

Cesium partly substituted salts $\text{Cs}_x\text{H}_{6-x}\text{P}_2\text{W}_{18}\text{O}_{62}$ of Wells–Dawson heteropolyacid as catalysts for ethyl-*tert*-butyl ether synthesis

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Dedicated to Professor Bogdan Marciniak on the occasion of his 65th Birthday

Abstract

A series of partly substituted cesium salts $\text{Cs}_x\text{H}_{6-x}\text{P}_2\text{W}_{18}\text{O}_{62}$ of Wells–Dawson heteropolyacid has been prepared. The samples were catalytically active at temperatures as low as 40 °C despite low specific surface area of the order of 1 m² g⁻¹. Activity in gas phase synthesis of ethyl-*tert*-butyl ether related to mass of non-neutralized acid reached maximum at $x=5$ and was higher than that of unsupported crystalline heteropolyacid. © 2006 Elsevier B.V. All rights reserved.

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1. Introduction

Heteropolyacids belonging to the strongest mineral acids are effective catalysts for many acid–base type catalytic reactions both in gas and liquid phase. Due to their high solubility in water and organic solvents the separation of heteropolyacid from the liquid reaction medium becomes difficult. This justifies the search for non-soluble forms of solid heteropolyacids. At the verge of eighties and nineties of XX century a series of papers has been published by Japanese authors dealing with the partly substituted cesium salts of Keggin type dodecaheteropolyacids such as $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ and $\text{Cs}_x\text{H}_{3-x}\text{PMo}_{12}\text{O}_{40}$ which were obtained by titration of free heteropolyacid with adequate amounts of cesium carbonate and evaporating the precipitate together with the supernatant liquid. In the series $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ the activity in an alkylation reaction on the samples with $x=1, 2$ was nearly zero but increased sharply at $x=2.5$ and again decreased to zero for $x=3$ [1]. The unique activity of the non-soluble catalysts with x about 2.5 has been subsequently confirmed in a number of publications by different authors. Its physico-chemical and catalytic properties have been recently reviewed by Okuhara [2]. It is interesting

that in this series the specific surface area at $x=0, 1$ and 2 was of the order of a few m² g⁻¹. However at $x=2.5, 3$ it was very much higher, reaching 135 and 150 m² g⁻¹, respectively [3]. This high specific surface area of $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ is an essential factor contributing to its high catalytic activity. In an earlier paper [4] it was presumed that $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ is a mixture of $\text{Cs}_2\text{HPW}_{12}\text{O}_{40}$ and $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$. This was supported by ³¹P NMR investigation [5]. However, more recently the same authors [6], basing on the X-ray diffraction data, claimed that the model of $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$ ultrafine nanocrystallites of the order of 1 nm covered epitaxially with $\text{H}_3\text{PW}_{12}\text{O}_{40}$ is adequate. According to them such crystallites are forming aggregates with voids of the size of the order 30 Å thus generating microporosity of the sample. On calcination at 300 °C the migration of Cs⁺ and H⁺ ions in the solid results in the formation of a nearly uniform solid solution with protons distributed randomly over the entire bulk.

As already said, catalysis on $\text{Cs}_{2.5}$ Keggin type catalyst was studied by many authors. Here, only few examples will be mentioned. It appeared to be a good catalyst for butane [7,8], butene [9,10] and pentane [11] isomerisation, esterification of benzoic [12] and acetic acids [13] and hydration of olefins [14].

Until now all experiments with cesium partly substituted heteropolyacids were carried out using dodecaheteropolyacids of Keggin type, predominantly $\text{H}_3\text{PW}_{12}\text{O}_{40}$. However, according to our knowledge no such investigations were undertaken with

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the cesium salts of Wells–Dawson type octadecaheteropolyacids. The latter HPAs, more active catalysts, are now the object of investigations in many laboratories. Taking into account the fact that both types of heteropolyacids, despite structural similarities, exhibit some distinct differences in the physico-chemical and catalytic properties, it was considered interesting to make in the present research an attempt to obtain a series of partly substituted cesium salts of Wells–Dawson $H_6P_2W_{18}O_{62}$ heteropolyacid and to test their physico-chemical and catalytic properties. Gas phase synthesis of ethyl-*tert*-butyl ether has been chosen as the catalytic test reaction. This reaction was earlier the object of our studies [15] in which $H_6P_2W_{18}O_{62}$ was used as the catalyst.

2. Experimental

Octadecadiphosphotungstic acid $H_6P_2W_{18}O_{62}$ has been obtained as described in Ref. [15]. After synthesis it was kept at room temperature in a desiccator over saturated solution of $Mg(NO_3)_2$. The hydrated sample was a greenish white fine powder. Its ^{31}P NMR spectrum exhibited a peak at -12.225 ppm characteristic of the α isomer and the doublet -11.499 and -10.737 characteristic of β isomer. The contents of $\alpha = 87.4\%$ and $\beta = 12.6\%$ were calculated from the intensities ratio. The absence of a peak at $+0.742$ ppm indicated that no contaminations with *o*-phosphoric acid or phosphates were present.

For salts synthesis cesium carbonate Cs_2CO_3 , 99% supplied by Aldrich was used. Partly substituted salts $Cs_xH_{6-x}P_2W_{18}O_{62}$ were obtained at the same conditions as it was done in Ref. [3] during the preparation of partly substituted salts of Keggin type $Cs_xH_{3-x}PW_{12}O_{40}$. Small portions of 0.1 M solution of Cs_2CO_3 were slowly added (1 cm^3 per 4 min) to the 0.08 M solution of $H_6P_2W_{18}O_{62}$ at vigorous mixing at room temperature. Cesium salt precipitated in form of milky suspension. It was kept overnight at room temperature and subsequently evaporated together with supernatant liquid on a water bath at $45\text{--}50^\circ\text{C}$. The preparations were then stored in a desiccator over saturated solution of $Mg(NO_3)_2$. Their composition corresponded to the formulas: $Cs_2H_4P_2W_{18}O_{62}$, $Cs_4H_2P_2W_{18}O_{62}$, $Cs_5HP_2W_{18}O_{62}$, $Cs_{5.5}H_{0.5}P_2W_{18}O_{62}$ and $Cs_6P_2W_{18}O_{62}$ for which the symbols: Cs_2D , Cs_4D , Cs_5D , $Cs_{5.5}D$ and Cs_6D were used, respectively. The experiments were carried out also with fresh crystalline heteropolyacid the composition of which corresponded to the formula $H_6P_2W_{18}O_{62}\cdot 19.4H_2O$ (HD).

The simultaneous differential scanning calorimetric (DSC) and thermogravimetric (TG, DTA) measurements were performed in the temperature range from ambient to 800°C with heating rate 25° min^{-1} using NETZSCH STA 409 PC Luxx apparatus. Measurements were carried out in helium flowing at a rate $50\text{ cm}^3\text{ min}^{-1}$. The mass of samples were in the range of 15–20 mg.

X-ray diffraction patterns were collected by Siemens D5005 powder diffractometer using $Cu\ K\alpha$ radiation (40 kV, 40 mA) and diffracted beam graphite monochromator. Patterns were collected in the range of two between 1.5 and 70° with the step size 0.02° , 3 s/step.

FTIR spectra were recorded with Excalibur 3000 Digilab spectrometer using KBr technique.

Specific surface area was measured using Quantachrome Nova 2000 apparatus. Samples were pretreated at 110°C for 3 h in vacuum.

Gas phase synthesis of ethyl-*tert*-butyl ether (ETBE) by ethanol to *i*-butene addition has been chosen as the catalytic test reaction. Before catalytic experiments samples were pretreated in helium stream at 95°C for 30 min. The experiments were carried out using a continuous flow microreactor ($\phi = 10\text{ mm}$). Helium carrier gas was first saturated with ethanol vapour (ethanol azeotrope, pure, supplied by POCh Gliwice) and then mixed with a stream of *i*-butene (*i*-butene, p.a., Aldrich). The composition of reaction mixture was fixed at the *i*-butene/ethanol molar ratio equal to 0.7 ($p_{i\text{-butene}} = 3.7\text{ kPa}$, $p_{\text{ethanol}} = 5.6\text{ kPa}$). An excess of ethanol was used in order to prevent the formation of *i*-butene oligomers at the catalyst surface. The catalytic reactor was connected on line with a Hewlett-Packard Ser II A gas chromatograph. Porapak QS column was used for chromatographic analyses. Catalyst samples 0.0362–0.250 g were mixed with such an amount of quartz grains as to obtain the 0.5 cm thick catalyst layer.

3. Results and discussion

TG, DTG and DSC curves of the samples are shown in Fig. 1a–c. The main loss of mass occurred at temperatures below 150°C , due to desorption of crystallization water and water adsorbed. The non-substituted heteropolyacid HD exhibits in this temperature region two DTG peaks at 70 and 135°C corresponding roughly to the formation of dodeca and trihydrates of the acid. The third DTG peak at 307°C is due to the dehydroxylation process, which is the departure of the so-called water of constitution [15]. Similar patterns of DTG peaks exhibit the sample Cs_2D . However, they are shifted to somewhat higher temperature. In the case of Cs_4D , Cs_5D , $Cs_{5.5}D$ and Cs_6D only one distinct peak below 100°C appears. All DTG peaks have their counterparts in endothermic DSC profile. Above 500°C all samples exhibit exothermic DSC peaks not accompanied by any change of the mass. This may indicate a phase transformation of the dehydrated products. However, it was difficult to correlate the temperatures and shapes of these peaks with the composition of the samples.

Fig. 2 shows the X-ray diffraction patterns of the samples: HD, Cs_2D , Cs_4D , Cs_5D , $Cs_{5.5}D$ and Cs_6D basing on which indexing was performed. Only weak reflexes of the crystalline hydrated heteropolyacid HD at $2\theta = 6.52^\circ$, 7.65° and possibly at 9.38° as well as at 17.57° appear in the X-ray diffraction pattern of Cs_2D sample. Cs_2D exhibits a quite distinct series of peaks at $2\theta = 6.73$, 9.75 , 12.16 , 13.68 , 24.45 , 25.65 and 28.64° which are not observed in a series of samples containing more cesium: Cs_4D , Cs_5D , $Cs_{5.5}D$ and Cs_6D . On the other hand, the patterns of all the samples show the same reflexes as the fully substituted cesium salt Cs_6D , namely 7.82 , 9.37 , 24.68 and 25.45° . The reflex 8.87° is found in patterns of all samples containing Cs.

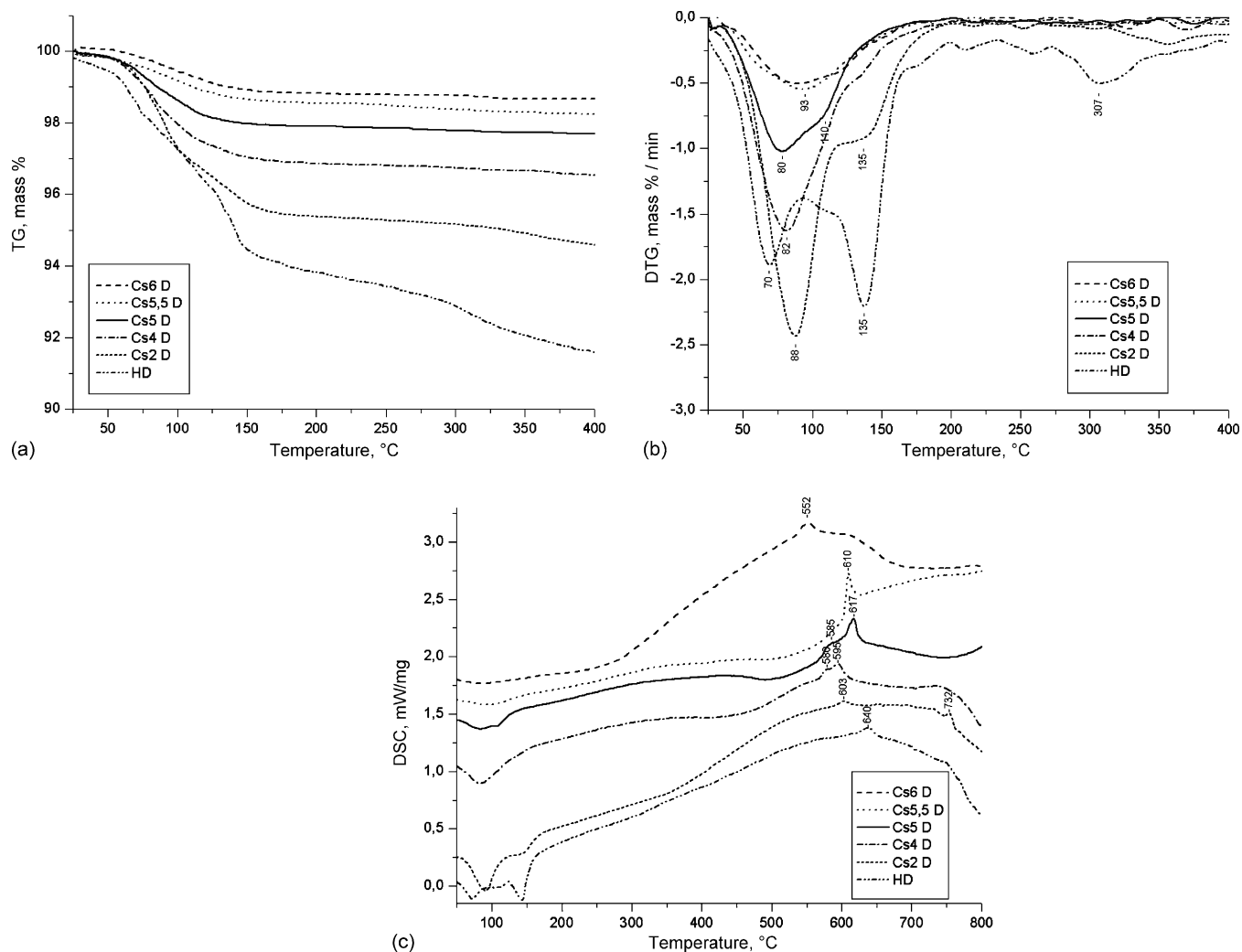


Fig. 1. Thermogravimetric analysis of cesium salts: (a) TG, (b) DTG and (c) DSC curves; rate heating $25^{\circ} \text{ min}^{-1}$.

The best results of indexing of diffraction patterns for all cesium containing samples were found in $P2_1/m$. The main crystal data are collected in Table 1. Pure HD acid crystallizes in $P2_1/m$ space group [16]. Both of these space groups and the changes

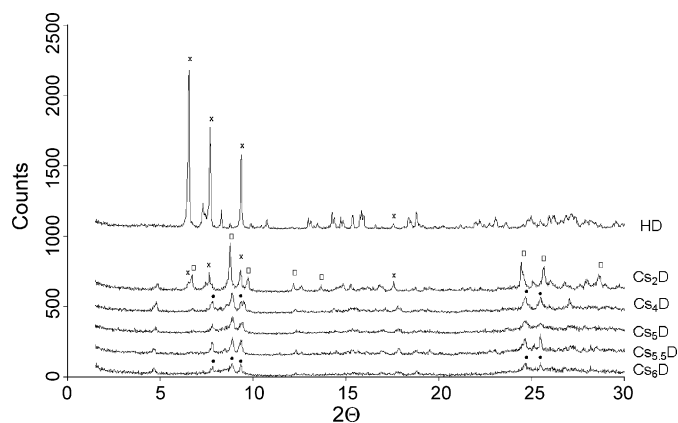


Fig. 2. The X-ray diffraction patterns of HD, Cs_2D , Cs_4D , Cs_5D , $\text{Cs}_{5.5}\text{D}$ and Cs_6D samples. Signs (x) and (●) mark the main reflexes characteristic for HD and Cs_6D , respectively; as (□) were marked reflexes of Cs_2D which were not found in Cs_6D and HD patterns.

of b period as well as values of other parameters imply high structural similarity of HD and all its cesium salts.

For samples containing not less than four cesium cations per Dawson anion the lattice parameters a , b and β are constant but period c increases with an increase of cesium concentration, which indicates the most probably substitution of cesium cations to the structure.

The attempts of indexing of Cs_2D diffraction pattern using only one phase was unsuccessful. The reasonable interpretation comes from the assumption of two coexisting phases; one of which close to structure of HD in $P2_1/m$ space group, and the second in $P2_1/m$ similar to other cesium salts. Nevertheless, some deviations of Cs_2D lattice parameters (parameter a and c in Table 1) from higher substituted Cs salts indicate some structural diversity of this phase. Hence, it can be concluded that the sample Cs_2D contains a phase different from both crystalline hydrated heteropolyacid and all other cesium substituted salts. The composition of this phase seems to indicate $\text{Cs}_2\text{H}_4\text{P}_2\text{W}_{18}\text{O}_{62}$ compound.

As the FTIR spectra in Fig. 3 show the phase mentioned above exhibits the same skeleton vibrations of Wells–Dawson anion as all other samples including HD and Cs_6D . Hence, it

Table 1
Calculated lattice parameters and size of crystallites for crystalline HD and Cs_xD (x = 2–6) samples

| Space group | Cs ₆ D P2/m (S.G. 10) | Cs _{5.5} D | Cs ₅ D | Cs ₄ D | Cs ₂ D | HD P2 ₁ /m (S.G. 11) |
|------------------------|-------------------------------------|---------------------|-------------------|-------------------|-------------------|------------------------------------|
| Z ^a | 4 | | | | | 2 |
| a (Å) | 14.28(1) | 14.265(3) | 14.28(1) | 14.382(3) | 14.849(2) | 14.029(2) |
| b (Å) | 29.82(1) | 29.849(4) | 29.84(1) | 29.74(1) | 29.864(4) | 15.183(3) |
| c (Å) | 19.07(1) | 19.078(4) | 18.99(1) | 18.807(4) | 18.373(2) | 18.441(3) |
| β (°) | 98.3(1) | 98.8(1) | 98.73(3) | 98.67(2) | 98.26(1) | 102.11(1) |
| V (Å ³) | 8032(6) | 8027(2) | 7997(4) | 7950(3) | 8063(2) | 3841(1) |
| Crystallites size (nm) | 20(1) | 39(2) | 25(2) | 29(1) | 46(1) | 700(20) |

^a Z, number of anions in elementary cell.

can be supposed that Cs₂D phase differs from others only by an arrangement of anions and cations, which is usually called the secondary structure of heteropoly compounds.

The Cs₂D salt is the primary product of heteropolyacid titration with cesium carbonate. It was formed after two thirds of the acid had been neutralized. However, on the further addition of the titrant the products containing only Cs₆D phase covered with different amounts of free acid in Cs₄D–Cs_{5.5}D salts are obtained. This indicates that during titration and evaporation, the transformation of Cs₂H₄P₂W₁₈O₆₂ into Cs₆P₂W₁₈O₆₂ takes place. This might include recrystallisation of the primary precipitate remaining in contact with the supernatant liquid or precipitation of crystalline Cs₆D in an excess of cesium ions. Precipitation might occur if Cs₂D is slightly more soluble in water than Cs₆D. In fact the highly Cs substituted samples, examined in microscope, appear to be composed of well crystallized grains of the size of a few microns. All samples exhibit definitely small specific surface area as is shown by the data presented in Table 2.

Fig. 4a and b shows a typical catalytic run. Two samples are compared: Cs₅D and crystalline HD, indicating higher activity of cesium salt in isobutene conversion. It is seen that conversion was constant over 6 h. Selectivity towards ETBE remains at 82%. Isobutene conversion is the highest at 40 °C and decreases with

increasing temperature which is typical of exothermic reversible reactions.

The activity can be expressed as follows: by the reaction rate related to mass of catalyst $r_{\text{cat}} = \alpha F / m_{\text{cat}}$, where α denotes fractional conversion of isobutene, F feed flow expressed in mol *i*-C₄/h and m_{cat} catalyst mass in grams. Alternatively, activity can be also defined as the reaction rate related to the mass of free heteropolyacid according to the formula $r_{\text{HPA}} = \alpha F / m_{\text{HPA}}$, where m_{HPA} is mass of free heteropolyacid. Both expressions are shown in Figs. 5 and 6 as the function of the number of cesium atoms substituted in HPA. Fig. 5. shows almost linear decrease of r_{cat} value with the increasing cesium content. On the other hand, as Fig. 6 shows, the activity related to the amount of free heteropolyacid r_{HPA} (proportional to the content of protons in the sample) increases and reaches a maximum for the sample Cs₅D. It is interesting that r_{HPA} value for all samples containing cesium at $x < 5.5$ is higher than that determined for crystalline HPA (sample HD) thus indicating that in acid cesium salts protons of the remaining non-neutralized acid become more active. As the protons content was smaller the effect was higher.

Considering the results obtained for Keggin type partly substituted cesium salts, discussed in the literature, in our Wells–Dawson type samples free heteropolyacid may either remain at the surface of Cs₆D phase crystallites in form of nanoclusters (as it was observed in the case of SiO₂ and TiO₂ supports [17]) or epitaxially adsorbed. Free heteropolyacid may also form a solid solution with Cs₆D if samples have been calcined at 200–300 °C. As our samples were never heated above 95 °C, hence the higher activity of free heteropolyacid has to be attributed to the so-called dispersion effect, connected with increasing accessibility of reagents to the dispersed acid.

The behaviour of cesium partly substituted Wells–Dawson heteropolyacid salts differs from that of Keggin type cesium salts, where not only r_{HPA} but also r_{cat} reaches maximum

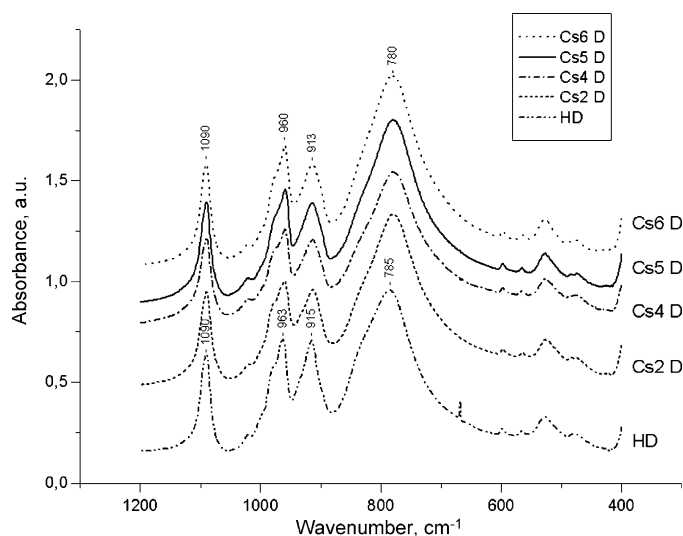
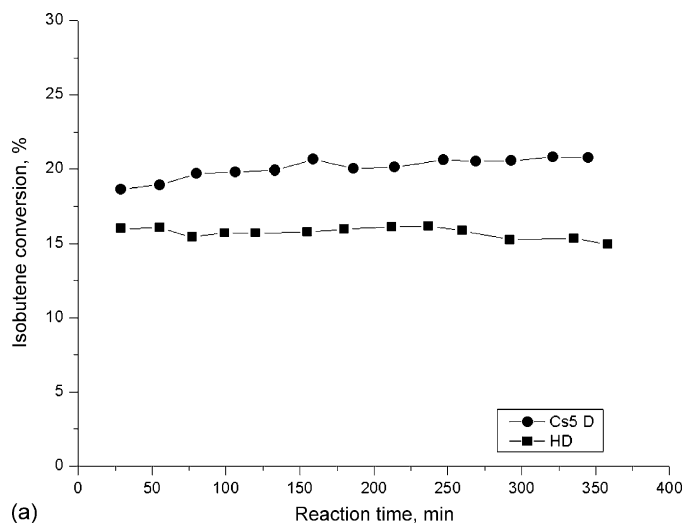


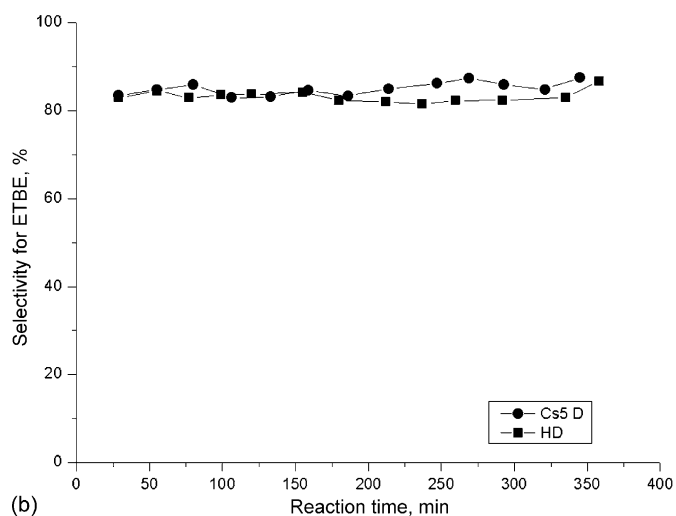
Fig. 3. FTIR spectra of cesium salts; range of Wells–Dawson structure vibrations.

Table 2
Specific surface area of cesium substituted salts Cs_xH_{6-x}P₂W₁₈O₆₂

| Sample | Specific surface area (m ² g ⁻¹) |
|---|---|
| Cs ₂ H ₄ P ₂ W ₁₈ O ₆₂ | 0.48 |
| Cs ₄ H ₂ P ₂ W ₁₈ O ₆₂ | 1.48 |
| Cs ₅ HP ₂ W ₁₈ O ₆₂ | 0.8 |
| Cs _{5.5} H _{0.5} P ₂ W ₁₈ O ₆₂ | ~0.1 |
| Cs ₆ P ₂ W ₁₈ O ₆₂ | 0.38 |



(a)



(b)

Fig. 4. Isobutene conversion (a) and selectivity for ETBE (b) at 40 °C; (■) crystalline HD sample, 0.0362 g, (●) Cs₅D salt sample, 0.25 g containing 0.0362 g of not neutralized HD.

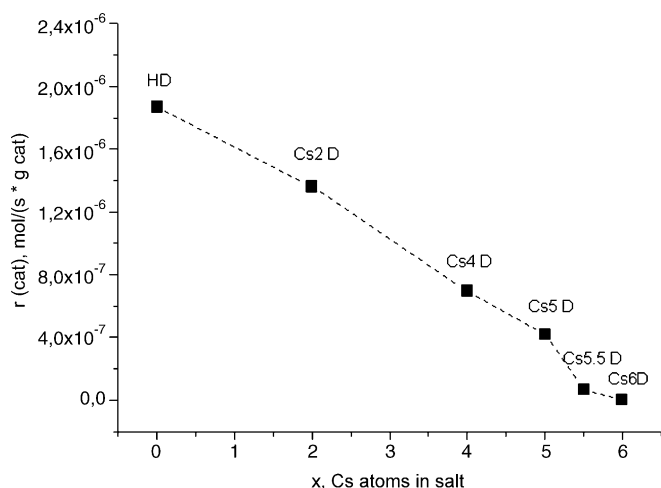


Fig. 5. Reaction rate related to mass of catalyst, r_{cat} , vs. number of cesium atoms substituted in salts.

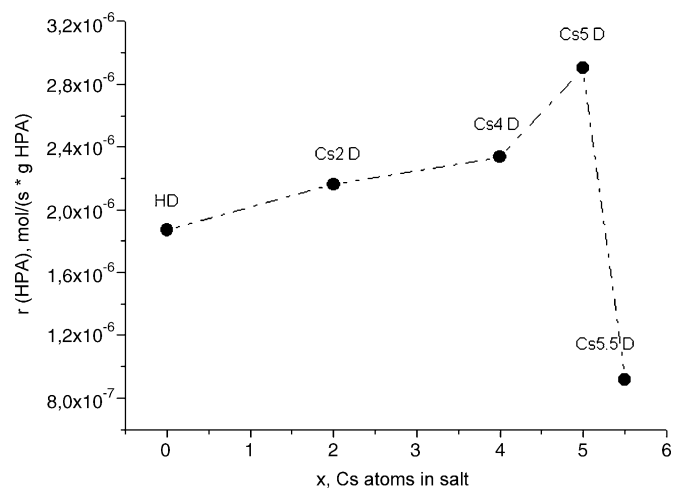


Fig. 6. Reaction rate related to mass of free heteropolyacid remaining in the sample, r_{HPA} , vs. number of cesium atoms substituted in salts.

at high substitution degree. This latter effect is evidently due to the fact mentioned above that, at $x=2.5$ in Keggin type $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$, specific surface area (small at $x=0-2$) reaches value as high as $135\text{ m}^2\text{ g}^{-1}$, while in Wells–Dawson type $\text{Cs}_x\text{H}_{6-x}\text{P}_2\text{W}_{18}\text{O}_{62}$ salts it remains low in all the samples (of order of $1\text{ m}^2\text{ g}^{-1}$). Moreover, it decreases with the increasing substitution degree. Even though we tried to obtain the product with larger surface area by both fast mixing aqueous solutions and also by using ethanol as the solvent only small increase in the specific surface area (till about $1.6\text{ m}^2\text{ g}^{-1}$) was noted.

4. Conclusions

Cesium partly substituted salts $\text{Cs}_x\text{H}_{6-x}\text{P}_2\text{W}_{18}\text{O}_{62}$ of Wells–Dawson heteropolyacid crystallize in $P2/m$ space group. Nevertheless, Cs₂D sample seems to be the primary product of heteropolyacid titration with Cs_2CO_3 with the formula $\text{Cs}_2\text{H}_4\text{P}_2\text{W}_{18}\text{O}_{62}$. Further introduction of cesium carbonate results in the transformation of $\text{Cs}_2\text{H}_4\text{P}_2\text{W}_{18}\text{O}_{62}$ into $\text{Cs}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ and highly substituted salts appeared to occur in the form of neutral salt covered with non-neutralized acid.

Wells–Dawson type partly substituted cesium salts are active catalysts in gas phase synthesis of ethyl-*tert*-butyl ether, ETBE. Their activity related to the mass of free HPA, higher than that of crystalline $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$, reaches the maximum for the sample Cs₅HP₂W₁₈O₆₂. Such behaviour may be attributed to the dispersion effect depending on the increasing accessibility of reagents to the dispersed acid.

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