3OH moles/KU)	Number of monolayers	CH_3OH moles/KU	Number of monolayers
22	8.53	16.1	69	5.8	25
	8.53	16.7	72	7.3	32
	8.53	16.3	70	6.9	30
40	8.53	4.2	18	2.1	9
	11.0	9.4	40	4.4	19
	14.9	11.4	49	5.2	22
80	8.53	1.33	6	−	−
	9.31	1.85	8	0	0

listed in Table 1. The amounts of sorbed methanol are expressed as the number of moles of CH_3OH per 1 Keggin unit (KU) and also as the corresponding number of monolayers (calculated under the assumption that specific surface area of the sorbent is 8 m^2 g^{-1} and the surface occupied by one CH_3OH molecule 1.65×10^{-19} m^2, which corresponds to the same packing as in the liquid methanol).

Sorption of isobutene on $H_4SiW_{12}O_{40}$ at 22°C and 8.53 kPa was very much weaker than that of methanol and only 0.34 C_4H_8/KU were taken up from which on evacuation 0.17 C_4H_8 molecules per KU remained. These values corresponded to 0.15 and 0.07 of isobutene monolayer thus indicating adsorption of C_4H_8 only on the external surface of the catalyst. At 80°C sorption of isobutene reached 0.28 C_4H_8 molecules per KU corresponding to 0.12 of monolayer. However, it has been recently suggested in Ref. [11] that sorption of isobutene may be enhanced by presorption of methanol. In
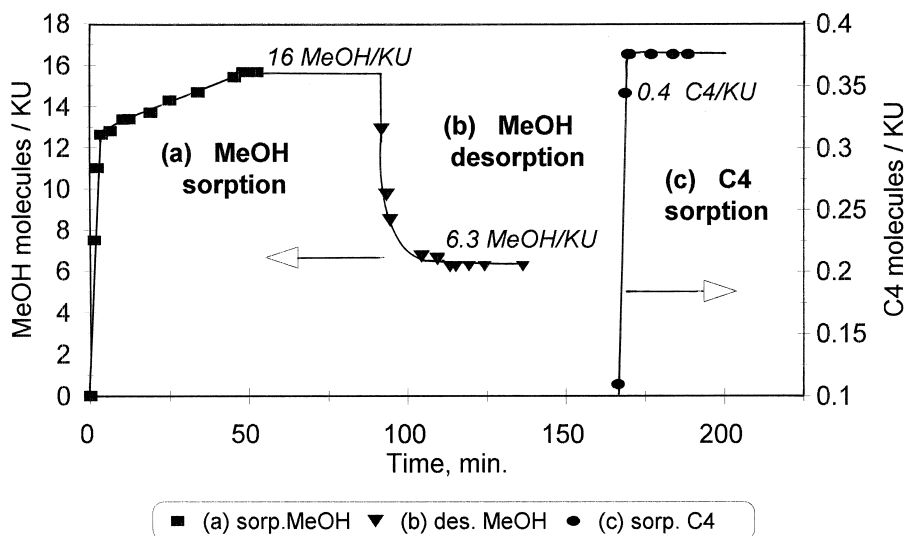

Fig. 4. Sorption of isobutene by $H_4SiW_{12}O_{40}$ at 22°C (c) after preadsorption of irreversibly bonded methanol (a and b).
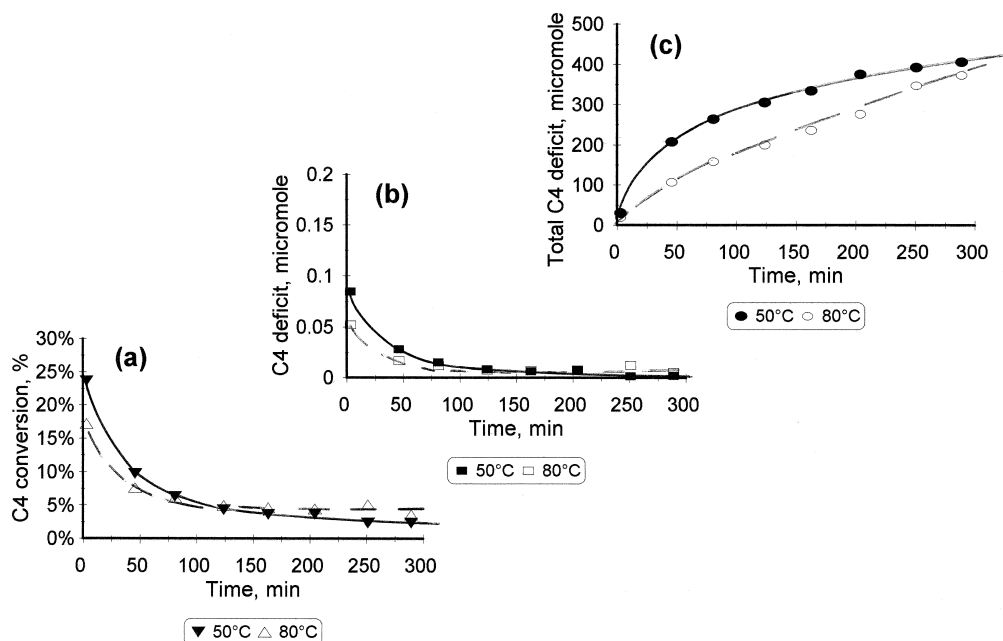
Fig. 5. The examples of the catalytic conversion of pure isobutene at 50°C and 80°C; (a) isobutene conversion (%), (b) deficit of isobutene (μmol sample^{-1}), (c) accumulated isobutene deficit (μmol sample^{-1}).

order to verify this suggestion we carried out an experiment the results of which are shown in Fig. 4.

Methanol was sorbed at 22°C and 8.5 kPa (Fig. 4a) and desorbed (b) thus giving the product containing 6.3 molecules CH_3OH/KU irreversibly sorbed. The subsequent uptake of isobutene (c) 0.4 C_4H_8/KU was within the experimental error the same as in the experiments without methanol preadsorption.

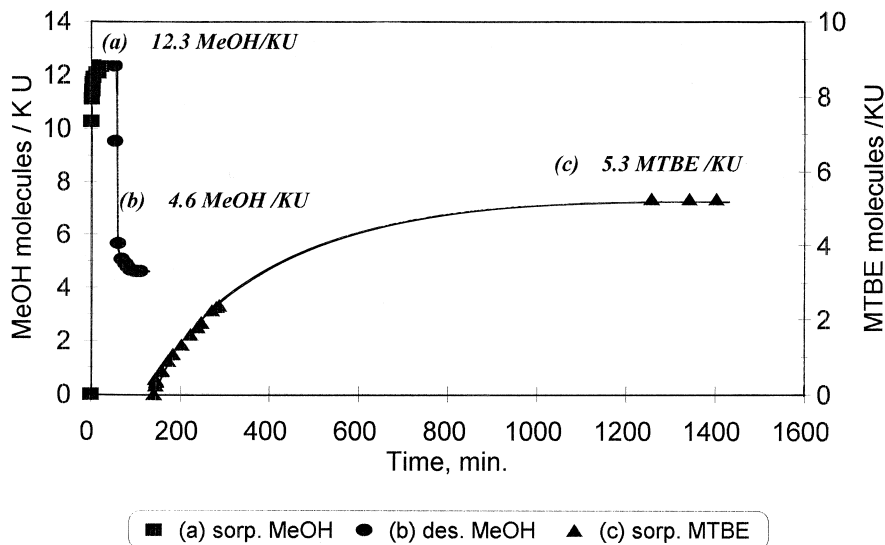Fig. 6. Sorption of MTBE by $H_4SiW_{12}O_{40}$ at 24°C (c) after preadsorption of irreversibly bonded methanol (a and b).

(a) initial state

R= 0.56
R= 0.43
R= 0.49
R= 0.73
R= 0.64

ln r

ln (p MeOH)

(b) steady state

R= 0.64
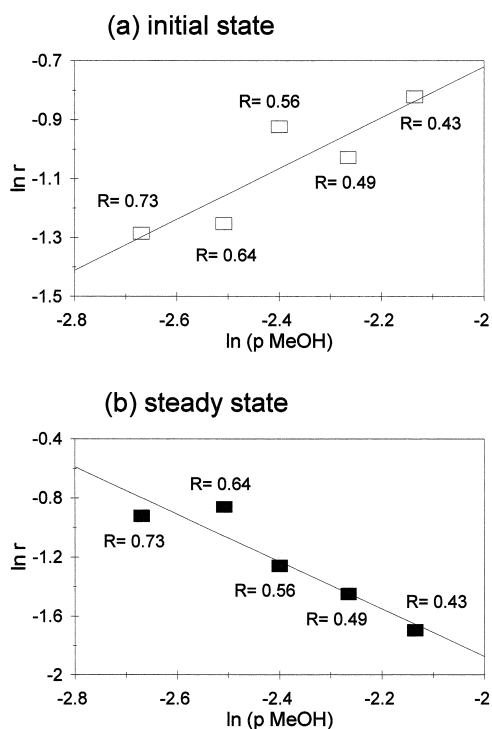R= 0.73
R= 0.56
R= 0.43
R= 0.49

ln r

ln (p MeOH)

Fig. 7. Logarithmic plots of rate of isobutene conversion at 40°C vs. methanol partial pressure, (a) initial period of the run, (b) steady state of the reaction.

Considering the tendency of olefins to oligomerize the experiments were also carried out in the catalytic reactor in which the amount of dehydrated $H_4SiW_{12}O_{40}$ was four time larger than in sorption experiments (0.2 g) and the run lasted 6 h. Isobutene partial pressure was 1.2 kPa in helium used as carrier gas. The only product detected at 80°C in the gas phase was isobutene dimer. The initial conversion 17% (Fig. 5) decreased in the course about 100 min to a constant level of 5%. However, selectivity was as low as about 25%. The rest of disappearing isobutene remained at the catalyst as it was indicated by the deficit in the mass balance (initial 0.099 μmol sample^{-1} and about 0.02 μmol sample^{-1} in the steady state) which was somewhat higher than that observed when at the same conditions of temperature and isobutene partial pressure the latter reacted with methanol at $p_{CH_3OH} = 9.98$ kPa (initial 0.051 mmol sample^{-1} and 0.016 mmol sample^{-1} at the steady

state). Considering the fact that no penetration of isobutene molecules into the bulk of HPA crystallites occurs we attributed the appearance of deficit to the formation of oligomers at the catalyst's surface in both cases. Darkening of the sample indicated the formation of coke.

Sorption of MTBE was investigated in the sorption balance at $p_{MTBE} = 8.6$ kPa. It was fast and in the course of 5–15 min reached a constant level of 0.95 at 22°C and 0.086 MTBE molecules per KU at 80°C which corresponded to 7–8 monolayers, respectively. Sorption was almost completely reversible at 80°C but at 22°C, roughly one third of adsorbed molecules remained at the catalyst.

In contrast to the case of isobutene the sorption of MTBE was distinctly enhanced by methanol preadsorption.

Fig. 6 shows that at 24°C and 8.6 kPa 12.3 molecules CH_3OH per KU were sorbed. After pumping off the system 4.6 molecules CH_3OH

(a) initial state

R= 0.21
R= 0.12
R= 0.18
R= 0.15
R= 0.09

ln r

ln (p C4)

(b) steady state

R= 0.21
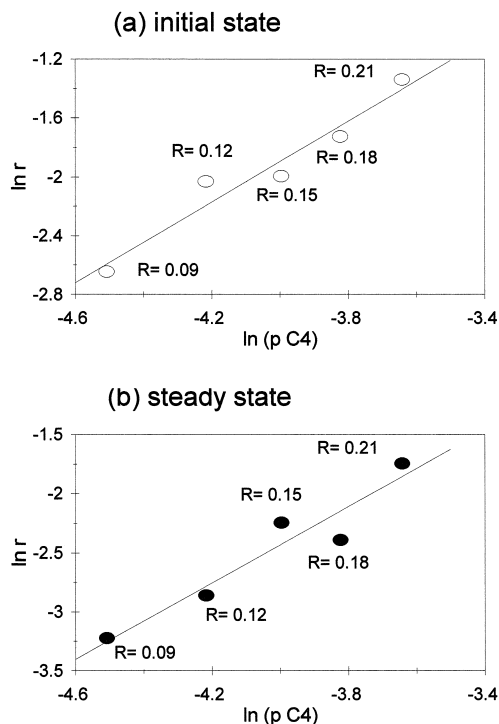R= 0.15
R= 0.18
R= 0.12
R= 0.09

ln r

ln (p C4)

Fig. 8. Logarithmic plots of rate of isobutene conversion at 40°C vs. isobutene partial pressure, (a) initial period of the run, (b) steady state of the reaction.

Table 2
Reaction orders

Temperature	Reaction order		
		Value	Correlation coefficient
With respect to CH_3OH			
40°C	initial	0.86 ± 0.26	0.7831
	steady state	-1.61 ± 0.33	0.8856
With respect to C_4H_8			
40°C	initial	1.38 ± 0.19	0.9461
	steady state	1.62 ± 0.28	0.9136
With respect to CH_3OH			
80°C	initial	0.44 ± 0.06	0.9043
	steady state	0.40 ± 0.06	0.9020
With respect to C_4H_8			
80°C	initial	0.97 ± 0.05	0.9853
	steady state	0.94 ± 0.14	0.9027

per KU remained. Subsequent sorption of MTBE (8.5 kPa) was much slower than that carried without preadsorption but the final uptake corresponded to 5.3 molecules MTBE per KU. At 80°C the sample containing 1 molecule CH_3OH per KU took up 1.8 molecules MTBE per KU.

Two series of experiments aiming to determine reaction order were carried out at 40 and 80°C. In one of them, the partial pressure of isobutene was constant and equal to 5.17 kPa while that of methanol vapours changed in particular experiments from 7 to 12 kPa.

In the second series, the partial pressure of methanol was kept constant and equal to 12.7 kPa while that of isobutene varied from 1.11 to 2.63 kPa. Figs. 7 and 8 show in the logarithmic scales the dependence of the initial and steady state isobutene conversion rate (μmol g^{-1} s^{-1}) on the partial pressure of methanol and that of isobutene. From the slope of the linear graphs reaction orders vs. methanol and isobutene were calculated. They are given in Table 2.

4. Discussion

Any discussion of the mechanism of MTBE formation on crystalline HPA—in our case

$H_4SiW_{12}O_{40}$—has to take into account the behaviour of the particular reagents at the contact with the catalyst. This has been studied in the present research gravimetrically using the sorption balance.

Polar molecules of methanol, similarly as the molecules of other alcohols, are known to penetrate the bulk of dodecaheteropolyacid crystallites forming so called pseudo-liquid phase [14], Highfield and Moffat [13] in their PAS–FTIR investigation have shown that methanol irreversibly bonded on $H_3PW_{12}O_{40}$ interacts strongly with protons contained in HPA forming protonated species $CH_3OH_2^+$ the presence of which must be assumed also in our case. They seem to be predominant species at 40°C and $p_{CH_3OH} = 8.61$ kPa when in the average 1.05 methanol molecules are sorbed per one proton (Table 1). This sorption is partly reversible and on pumping off the system still one methanol molecule remains in the solid per two protons. It may be suggested that in this latter case each methanol molecule is bonded by two hydrogen bonds to two neighbouring Keggin units:
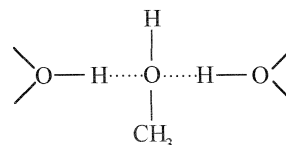
At the same temperature and $p_{CH_3OH} = 11$ kPa in the average 2.35 CH_3OH molecules correspond to one proton indicating the formation of protonated dimer $(CH_3OH)_2H^+$ the species the presence of which in $H_3PW_{12}O_{40}$ was proved by Lee et al. [15,16]. Similarly the predominant formation of $(CH_3OH)_3H^+$ trimer at 40°C and 14.9 kPa as well as $(CH_3OH)_4H^+$ tetramer at 40°C and 8.53 kPa seems very much probable.

The comparison of the graphs (a) in Fig. 1 representing isobutene conversion in the course of catalytic run with the graphs (d) representing the growth of the accumulated methanol deficit

indicates that despite the fact that steady state of catalytic reaction was reached after some 70 min the sorption of methanol was not brought to a standstill at the same time. In the case of sample $R = 0.09$ the saturation of solid with methanol was reached after 200 min and in that of sample $R = 0.73$ it was not reached even after 6 h.

At the steady state of catalytic reaction the concentration of the adsorbed isobutene at the surface as well as that of methanol and protons in the next-to-surface layer must be constant. However, continuation of methanol sorption indicates that the equilibrium exists only between methanol in the gas phase and methanol in the next-to-surface layer but there is no equilibrium between methanol in the bulk of HPA crystallites.

In contrast to methanol, the uptake of non-polar isobutene was very weak and the coverage observed at 8.53 kPa (the pressure of the similar order as it has been used in the catalytic experiments) at 22 and 80°C corresponded only to 0.148 and 0.074 of monolayer, respectively. This indicates that no penetration of isobutene into the bulk of HPA crystallites occurred. However, in the catalytic experiments certain deficit of isobutene was observed although in most cases very much lower than that of methanol (the exceptions will be discussed later). It was attributed to the formation of oligomers which at higher temperatures transform into carbonaceous deposit, coke, which results in darkening of catalysts, observed by us in sorption experiments at 250°C. The suggestion of Shikata et al. [11] that sorption of methanol enhances the penetration of isobutene into the bulk of HPA crystallites was not confirmed in our experiments. As Fig. 4 shows 0.05 g sample of $H_4SiW_{12}O_{40}$ containing irreversibly bonded about 6 molecules of CH_3OH per one KU adsorbed at room temperature 0.38 C_4H_8/KU which is very much similar to 0.34 C_4H_8/KU observed when sorption was carried out on the pristine dehydrated sample. The enhancement of isobutene sorption by methanol was also not

observed at 80°C. All these facts justify the conclusion that the catalytic formation of MTBE occurs only on the external surface of $H_4SiW_{12}O_{40}$ crystallites or in their next-to-surface layers.

As already mentioned in Section 3, the sorption of MTBE on pristine dehydrated $H_4SiW_{12}O_{40}$ sample is much more limited than that of methanol. At 22 and 80°C ($p_{MTBE} = 8.53$ kPa), it approaches to one molecule per KU. Only 30% of this amount is bonded irreversibly at 22°C and less than 5% at 80°C. Weaker bonding is evidently due to the lower dipole moment. Steric factor may also be important hindrance in the bulk diffusion. However, in contrast to isobutene the sorption of MTBE is strongly enhanced by presorption of methanol. In the experiments described in the precedent section the increase in sorption of MTBE due to presorption of methanol was about 5-fold at room temperature and it doubled at 80°C. Sorption of MTBE may be one of the reasons of appearance of deficit in mass balance of the catalytic runs.
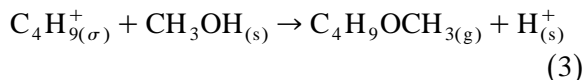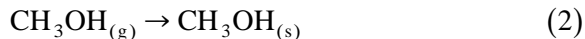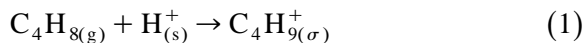
Information concerning the interaction of reagents with the catalyst in the course of catalytic reaction was also obtained by calculating the mass balance from the results of particular chromatographic analyses. Fig. 1c shows that the deficit of methanol at 40°C was always much higher than that of isobutene which justifies the conclusion that sorption of methyl-*tert*-butyl ether was unimportant and methanol penetrated the HPA crystal lattice without transformation changing its composition while small deficit of isobutene was mainly due to its adsorption and formation of oligomers. Methanol deficit decreased with time and hence the total amount of missing methanol tended to reach a constant level as it is shown in Fig. 1d. In the case of run $R = 0.09$ at 40°C, this value corresponded to the uptake of about 16.5 moles CH_3OH per 1 KU. The value comparable to values reached during independent sorption experiments (Table 1). Sorption of methanol in the case of run $R = 0.73$ at same temperature in

which methanol partial pressure in the feed was twice as lower did not reach full saturation in the course of run lasting 6 h but after this time composition of catalyst corresponded to the formula $H_4SiW_{12}O_{40}$ 3.3 CH_3OH. Different results were obtained at 80°C. In most cases molar ratio of deficit of methanol and isobutene was close to one which indicated that it was the reaction product methyl-*tert*-butyl ether which remained in the catalyst. At the moment when run $R = 1.14$ (190 min) has been interrupted (Fig. 2d) the composition of the catalyst sample corresponded to the formula $H_4SiW_{12}O_{40}$ 5.47 MTBE and in the case of $R = 1.67$ run (116 min) to $H_4SiW_{12}O_{40}$ 3.3 MTBE.

Let us now discuss the possible mechanism and kinetics of MTBE formation. MTBE synthesis from isobutene and methanol similarly as the formation of *tert*-butyl alcohol from isobutene and water belongs to the class of reactions classified as electrophilic addition. It is generally accepted that carbocation forming e.g. on Brönsted acid sites is involved in the rate determining step. In our case this will be *tert*-butyl carbenium ion reacting subsequently with methanol molecule. The peculiarity of this reaction occurring on crystalline heteropolyacids as catalysts is the fact that one reagent, isobutene, remains only at the surface of crystallites as adsorbed species while the other one, methanol, penetrates their bulk. Also protons are supplied from the bulk. Protons forming hydrogen bonds between Keggin units in the dehydrated HPA and relatively loosely bonded, called here 'free protons', may be trapped by methanol molecules penetrating the solid and thus forming protonated monomers or protonated clusters. Basing on the above described experiments it may be assumed that equilibria between methanol in gas phase and methanol in the next-to-surface layer are establishing relatively fast and that there is also fast equilibrium between free protons and methanol molecules in this layer.

Reaction scheme on the basis of which we propose to interpret our kinetic results must comprise—at least—the following steps:

$$C_4H_{8(g)} + H^+_{(s)} \rightarrow C_4H^+_{9(\sigma)} \tag{1}$$

$$CH_3OH_{(g)} \rightarrow CH_3OH_{(s)} \tag{2}$$

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

where: g and s—molecules in the gas or solid phase, σ—molecules adsorbed at the surface,

$$nCH_3OH_{(s)} + H^+_{(s)} \rightleftarrows (CH_3OH)_nH^+_{(s)} \tag{4}$$
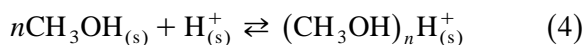
Eq. (4) comprises in fact a series of equations with different integral values of n. In the further discussion we shall use the overall equilibrium formula

$$K_4 = \frac{\left[(CH_3OH)_nH^+_{(s)}\right]}{\left[CH_3OH_{(s)}\right]^n\left[H^+_{(s)}\right]} \tag{5}$$

($[H^+_{(s)}]$ is concentration of free protons in the solid) assuming that integral value of n approximates the state in which a protonated cluster with n methanol molecules predominates and the fractional value of n will indicate the predominance of two clusters differing in n by unity and present in the comparable concentrations.

Let us now assume that reaction (3) is the rate determining step. Reaction rate will be then expressed by the equation:

$$r = k_3\left[C_4H^+_{9\,(\sigma)}\right]\left[CH_3OH_{(s)}\right] \tag{6}$$

Assuming virtual equilibria of reactions (1) and (2), we obtain:

$$K_1 = \frac{\left[C_4H^+_{9\,(\sigma)}\right]}{p_{C_4H_8}\left[H^+_{(s)}\right]} \tag{7}$$

$$K_2 = \frac{\left[CH_3OH_{(s)}\right]}{p_{CH_3OH}} \tag{8}$$

($p_{C_4H_8}$ and p_{CH_3OH} are partial pressures of

isobutene and methanol in the gas phase) and then from Eqs. (6)–(8),

$$r = k_3 K_1 K_2 [\mathrm{H}_{(s)}^+] \, p_{\mathrm{C_4H_8}} \, p_{\mathrm{CH_3OH}} \qquad (9)$$

At the initial state of the reaction when the concentration of methanol in the solid is small in comparison to the concentration of free protons the latter can be assumed as constant and equal to the initial one $[\mathrm{H}_{(s)}^+]_0$ reaction (9) turns into:

$$r = \alpha p_{\mathrm{C_4H_8}} \, p_{\mathrm{CH_3OH}} \quad \text{where}$$
$$\alpha = k_3 K_1 K_2 [\mathrm{H}_{(s)}^+]_0 \qquad (10)$$

In fact, initial reaction order 0.86 with respect to methanol is near to the expected value. On the other hand reaction order with respect to isobutene 1.29 indicates deviation from the proposed model suggesting parallel occurring of a bimolecular reaction. The most plausible eventuality would be bimolecular formation of isobutene dimer 2,5-dimethyl-3-hexene which on further reaction with methanol would produce one molecule of MTBE and regenerate one molecule of isobutene.

At the steady state of catalytic reaction the concentration of free protons must markedly decrease owing to the reaction (4). Its concentration evaluated from Eqs. (5) and (8) expressing the equilibrium of reaction (2) is given by:

$$[\mathrm{H}_{(s)}^+] = \frac{1}{K_4 K_2^n} [(\mathrm{CH_3OH})_n \mathrm{H}_{(s)}^+] \, p_{\mathrm{CH_3OH}}^{-n} \quad (11)$$

and hence,

$$r = \frac{k_3 K_1}{K_2^{n-1} K_4} p_{\mathrm{C_4H_8}} \, p_{\mathrm{CH_3OH}}^{1-n} [(\mathrm{CH_3OH})_n \mathrm{H}_{(s)}^+] \qquad (12)$$

The concentration of the predominant cluster at low values of $[\mathrm{H}_{(s)}^+]$ may be approximated by the equation $[(\mathrm{CH_3OH})_n \mathrm{H}_{(s)}^+] \approx c_{\mathrm{CH_3OH}}$, where $c_{\mathrm{CH_3OH}}$ is the total concentration of methanol in next-to-surface layer (both concentrations being expressed as molecules of $\mathrm{CH_3OH/KU}$). Then we transform Eq. (11) into:

$$r = \frac{k_3 K_1}{K_2^{n-1} K_4} p_{\mathrm{C_4H_8}} \, p_{\mathrm{CH_3OH}}^{1-n} c_{\mathrm{CH_3OH}} \qquad (13)$$

At 40°C, the empirical dependence of $c_{\mathrm{CH_3OH}}$ on $p_{\mathrm{CH_3OH}}$ within the limits of methanol partial pressure 8.53 and 14.9 kPa (overlapping with the $p_{\mathrm{CH_3OH}}$ range in which determination of reaction order with respect to $\mathrm{CH_3OH}$ was carried out) was obtained by fitting the data presented in Table 1 in an exponential equation (correlation coefficient 0.9327):

$$c_{\mathrm{CH_3OH}}(\mathrm{CH_3OH} \text{ molecules/KU})$$
$$= 0.109 \, p_{\mathrm{CH_3OH}}^{1.76} \qquad (14)$$

Inserting this into Eq. (13) gives:

$$r = \frac{0.109 k_3 K_1}{K_2^{n-1} K_4} p_{\mathrm{C_4H_8}} \, p_{\mathrm{CH_3OH}}^{1-n} \, p_{\mathrm{CH_3OH}}^{1.76}$$
$$= \beta p_{\mathrm{C_4H_8}} \, p_{\mathrm{CH_3OH}}^{2.76-n} \qquad (15)$$

In fact the reaction order with respect to methanol observed at the steady state at 40°C was equal to -1.61 corresponding to $n \approx 4$ suggesting that in the next-to-surface layer of the catalyst equilibrated with methanol in gas phase a tetrameric species is the predominant cluster.

As has already been mentioned, the initial reaction order with respect to methanol (determined on the basis of first chromatographic analysis carried out after 3 min since the beginning of the run) was positive and assumed value about one. It corresponds to the situation in which the concentration of methanol in the next-to-surface layer is still negligible. However, one can expect that with time when the system moves to the steady state and equilibrium between methanol in gas phase and next-to-surface layer represented by empirical Eq. (14) the reaction order with respect to methanol will decrease and even assume more and more negative values. In fact reaction orders calculated on the basis of the second analysis (carried

out after 40 min) and the third ones (carried out after 80 min) were -0.98 and -1.23, respectively.

The fact that the formation of pseudo-liquid phase in $H_4SiW_{12}O_{40}$ absorbing mainly methanol occurs at the initial stage and accelerates the reaction but then transforms into the low-activity state at the latter stage of reaction by absorbing a large amount of methanol was also observed and discussed previously in similar way by Shikata et al. [11].

At 80°C, there was not any change of reaction orders as determined at the initial stage and at the steady state of the catalytic reaction. The equilibrium concentration of methanol (Table 1) is much lower than that at 40°C. It corresponds to 0.33 CH_3OH/H^+ at 8.53 kPa and 0.46 CH_3OH/H^+ at 9.31 kPa. Hence the same approximation can be introduced as those leading to Eq. (9) according to which both reaction orders should be equal to one. In fact reaction order with respect to isobutene is close to one (Table 2) but the order with respect to methanol decreased to about 0.5 suggesting that at this temperature reaction is diffusion controlled. The case of the reaction $A + B \rightarrow C$ on porous catalyst in which only one reagent is diffusionally controlled and both exhibit reaction order one at the freely accessible catalyst surface has been discussed by Satterfield [17]. He has shown that on porous catalyst reaction order of the component diffusionally limited remains unity while the reaction order of the component diffusionally *not* limited decreases to 0.5. Hence we can conclude that in the case of our reaction occurring on highly porous catalyst at 80°C there are diffusion limitations of isobutene while there are not for methanol. This is in agreement with the fact that diffusion coefficient (molecular or Knudsen) of isobutene must be lower than that of methanol the molecular mass of which is almost twice lower. The conclusion that at 80°C reaction was diffusion controlled is strongly supported by the estimation of apparent activation energy which was as low as 25 kJ mol^{-1} (6 kcal mol^{-1}).

Let us now discuss the case in which reaction (1) is taken as the rate determining step. Kinetic equation would have then the following form:

$$r = k_1 \, p_{C_4H_8}[H^+_{(s)}] \qquad (16)$$

At the initial stage $[H^+_{(s)}]$ can be taken as constant and the reaction rate would be of the order one with respect to isobutene but of the order zero with respect to methanol in disagreement with the experimental results.

At the steady state of reaction $[H^+_{(s)}]$ is expressed by Eq. (11) and

$$r = \frac{k_1}{K_4 K_2^n} p_{C_4H_8} \, p_{CH_3OH}^{-n}[(CH_3OH)_n H^+_{(s)}] \quad (17)$$

Substituting $[(CH_3OH)_n H^+_{(s)}] \approx 0.109 \, p_{CH_3OH}^{1.76}$, we obtain

$$r = \frac{0.109 \, k_1}{K_4 K_2^n} p_{C_4H_8} \, p_{CH_3OH}^{1.76-n} = \gamma p_{C_4H_8} \, p_{CH_3OH}^{1.76-n}$$
$$(18)$$

Eq. (18) has an analogous form as Eq. (15) leading to somewhat lower value of n ($n \approx 3$) but differs by the values of constants which can not be determined on the basis of our experimental results. We can only conclude that both equations qualitatively explain the negative values of reaction order with respect to methanol observed at later stages of catalytic run at 40°C.

The above proposed mechanism of catalytic formation of MTBE on dodecatungstosilicic acid catalyst enables also to understand the shape of the conversion vs. time or MTBE yield vs. time curves. In run $R = 0.09$ represented in Fig. 1a carried out at 40°C, $p_{C_4H_8} = 11.4$ kPa and $p_{CH_3OH} = 13.0$ kPa initial conversion decreases with time and the steady state is reached after 70–100 min. Initial sorption of methanol is fast as it is shown by high methanol deficit calculated from the first chromatographic analysis (Fig. 1c) and deactivation according to our model is due to the gradual decrease of the concentration of free protons bonded in the protonated methanol clusters.

However, in a few cases when partial pressure of isobutene was high and that of methanol low we observed an increase of conversion before steady state has been established. Such case is represented by the run $R = 0.73$ in Fig. 1a in which partial pressures were $p_{C_4H_8} = 52.7$ kPa and $p_{CH_3OH} = 7.12$ kPa. The absolute initial reaction rate 0.277 μmol $C_4H_8/(s \cdot g$ catalyst) was much higher than that in run $R = 0.09$ equal to 0.071 μmol $C_4H_8/(s \cdot g$ catalyst). The fact that initial sorption of methanol (Fig. 1c) was definitely low suggests that reaction was slowed down by too small initial concentration of methanol in the next-to-surface layer, i.e., at this stage it was reaction (2) which was rate determining step.

5. Conclusions

Due to the fact that one polar substrate, methanol, may penetrate the crystal lattice of dodecatungstosilicic acid while the non polar one, isobutene, remains only at the surface the investigated catalytic system is fairly complicated and reaction mechanism depends not only on the concentration of reagents in the feed, their adsorption on the surface but also on their sorption by the whole volume of the catalyst. The information about this sorption was obtained on the basis of direct sorption experiments carried out with sorption balance as well as on the basis of calculations of mass balance during the catalytic experiments. The farmer have shown that methanol easily penetrates the bulk of HPA crystallites while isobutene remains on the surface of HPA pristine as well as saturated with methanol. This justified conclusion that reaction occurs on the surface with the participation of protons and methanol molecules supplied from the bulk (reaction of bulk type II according to classification of Misono [18].

The study of mass deficit indicated that in the steady state of the catalytic reaction at which constant concentration of reagents at the surface and in the next-to-surface layer has to be pre-

served the sorption of methanol may continue up to the full saturation of the bulk. This shows that at the steady state an equilibrium exists between methanol in the gas phase and that in the next-to-surface layer but there is not necessarily equilibrium of methanol between next-to-surface layer and the bulk.

The particularity of this catalytic process that at 40°C reaction order with respect to methanol was positive and about one at the initial period of the run but negative at the steady state was interpreted on the basis of the proposed reaction scheme including the formation of *tert*-butyl carbenium ion due to the surface reaction of isobutene with 'free' protons supplied by the solid. A system of kinetic equations was obtained assuming that the reaction of surface carbocation with methanol supplied from the next-to-surface layer is the rate determining step. According to it the surface concentration of carbocations depends on the concentration of the 'free' protons, i.e., the protons forming hydrogen bonds between Keggin units. This concentration depends on its turn on the concentration of methanol in the bulk forming protonated monomeric species $CH_3OH_2^+$ and/or protonated clusters $(CH_3OH)_nH^+$.

At the very beginning of the run the concentration of the methanol in the next-to-surface layer is still very low and the concentration of 'free' protons practically constant. Assuming proportionality of methanol concentration in the next-to-surface layer to its pressure in the feed we obtain an equation of the first order with respect both to methanol and to isobutene. On the other hand at the steady state when equilibrium is reached between methanol in the gas phase and the next-to-surface layer the concentration of 'free' protons decreases with the increase of concentration of methanol in the solid thus slowing down the catalytic reaction which results in the negative order of reaction with respect to methanol.

It should be noticed that in fact reaction order with respect to isobutene at 40°C is higher than one thus suggesting parallel bimolecular reac-

tion. This might be the formation of protonated isobutene dimer 2,5-dimethyl-3-hexene which on further reaction with methanol would produce one molecule of MTBE and regenerate one molecule of isobutene. At 80°C, the concentration of methanol in the solid is much lower than that at 40°C reaction order with respect to isobutene is close to unity and that with respect to methanol about 0.5 both at the initial stage and at the steady state. Such situation corresponds to the case of reaction $A + B \rightarrow C$ on porous catalyst in which one component, e.g., A suffers diffusional limitation but at the non porous catalyst reaction is of the order one with respect to both reagents. As it has been shown by Satterfield [17] at the porous catalyst reaction order with respect to the component A remains one but with respect to component B not suffering diffusional limitations decreased to 0.5. Hence it has been concluded that in our case at 80°C catalytic reaction on highly porous catalyst is most probably diffusion controlled due to the diffusional limitation suffered by isobutene. Another possibility is an explanation in terms of Langmuir–Hinshelwood kinetic model using Langmuir isotherm. The low apparent activation energy would be in this case connected with high adsorption heat of methanol.

Acknowledgements

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