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The Effect of Proton Hydration in Wells-Dawson and Keggin Type Heteropolyacids on their Catalytic Activity in Gas Phase ETBE Synthesis

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Abstract The influence of proton hydration in Wells-Dawson $H_6P_2W_{18}O_{62}$ (HP2W) and Keggin $H_3PW_{12}O_{40}$ (HPW) type heteropolyacids on their catalytic activity in ethyl-tert-butyl ether (ETBE) synthesis in gas phase was investigated. In the case of samples with the content of crystallisation water per one proton below 0.8 ($[H_2O]/[H^+] < 0.8$), the catalytic activity related to the mass unit of the HP2W was higher than that of the HPW in accordance with the order of proton concentration in mass unit. On the other hand, the activity related to one mole of protons indicated higher activity in the HPW than in the HP2W in accordance with the order of acid strength. In the series of samples with $[H_2O]/[H^+] > 0.8$ the activity was much higher for the HP2W than the HPW and maximum of both catalytic activity and ethanol sorption capacity was observed for the HP2W. The possible role of the secondary structure of the hydrates was discussed.

Keywords ETBE · Wells-Dawson · Keggin · Heteropolyacid · Ethanol · Isobutene

1 Introduction

Heteropolyacids (HPA) exhibit specific structure of oxyanions in which one or several atoms, called heteroatoms, are the centres around which a system of $[MO_6]$ octahedrons (M = W, Mo, V, Nb, or Ta) is coordinated. The most frequently used in catalytic research are dodecaheteropolyacids of Keggin structure, e.g. $H_3PW_{12}O_{40}$, and octadecaheteropolyacids of Wells-Dawson structure, e.g. $H_6P_2W_{18}O_{62}$. In crystalline HPAs the structure of anions is usually called the primary structure, while the crystal lattice built of anions and protons or other counter cations, solvated or not, is forming the secondary structure.

Due to the large size of anions the negative charge of heteropolyanions is smeared over their external surface (comprising 36 and 55 oxygen atoms in the case of above mentioned examples), therefore protons are weakly attracted in the HPA. As a result, the acid strength of many HPAs is higher than that of the mineral acids HCl, H_2SO_4 or HNO_3, and even so strong acids as $HClO_4$ and CF_3SO_3H [1, 2]. HPAs are effective catalysts in many acid catalyzed reactions: esterification and reactions of esters [3], synthesis of ethers [4–6], hydration of olefins [7] and dehydration of alcohols [4, 84,] occurring both in liquid and gas phase [9] among others. The acidity series of dodeca and octadecaheteropolyacids based on the determination of the pK_a values in solutions differed dependently on the investigated solvent [2].

Acid strength of solid heteropolyacids was characterized semi-quantitatively by calorimetric measurements of the heat of ammonia sorption from gas phase at 150 °C, leading to the following series: $H_3PW_{12}O_{40}$ (200 kJ mol^{-1}) > $H_4SiW_{12}O_{40}$ > $H_6P_2W_{21}O_{71}(H_2O)_3$ > $H_6P_2W_{18}O_{62}$ (155 kJ mol^{-1}) [2–11]. The acid strength of $H_4SiW_{12}O_{40}$ [12] and $H_6P_2W_{18}O_{62}$ [13] determined at 25 °C with the same technique gave similar but somewhat lower results ($\Delta H = -132.9$ kJ mol^{-1} and $\Delta H = -127.9$ kJ mol^{-1}, respectively).

Solid heteropolyacids exhibit unusual sorption properties showing so called "pseudo-liquid phase" behaviour [14]. Polar molecules such as H_2O, NH_3, amines and alcohols not only are adsorbed on the external surface of HPA crystallites but also penetrate their bulk where they interact with loosely bonded protons, thus forming

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protonated monomers or protonated clusters [14–17]. The exact form and contribution of the clusters depend on the type of heteropolyacid or sorption temperature. At 150 °C ammonia sorption [10] corresponded to 3 NH_3 molecules per one $H_3PW_{12}O_{40}$ unit and about 5 NH_3 per one $H_6P_2W_{18}O_{62}$ unit thus indicating the predominance of absorbed ammonia as NH_4^+ ion. On the other hand at room temperature, 6 NH_3 molecules were uptaken per one $H_3PW_{12}O_{40}$ unit and about 12 NH_3 per one $H_6P_2W_{18}O_{62}$. This indicated the predominant sorption of ammonia in the form of a protonated dimer $N_2H_7^+$. The NH_4^+ and $N_2H_7^+$ units could also be differentiated on the basis of their IR spectra [13, 18].

Generally, the sorption processes are fast, indicating that at least a part of the absorbed molecules exhibits high mobility. In the contrast to the polar molecules the nonpolar ones can be adsorbed physically or chemisorbed only at the external surface of the HPA crystallites and they do not penetrate the bulk.

Catalytic activity of the Keggin type HPW and the Wells-Dawson type HP2W heteropolyacids has been compared for several acid catalyzed reactions occurring in gas [19–22] and liquid [23] phases. Catalytic activity of the HP2W and the HPW [20, 21] was investigated in methyl-tert-butyl ether (MTBE) synthesis in gas phase (30–110 °C). The authors stated that solid acid of the Wells-Dawson type $H_6P_2W_{18}O_{62}$, was more active catalyst than the Keggin type $H_3PW_{12}O_{40}$ despite higher acid strength of the latter one. Their experiments were however carried out in the absence of water.

Some authors indicated that water may play an important role in the catalytic activity of heteropolyacids [24–26]. Bardin et al. [26] studied the effect of temperature pretreatment conditions (100–300 °C) on the catalytic activity of the Keggin type HPA, $H_3PW_{12}O_{40,}$ in isomerisation of 1-butene. They observed a decrease in activity as pretreatment temperature was increased over 100 °C. This fact has been ascribed to the departure of crystallisation water from the HPA crystallites. Poźniczek et al. [27] observed similar effect investigating the influence of preheating on the activity of the $H_6P_2W_{18}O_{62}$ in the catalytic synthesis of ethyl-tert-butyl ether (ETBE). They stated that samples activated at or above 150 °C exhibited much lower activity than those pretreated at 95 °C containing about eight water molecules per one anion. It was also shown in the separate experiments that parallel to the changes in catalytic activity the changes in the ethanol sorption capacity of the catalysts occurred. The latter was definitely lower for the samples pretreated at 150 °C than those pretreated at 95 °C. Gambaro and Briand [28] observed a similar effect in the study of isopropanol sorption on Wells-Dawson catalysts. Baronetti et al. [4] investigated the effect of HP2W preheating temperature on its catalytic activity in MTBE synthesis. They stated that $H_6P_2W_{18}O_{62}$ $28H_2O$ sample preheated at or below 200 °C exhibited practically constant catalytic activity. When activation temperature was increased to 400 °C, causing dehydration of the acid, catalytic activity dropped to zero. The authors suggested that in anhydrous acids protons are trapped between the primary units, being inaccessible to the reagents.

The effect of water vapour in the feed of gas phase synthesis of ETBE on dehydrated (devoid of crystallisation water) solid $H_6P_2W_{18}O_{62}$ was studied by us [29]. It was showed that the positive reaction order with respect to isobutene, one of the reactants, and the negative reaction order with respect to the second reactant, ethanol, were independent of the presence or absence of water vapour in the feed.

All the above results strongly suggest that the presence of the crystallisation water in heteropolyacids participating in the formation of the secondary structure plays an essential role in catalysis and without taking it into account no comparison between Keggin and Wells-Dawson heteropolyacids can be done. It should be stressed here that water of crystallisation in solid heteropolyacids is present in the form of protonated clusters [30, 31]. The hydration of protons is also considered to be an essential factor in their acidity and hence catalytic activity [32].

The aim of the present investigation was to compare two the most frequently studied Keggin and Wells-Dawson heteropolyacids, $H_3PW_{12}O_{40}$ and $H_6P_2W_{18}O_{62}$, as the catalysts and sorbents. For both acids the content of crystallisation water and hence the degree of proton hydration can be conveniently changed by different heat treatment. Gas phase synthesis of ethyl-tert-butyl ether (ETBE) has been chosen as the catalytic test reaction, while sorption of ethanol (EtOH) vapour as a test of the sorption capacity was chosen.

2 Experimental

The samples of heteropolyacids: Keggin type $H_3PW_{12}O_{40}$ (HPW), Aldrich p.a. and Wells-Dawson type $H_6P_2W_{18}O_{62}$ (HP2W) prepared according [4, 27, 33] were kept over 2saturated solution of $Mg(NO_3)_2$. Their composition after equilibration at room temperature corresponded to the formulas: $H_3PW_{12}O_{40} \cdot 26.6H_2O$ and $H_6P_2W_{18}O_{62} \cdot 28.8H_2O$.

ETBE synthesis in the gas phase electrophilic addition of ethanol (EtOH) to isobutene was used as a catalytic test reaction. Catalytic experiments were carried out in a flow microreactor ($\phi = 10$ mm) connected on line with the gas-chromatograph with Porapak QS filled column. Helium used as carrier gas in catalytic tests was saturated with ethanol vapour and subsequently mixed with a stream of

Table 1 Composition of heteropolyacid samples as a function of the pretreatment temperature

Pretreatment temperature °C (activation time, min)	Samples composition	H_2O/H^+
Wells-Dawson type HPA		
40 (140)	$H_6P_2W_{18}O_{62} \cdot 18\ H_2O$	3.00
80 (30)[a]	$H_6P_2W_{18}O_{62} \cdot 8.6\ H_2O$	1.43
95 (30)[a]	$H_6P_2W_{18}O_{62} \cdot 8.0\ H_2O$	1.33
128 (30)[a]	$H_6P_2W_{18}O_{62} \cdot 5.4\ H_2O$	0.90
150 (30)[a]	$H_6P_2W_{18}O_{62} \cdot 3.0\ H_2O$	0.50
200 (30)[a]	$H_6P_2W_{18}O_{62} \cdot 2.8\ H_2O$	0.47
300[a]	$P_2W_{18}O_{59}$	–
Keggin type HPA		
40 (140)	$H_3PW_{12}O_{40} \cdot 6.0\ H_2O$	2.00
100 (30)	$H_3PW_{12}O_{40} \cdot 4.8\ H_2O$	1.60
150 (30)	$H_3PW_{12}O_{40} \cdot 3.0\ H_2O$	1.00
200 (60)	$H_3PW_{12}O_{40} \cdot 2.5\ H_2O$	0.83
220 (120)	$H_3PW_{12}O_{40}$	–

[a] Data taken from [29], carried out at the same apparatus and conditions as in the present research

isobutene. Feed flow rate was 30 $cm^3\ min^{-1}$. The composition of the reaction mixture fixed at the isobutene/ethanol molar ratio equal to 0.7 ($p_{C4H8} = 3.2$ kPa, $p_{C2H5OH} = 5.1$ kPa) was used in all catalytic tests. Before the catalytic experiments the pristine samples (0.45 g of HP2W and 0.60 g of HPW) mixed with quartz grains were pretreated in situ in the helium stream at temperatures between 40 and 220 °C. All catalytic experiments were carried out at 40 °C. In a parallel series of separate experiments the content of crystallisation water was determined in the samples pretreated in the same conditions as for the catalytic tests (Table 1). The loss of water during this treatment was determined gravimetrically. The main product of the catalytic reaction at 40 °C was ETBE. Only traces of TBA were discovered. Isobutene conversion in all cases reached a constant level after a few minutes and stayed constant during the whole catalytic test (up to 7 h).

The rate of isobutene catalytic consumption with respect to anhydrous catalyst mass, r_m, and also with respect to the number of protons in an anhydrous sample r_{H^+}, were calculated from equations:

$$r_m\left[\mathrm{mol}\cdot\mathrm{h}^{-1}\mathrm{g}^{-1}\right] = F\frac{X_{\mathrm{IB}}}{m} \tag{1}$$

$$r_{H^+}\left[\mathrm{mol}\cdot\mathrm{h}^{-1}(\mathrm{molH}^+)^{-1}\right] = F\frac{X_{\mathrm{IB}}}{n} \tag{2}$$

where: F—the velocity of isobutene flow in the feed [mole·s^{-1}], m—the mass of anhydrous catalyst [g], n—the number of H^+ moles in the sample of catalyst, X_{IB}—the conversion of isobutene expressed as a molar fraction. At standard conditions of temperature and substrate partial pressures, both r_m and r_{H+} were taken as the measure of sample's activity.

The sorption of anhydrous ethanol (p.a. POCh.) was studied by means of a quartz spring sorption balance (sensitivity 0.6828 mm mg^{-1}) connected to a vacuum system. Before sorption the samples were evacuated in situ at temperatures 100–220 °C for the HPW and 40–210 °C for the HP2W thus, reaching different content of crystallisation water. The adequate pretreatment conditions allowed obtaining a series of differently hydrated heteropolyacids. After pretreatment the samples were cooled to 40 °C and sorption experiments were carried out at ethanol pressure 5.1 kPa.

Thermometric titrations of the anhydrous powdered samples (~2 g suspension in 100 cm^3 of toluene) with 1 M *n*-butylamine solution in toluene were carried out as described in [34].

X-ray diffraction patterns were collected using Siemens D5005 diffractometer (Cu Kα radiation, 40 kV, 40 mA) equipped with diffracted beam graphite monochromator. The patterns were collected in the range of $2\Theta = 1.5$–$90°$, step size 0.02°. The patterns were decomposed in the range 1.5–65° of 2Θ by LeBail method using TOPAS R2.1 programme. The crystallites size was calculated by Lvol-IB method.

3 Results and Discussion

3.1 Catalytic Results

The catalytic activity related to the catalyst mass unit, r_m, is shown in Fig. 1 as a function of the number of crystallisation water molecules per one proton $[H_2O]/[H^+]$ (called here proton hydration). It is seen that r_m was higher for the Wells-Dawson heteropolyacid (HP2W) than that of the Keggin type (HPW) within the whole range of $[H_2O]/[H^+]$.

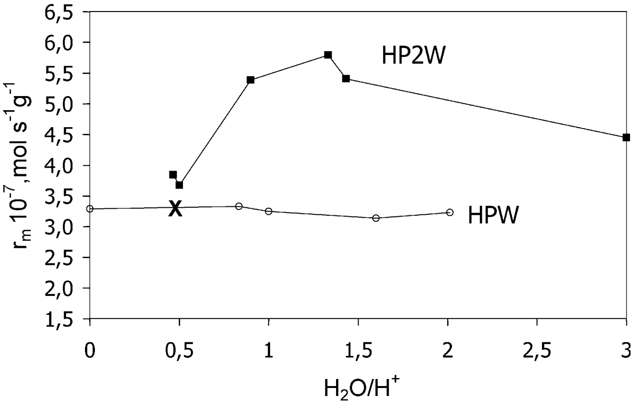

Fig. 1 Catalytic activity r_m related to mass of catalyst as the function of proton hydration: ■, HP2W; ○, HPW; X, HPW interpolated value

Similar results were observed by Shikata et al. [22] in the gas phase synthesis of methyl-tert-butyl ether (MTBE) and also by Maksimov and Kozhevnikov [35] the same reaction in liquid phase. It is striking in Fig. 1 that the activity r_m of the HPW is almost independent of the proton hydration while activity of the HP2W is relatively low at hydration degree as low as $[H_2O]/[H^+] \approx 0.5$ but increases with the increase of $[H_2O]/[H^+]$ to 1.3.

Figure 2 shows the catalytic activity of the investigated catalysts related to one mole of protons r_{H+} as a function of proton hydration $[H_2O]/[H^+]$. It is seen that the curves representing the activity of the particular types of heteropolyacids preserve similar shape as those in Fig. 1. However, the relative position of both curves is different: at the low $[H_2O]/[H^+]$ the activity of the HPW expressed as r_{H+} is higher than that of the HP2W and the opposite is observed when $[H_2O]/[H^+] \geq 0.8$.

3.2 Proton Hydration Degree $[H_2O]/[H^+] < 0.8$

Let us discuss at first the case of low content of crystallisation water in the sample. At the same hydration degree $[H_2O]/[H^+] \approx 0.5$ approximately a half of protons in both catalysts is present in the form of H_3O^+ ions and a half remains not hydrated forming hydrogen bonds between the HPA anions. In this situation when comparing the rate of isobutene catalytic consumption with respect to anhydrous catalyst mass, $r_{m(\mathrm{HP2W})}$ and $r_{m(\mathrm{HPW})}$, the concentration of protons (playing the role of Brønsted acid centres) in a unit mass of the catalyst is different. It follows from stoichiometry that the concentration of protons in the HP2W (1.37 mmol H^+/g) is higher by the factor 1.3 than that in the HPW (1.04 mmol H^+/g). This can be compared with the experimental ratio of $r_{m\ (\mathrm{HP2W})}/r_{m\ (\mathrm{HPW})}$ which is equal to 1.15 at $[H_2O]/[H^+]=0.5$ thus suggesting that at the same proton hydration degree it is proton concentration which predominantly determinates observed higher activity (per mass) of the Wells-Dawson heteropolyacid.

Now the activity of protons should be compared at the similar $[H_2O]/[H^+]$ value and expressed as the activity related to one proton r_{H+}. As Fig. 2 shows, $r_{H+(\mathrm{HP2W})}$ is smaller than $r_{H+(\mathrm{HPW})}$ at low content of water in accordance with the order of their acid strength characterised by the heat of ammonia sorption [10, 11]. Such order of the acid strength was also confirmed in the present investigation by the thermometric titration of dehydrated heteropolyacids with *n*-butylamine. The initial value of ΔH equal to 167 kJ/(mol amine) was obtained for the HPW and 131 kJ/(mol amine) for the HP2W.

The above results justify the conclusion that at the low proton hydration degree the catalytic activity of the investigated heteropolyacids is governed by both the concentration of protons in the bulk and their acid strength.

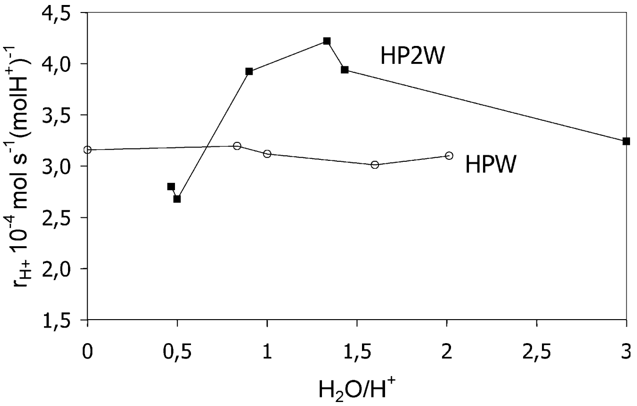

Fig. 2 Catalytic activity rH^+ related to one mole of protons as the function of proton hydration

3.3 Proton Hydration Degree $[H_2O]/[H^+] > 0.8$

The samples of HP2 W and HPW containing higher content of the crystallisation water and hence exhibiting higher proton hydration degree $0.8 < [H_2O]/[H^+] < 3.0$ were obtained by preheating the pristine hydrated heteropolyacids at temperatures ranging from 128 to 40 °C. Catalytic activity of the Keggin type samples of different degree of hydration is virtually constant. At the same time the Wells-Dawson samples reaches a distinct maximum at $[H_2O]/[H^+] \approx 1.3$. In this case, the ratio of $r_{m(\mathrm{HP2W})}/r_{m(\mathrm{HPW})}$ is as high as 1.84 and the distinct increase of $r_{m(\mathrm{HP2W})}$ in respect to $r_{m(\mathrm{HPW})}$ cannot be ascribed exclusively to the differences in the concentration of protons for a unit mass as it was done in point 3.2. The more, the order of activities $r_{H+(\mathrm{HP2W})} > r_{H+(\mathrm{HPW})}$ is not in accordance with the order of the acid strength determined for the anhydrous samples by the heat of ammonia sorption.

It was suggested in our previous paper [27] that the shape of the curve representing $r_{m\ (\mathrm{HP2W})}$ as a function of the proton hydration may be correlated with the ethanol sorption capacity which can be analyse by spring balance. This was also confirmed in the present investigation for both, the Wells-Dawson and the Keggin type samples. This is seen in Fig. 3a, b where the hollow points show ethanol sorption capacity (EtOH/HPA molecule) and the full ones the catalytic activity (r_{H+}). The observed parallelism suggests that it is the bulk concentration of ethanol which may be the dominant factor determining the differences between activities observed for the particular series of heteropolyacids, Keggin or Wells-Dawson type. It should be observed that the calculated mass balance indicates sorption of ethanol in the course of catalytic reaction [27] which in fact reaches maximum in the case of the HP2W sample with $[H_2O]/[H^+] \approx 1.3$

We therefore believe that different catalytic behaviour of the HP2W and the HPW within $0.8 < [H_2O]/[H^+] < 3.0$

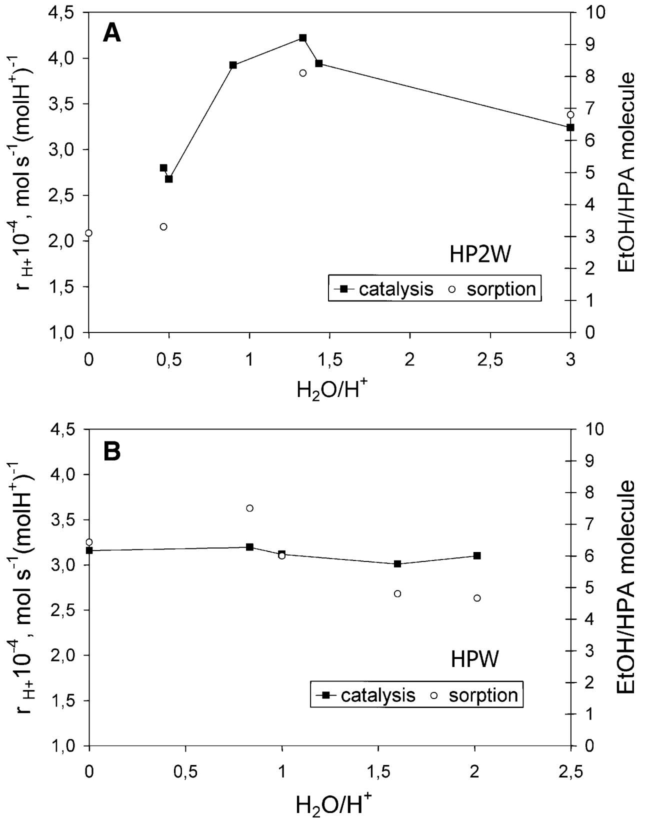

Fig. 3 (**a**) Catalytic activity as compared with the ethanol sorption capacity of HP2W as the functions of proton hydration: ■, catalytic activity; ○, sorption capacity. (**b**) Catalytic activity as compared with the ethanol sorption capacity of HPW as the functions of proton hydration: ■, catalytic activity; ○, sorption capacity

range is due to the differences in the secondary structure of the acids. The structure of the HP2W with $[H_2O]/[H^+] \approx 1.3$ (containing $8H_2O$ molecules per one anion) would be much more loose then that of HPW with the same $[H_2O]/[H^+]$. This might be also the result of the different size and shape of Wells-Dawson and Keggin anions.

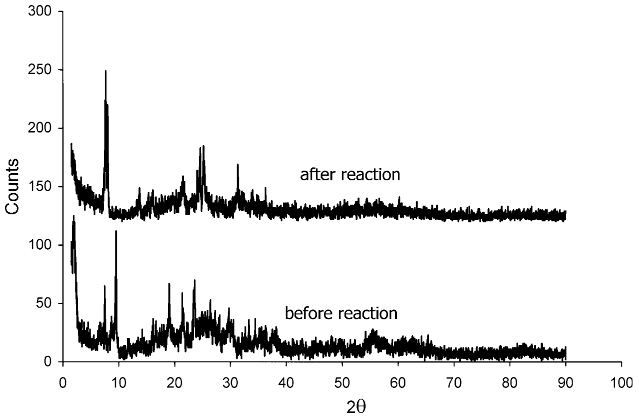

Fig. 4 X-ray patterns for HP2W $8H_2O$

The X-ray diffraction patterns of the HP2W · 8.0 H_2O sample activated at 95 °C and the same sample after the catalytic run are shown in Fig. 4. Both samples were of fine crystalline making structure refinement by Rietveld method impossible. However, using the above patterns we performed LeBail decompositions obtaining lattice parameters and crystallite sizes of both samples. For the sample activated at 95 °C we found the triclinic crystal system with cell parameters $a = 14.09$ Å, $b = 43.50$ Å, $c = 18.25$ Å, $\alpha = 91°$, $\beta = 100.9°$, $\gamma = 90.9°$. These parameters differ from those published for $H_6P_2W_{18}O_{62} \cdot 23.5\ H_2O$ [36] by triclinic space group versus monoclinic one and by approximately tripled b period (43.50 Å vs. 14.20 Å). It suggests that decrease of hydration water causes some structural changes of the investigated sample. No X-ray data of lower hydrates are given in literature. For the sample after the catalytic run we found the following lattice parameters in monoclinic system: $a = 12.15$ Å, $b = 12.21$ Å, $c = 18.10$ Å, $\beta = 102.4°$. In comparison to $H_6P_2W_{18}O_{62} \cdot 23.5\ H_2O$ there is visible significant shortening of a and b periods suggesting removing of water from the space between Dawson anions. The analysis of our X-ray data indicates that the average size of crystallites increased from about 7.5 nm in the freshly activated sample to 22.4 nm after the catalytic test. The inspection of the data did not exclude the presence of more than one phase in the sample after the test. The complicated structure of highly hydrated $H_6P_2W_{18}O_{62}$ samples and their catalytic properties signalled in the present publication deserves further investigation.

4 Conclusion

At the low proton hydration degree such as $[H_2O]/[H^+]=0.5$ there are two factors predominately influencing the catalytic activity of the investigated samples: one is the proton concentration in the bulk and second, their acid strength. At the proton hydration $[H_2O]/[H^+] > 0.8$ HP2W exhibits specific secondary structure enabling higher ethanol sorption capacity than that of the HPW.

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References

1. Misono M, Okuhara T (1993) CHEMTECH 23:23
2. Timofeeva MN (2003) Appl Catal A: Gen 256:19
3. Hu Ch, Hashimoto M, Okuhara T, Misono M (1993) J Catal 143:437
4. Baronetti G, Briand L, Sedran U, Thomas H (1998) Appl Catal A: Gen 172:265

5. Bielański A, Lubańska A, Poźniczek J, Micek-Ilnicka A (2003) Appl Catal A: Gen 256:153
6. Bielański A, Lubańska A, Micek-Ilnicka A, Poźniczek J (2005) Coord Chem Rev 249:2222
7. Ivanov AV, Zausa E, Ben Taarit Y, Essayem N (2003) Appl Catal A: Gen 256:225
8. Highfield JG, Moffat JB (1985) J Catal 95:108
9. Briand L, Baronetti G, Thomas H (2003) Appl Catal A: Gen 256:37
10. Lefebvre F, Cai FXL, Auroux A (1994) J Mater Chem 4:125
11. Auroux A, Vedrine JC (1985) Stud Surf Sci Catal 20:311
12. Lalik E, Micek-Ilnicka A, Groszek AJ, Bielański A (2003) Phys Chem Chem Phys 5:3606
13. Micek-Ilnicka A, Gil B, Lalik E (2005) J Mol Struct 740:25
14. Misono M, (1985) Stud Surf Sci Catal 20:147
15. Małecka A, Poźniczek J, Micek-Ilnicka A, Bielański A (1999) J Mol Catal A: Chem 138:67
16. Micek-Ilnicka A (2006) J Mol Catal A: Chem 260:170
17. Lubańska A, Bielański A (2004) J Mol Catal A: Chem 224:179
18. Micek-Ilnicka A, Gil B (2007) Vib Spectrosc 43:435–439
19. Oulmekki A, Lefebvre F (1992) RKCL 48 2:593
20. Oulmekki A, Lefebvre F (1992) RKCL 48 2:601
21. Shikata S, Okuhara T, Misono M (1995) J Mol Catal A: Chem 100:49
22. Shikata S, Misono M, (1998) Chem Commun 1293
23. Li G, Ding Y, Wang J, Wang X, Suo J, (2007) J Mol Catal A: Chem 262:67
24. Essayem N, Coudurier G, Vedrine J, Habermacher D, Sommer J (1999) J Catal 183:292
25. Bardin BB, Bordawekar SV, Neurock M, Davis RJ (1998) J Phys Chem B 102:10817
26. Bardin BB, Davis RJ (2000) Appl Catal A: Gen 200:219
27. Poźniczek J, Micek-Ilnicka A, Lubańska A, Bielański A (2005) Appl Catal A: Gen 286:52
28. Gambaro L, Briand L (2004) Appl Catal A: Gen 264:151
29. Micek-Ilnicka A (2007) J Mol Catal A: Chem 277:252
30. Brown GM, Noe-Spirlett MR, Busing WR, Levy HA (1977) Acta Cryst B 33:1038
31. Bielański A, Małecka-Lubańska A, Micek-Ilnicka A, Poźniczek J (2000) Top Catal 11/12:43
32. Okuhara T, Mizuno N, Misono M (1996) Adv Catal 41:113
33. Lyon DK, Miller WK, Nowet T, Domaille PJ, Evitt E, Johnson DC, Finke RJ (1991) Am Chem Soc 113:7209
34. Micek-Ilnicka A, Bielański A, Derewiński M, Rakoczy J (1997) RKCL 61:1–33
35. Maksimov GM, Kozhevnikov IV (1989) RKCL 39:317
36. Sergienko VS, Porai-Koshits MA, Kiselev SV, Butman LA, Chuvaev VF (1983) Zh Neorg Khim 28:1197