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Methanolysis of Castor Oil Catalysed by Solid Potassium and Cesium Salts of 12-Tungstophosphoric Acid

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Abstract Methanolysis of castor oil to methyl esters, a key step in Biodiesel production, was studied with the use of KOH, H_2SO_4 and 12-tungstophosphoric acid ($H_3PW_{12}O_{40}$, HPW) as the homogeneous catalysts. Reaction was also performed in the presence of solid salts of HPW, namely $M_xH_{3-x}PW_{12}O_{40,}$ where M = K or Cs and x = 2, 2.5 and 3 (abbreviated as K2, K2.5, K3 and Cs2, Cs2.5, Cs3, respectively). The HPW salts were precipitated by K_2CO_3 and Cs_2CO_3 or CsCl. Their properties were characterized by BET, electron microscopy (SEM, EDS) and colloidal particles size distribution (laser diffraction technique). The potassium doped HPW samples, K2 and K2.5, prove to be much more active catalysts (ca. 3 times) than their Cs-containing analogues. Among the K, Cs salts, K2 salt was the most active catalyst. The activity of catalysts was found to depend on preparation stages such as the temperature of drying or annealing and aging of the samples. Microscopic studies evidenced colloidal form of Cs and K salts particles under the catalytic reaction. The size of colloidal particles was found to depend upon the type of cation, Cs^+ or K^+, as well as the "history" of catalysts preparation (temperature of drying). Based on the results obtained in this work, we concluded that activity was determined by the accessibility of the reactants to acid sites which is facilitated by the high surface area and open structure of the colloidal form. This may lead to better utilization of acid sites and higher activity of samples with lower content of K^+ or Cs^+ cations in the HPW.

Keywords Biodiesel · Transesterification · Castor oil · Heteropolyacid

1 Introduction

The production of biodiesel (fatty acid methyl esters, FAME) as a fuel in diesel engines greatly increased due to its environmental benefits. Biodiesel can be produced from renewable sources like vegetable oils, animal fats and recycled greases (from food industry). In transesterification with methanol (methanolysis), the triglycerides (TG) of fatty acids (C_{14}–C_{20}) are converted into respective fatty acid methyl esters (FAME) and glycerol as a by-product (Scheme 1). Transesterification reaction is catalysed by bases, acids as well as enzymes. The most commonly tested vegetable oils included palm oil, soybean oil, sunflower oil, coconut oil and rapeseed oil. Castor oil derived from *Riccinus communis* plants is mentioned frequently in the literature as a potential raw material for biodiesel, however its transesterification has been studied only by Meneghetti et al. [1, 2]. The main constituent of castor oil is triglyceride of 12-hydroxy-9-octadecenoic acid (ricinoleic acid, Scheme 1). Due to the presence of OH group at C-12 carbon, castor oil exhibits unique chemical and physical properties. For example it is completely miscible with alcohols (methanol, ethanol) even at room temperature. As a consequence, in acid and basic transesterification catalysis, castor oil and methanol form a homogeneous phase. This is not the case with typical vegetable oils (Scheme 2).

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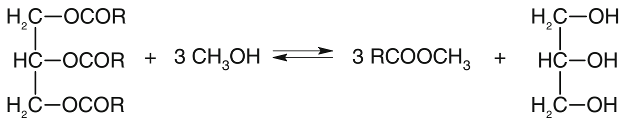
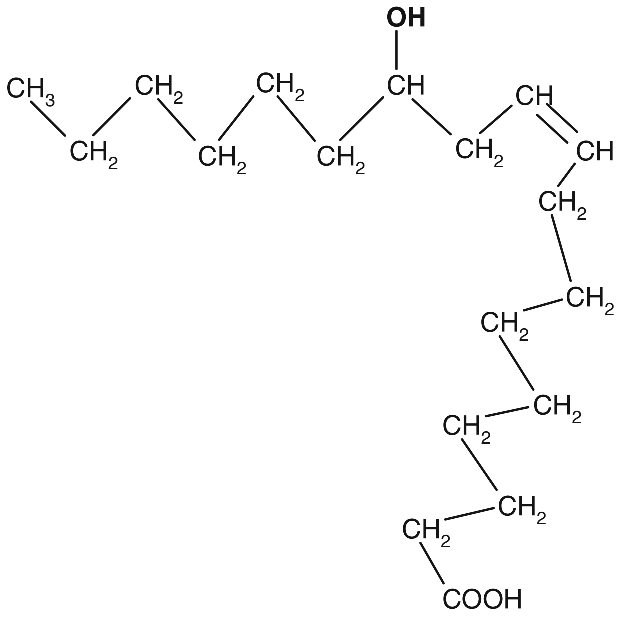


Scheme 1 Transesterification of triglyceride with methanol



Scheme 2 Ricinoleic acid

Most often the syntheses of bio-esters use homogeneous alkaline catalysts, such as K- or Na- alkoxides or hydroxides. The usage of homogeneous base catalyst suffers from significant limitation due to undesirable side reaction such as saponification, which creates serious problem of product separation. Therefore, acid catalysts have the potential to replace base catalysts [3]. However, requirement of high temperature, high molar ratio of alcohol to oil and serious corrosion problems make the use of homogeneous acid catalysts non-practical. These problems can be partially avoided by employing solid acid catalysts. In view of recently published papers [3, 4], solid acids of moderate to strong acid sites and hydrophobic surface would be preferred catalysts.

The Keggin-type heteropolyacids (HPA) present a potential interest since they are known to be very strong Brőensted acids and are effective catalysts in number of reactions (isomerization, hydration, esterification, alkylation, hydrolysis) performed in both homogeneous and heterogeneous conditions [5–13]. Heteropolyacids, namely $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, $H_3PMo_{12}O_{40}$ and $H_4SiMo_{12}O_{40}$, have already been successfully used as soluble, homogeneous catalysts in the transesterification of rapeseed oil with ethanol under mild conditions (atmospheric pressure and temperature 60–85 °C) [14]. At equivalent H^+ concentrations HPA-catalysed transesterification achieves higher reaction rates than conventional mineral acids (H_2SO_4, H_3PO_4) due to higher acid strength of HPA [15]. However, the main disadvantage of the usage of HPA is their solubility in water and polar solvents. In order to overcome this problem, the salts of HPA with large monovalent cations such as Cs^+, NH_4^+, K^+ and Ag^+ which are insoluble in water can be used. By combining various proportions of cations and heteropolyacid, a range of insoluble, microporous solid catalysts of different acidity, surface area and crystallinity can be obtained [16–21]. Insoluble salts of $H_3PW_{12}O_{40}$ consisting of various contents of NH_4^+, K^+, Cs^+ and Ag^+ cations have already been studied in number of catalytic reactions [8–13, 22].

The majority of studies have been devoted to $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (Cs2.5) salt because of its unique properties resulting in strong surface acidity and higher activity than that of parent HPW [23–25]. The results obtained by Chai et al. showed that $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ is also an excellent solid acid catalyst for the transesterification of vegetable oil (*Eruca sativa Gars)*, at temperature 20–60 °C [26]. Quite recently, cesium salts $Cs_xH_{3-x}PW_{12}O_{40}$ of various Cs content ($x = 0.9$–3) were successfully tested as the solid catalysts in methanolysis of tributyrin, a model compound of natural triglycerides [27]. In these studies, the activity of cesium salts increased with Cs content up to $x = 2.0$–2.3, then dropped rapidly. The optimum performance found for Cs loading of $x = 2$–2.3 correlated well with the density of accessible surface acid sites which was probed by α-pinene isomerization, NH_3 adsorption calorimetry and surface area measurements [27]. The NH_4^+ and K^+ salts of HPW were found to be highly active in the esterification reactions [10, 22]. Thus, insoluble K^+, Cs^+, and NH_4^+ salts of $H_3PW_{12}O_{40}$ are promising candidates as solid catalysts for esterification and transesterification reactions, i.e. for reactions proceeding in the course of bio-ester formation using natural oils. In this context, studies concerning the activity of insoluble potassium and cesium salts of $H_3PW_{12}O_{40}$ in methanolysis of natural oil, namely castor oil are undertaken in the present work. To the best of our knowledge we report for the first time on castor oil methanolysis catalysed by solid acid catalysts. In the research the activities of potassium salts with different degree of exchange, namely $K_2HPW_{12}O_{40}$ (K2), $K_{2.5}H_{0.5}PW_{12}O_{40}$ (K2.5) and $K_3PW_{12}O_{40}$ (K3), are compared with those for their Cs-HPW analogues.

2 Experimental Section

2.1 Catalysts Preparation

A commercially available 12-tungstophosphoric acid ($H_3PW_{12}O_{40}$, HPW, Merck) was used to prepare the Cs and K-salts. Prior to the salts preparation, HPW sample was analysed by DTG method to determine the content of water. To prepare potassium salts $K_xH_{3-x}PW_{12}O_{40}$ of various K contents $x = 2$, 2.5 and 3 (denoted as K2, K2.5 and K3) the solution of K_2CO_3 (POCH) was used.

The cesium salts $Cs_xH_{3-x}PW_{12}O_{40}$ of various Cs contents $x = 2$, 2.5 and 3 (denoted as Cs2, Cs2.5 and Cs3), were prepared using Cs_2CO_3 or CsCl (Aldrich) as the substrates. The corresponding salts are termed as CsX–CO_3 or CsX–Cl, respectively. The Cs or K content (x) in final salts was adjusted by the amount of precipitating solutions (Cs_2CO_3, CsCl and K_2CO_3) added.

The Cs or K-salts were prepared as described before [28]. The stoichiometric quantities of cesium carbonate, cesium chloride or potassium carbonate were added to aqueous solutions of the 12-tungstophosphoric acid. The concentrations of HPW and potassium or cesium salts solutions were 0.10 M and 0.04 M, respectively. The preparations were performed at ambient temperature without stirring. In standard procedure, the resulting white colloidal solution of Cs, K-salts was slowly evaporated overnight in the oven at 313 K to dryness. In some cases, the evaporation of colloidal solution was carried out at higher temperature, 353 K. The resulting solid was ground into white powder.

Prior to the catalytic tests all the samples were dried at 393 K in order to remove water of crystallization.

2.2 Characterization of Catalysts

2.2.1 Nitrogen Physisorption Measurements

The specific surface areas of samples were calculated from the nitrogen adsorption–desorption isotherms at 77 K in an Autosorb-1, Quantachrome equipment. Prior to the measurements, the samples were preheated and degassed, under vacuum at 473 K for 2 h.

2.2.2 Scanning Electron Microscopy

The studies were carried out by means of electron microscope JSM-5800 (Jeol) coupled with an energy dispersive X-ray spectrometer Link ISIS 300, Oxford Instruments Ltd. (Si[Li] detector, ATW-atmospheric thin window, resolution 131 eV for MnKα at 10,000 counts). EDS analysis was performed by means of Field Emission Scanning Electron Microscope JEOL JSM-7500 F.

2.2.3 Colloid Particles Characterization

The size distribution of catalyst particles in the colloidal solution after the precipitation of cesium or potassium salts was analyzed using Laser Diffraction Particle Size Analyzer LS 13 320 (Beckman Coulter Inc.). The sizes of particles were measured in the range of 40 nm to 2,000 μm.

2.3 Catalytic Tests

The transesterification reaction was carried out in a 100 cm^3 glass reactor at atmospheric pressure. Reactor was equipped with a reflux condenser, magnetic stirrer, and a tube for sampling the solution. Reaction was performed using 0.5 g of catalyst, 6 g of castor oil, and 7.6 cm^3 of methanol (Fluka).

This composition corresponded to molar ratio of methanol/oil/catalyst equal to 29/1/0.025. In catalytic experiment castor oil and internal standard (eicosane) were introduced to the reactor and heated up to 60 °C. Methanol was introduced and after reaching temperature of 60 °C the catalyst was added. Typically, methanolysis was carried out for 3 h at 60 °C and the samples were withdrawn at appropriate time intervals. The analysis of methyl esters was performed with a gas chromatograph PE Clarus 500 equipped with a flame ionisation detector under conditions: capillary column Elite-5 MS (30 m × 0.25 mm × 0.25 μm coating) with helium as a carrier gas (flow rate 1 mL/min) and the injection temperature 260 °C. Product separation was obtained using temperature ramp 120 °C for 1 min, 10 °C/min to 180 °C, 7 °C/min to 260 °C hold for 15 min.

HPLC analysis was used to determine the composition of starting castor oil. In selected catalytic experiments the concentration change of castor oil during the methanolysis reaction was analysed by HPLC. The analysis was carried out under following conditions: chromatograph Knauer K-500, RI detector, column SiO_2 10 cm × 0.2 cm, $d_p = 5$ μm, mobile phase n-heptane, 12 vol.% THF, 2 vol.% diisopropylether, 0.2 vol.% diglyme, flow rate 1 cm^3/min. For the analysis 100 μL of the sample (castor oil or reaction mixture) was added to 1 cm^3 of mobile phase.

The results of HPLC analysis showed that castor oil (Microfarm, Poland) was composed entirely (ca. 90%) of triglyceride of ricinoleic acid. From HPLC analysis trace amounts of di- and mono-glycerides of ricinoleic acid and free ricinoleic acid were also observed. By using analytical standards, the content of free ricinoleic acid was determined to be below 0.1 wt%.

GC analysis showed that methanolysis of castor oil produced bio-esters composed entirely of methyl ricinoleate (87.44 wt%) and trace amounts of methyl-esters of typical fatty acids. Using analytical standards the content of methyl esters of linoleic, oleic, stearic, palmitic, linolenic and others acids was determined to be 5.05, 3.88, 1.4, 1.28 and 0.56, 0.39 wt%, respectively. These analytical results showed that the composition of our castor oil was practically the same as that reported by Drown et al. [29]. Thus, for the castor oil molecular weight of 928 g/mol was assumed [29].

For GC analysis the sample of reaction mixture (40 μL) taken from the reactor was added to 1 cm^3 of hexane. Then, the mixture was shaken to separate the catalyst and the solution obtained after filtration was analysed by GC method. A sample (1 μL) of this solution was injected to GC and fatty acid methyl esters (FAME) were quantified using an internal standard method.

To determine the maximum yield of methyl esters the methanolysis of castor oil was performed in the presence of soluble KOH at the same methanol to oil ratio. Reaction was carried out up to the complete transformation of all triglycerides present in castor oil to methyl esters, controlled by HPLC.

The obtained methyl esters were separated from glycerol phase by extraction (3 times) with hexane–water. Then, the upper phase was evaporated to remove hexane and weighted. The known amounts of methyl esters were analysed by GC using the same procedure as the one in typical analysis. The area of GC peaks for individual fatty acid methyl esters were calculated and their cumulative content was assumed to be the maximum yield (100%) corresponding to complete methanolysis of our castor oil. For the calibration curves the mixtures were prepared by weighing known amounts of castor oil, methanol and methyl esters obtained in methanolysis of castor oil (in the presence of KOH). The individual components were mixed in proportions corresponding to various conversions of triglycerides, from 5 to 100%. From the obtained areas of GC peaks the calibration factors were calculated and they were used to determine the yield of methyl esters in catalytic studies. Thus, the methyl esters yield in catalytic experiments was expressed in terms of the percentage of methyl esters produced.

In selected catalytic experiments the composition of reaction mixture in the course of methanolysis was determined by HPLC. These experiments were performed taking into account that methanolysis is a consecutive reaction proceeding via di- and mono-glycerides. In all studied solutions, the content of triglycerides decreased against reaction time, whereas no peaks originating from di- and mono-glycerides were observed.

For the microscopic studies (SEM) the catalysts (Cs, K-salts) were separated from the reagents solution after the methanolysis of castor oil by centrifugation performed several times.

3 Results and Discussion

3.1 Methanolysis of Castor Oil in Homogeneous Conditions

To obtain general information concerning the yield of methyl esters (FAME) which can be achieved from the present castor oil conventional catalytic systems including KOH and H_2SO_4 as the homogeneous catalysts are studied. It should be stressed that in both cases, acid and base-catalysis, all the reagents form a homogeneous mixture because castor oil is well soluble in methanol.

The activities of homogeneously acting KOH and H_2SO_4 catalysts are compared in Fig. 1 presenting the yield to bio-ester against reaction time. The results clearly show that efficiency of acid-catalysis is of similar order to that of alkaline catalysis. This finding is close to that observed by Meneghetti et al. [1, 2]. On the other hand, for typical vegetable oils like rapeseed, sunflower, etc. which are not miscible with methanol and form separate phases, homogeneous acid-catalysed transesterification is ca. 4,000-times slower process compared to base-catalysed reaction [3, 4]. As mentioned before, this different behaviour of castor oil–methanol system may be related to the structure of triglyceride of ricinoleic acid, which contains OH group. In our investigations methanolysis of castor oil was also studied in the presence of homogeneously acting $H_3PW_{12}O_{40}$ acid (Fig. 2). Prior to the catalytic tests the HPW sample was dried for 18 h at 503 K as reported earlier [14]. Methanolysis of castor oil was performed using various concentrations of HPW and the obtained HPW activity was compared to that of H_2SO_4. In order to compare reactivities of HPW and H_2SO_4, specific activity (SPC) defined as the yield to bio-ester (obtained after 30 min of reaction) related to one stoichiometric proton in HPW or H_2SO_4, was introduced (Fig. 2). The calculated specific activity (SPC) of HPA was higher than that of H_2SO_4. This result is consistent with the literature data for transesterification of rapeseed oil with ethanol in the presence of various HPA and mineral H_2SO_4 acid [14].

3.2 Heterogeneous Conditions

The acidic salts of heteropolyacids with large monovalent cations such as NH_4^+, K^+ and Cs^+ form heterophase mixtures and their final formula is an average of pure hetropolyacid and neutral salt. The Cs-salts of $H_3PW_{12}O_{40}$ at Cs >2, namely Cs2 and Cs2.5 formed solid solution of HPW in neutral cesium salt [24]. The structure of $K_xH_{3-x}PW_{12}O_{40}$ salts with the content of K^+ cations changing within the range $2 \leq x < 3$ consists of $K_3PW_{12}O_{40}$ core covered by surface layer of amorphous $H_3PW_{12}O_{40}$ [28, 30]. It has been shown that in fresh K2 and K2.5 salts

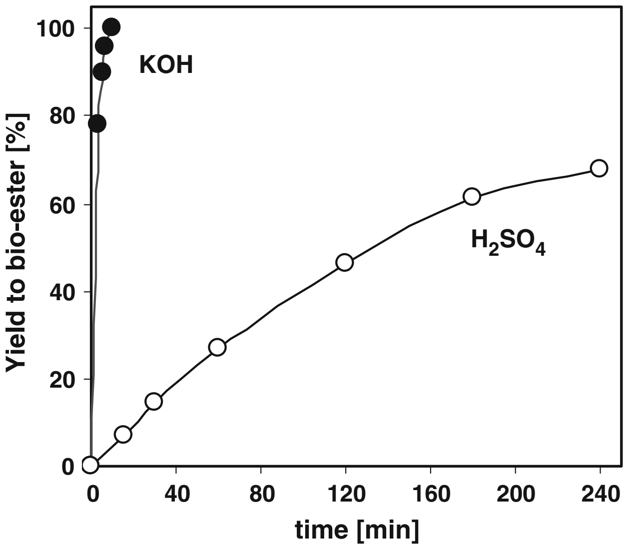


Fig. 1 Formation of methyl esters (percentage yield) in the transesterification of castor oil with methanol catalysed by conventional homogeneous catalysts KOH and H_2SO_4. The reaction conditions were: molar proportion of MeOH/oil/OH^- or H^+ = 29:1:0.05, temperature 60 °C

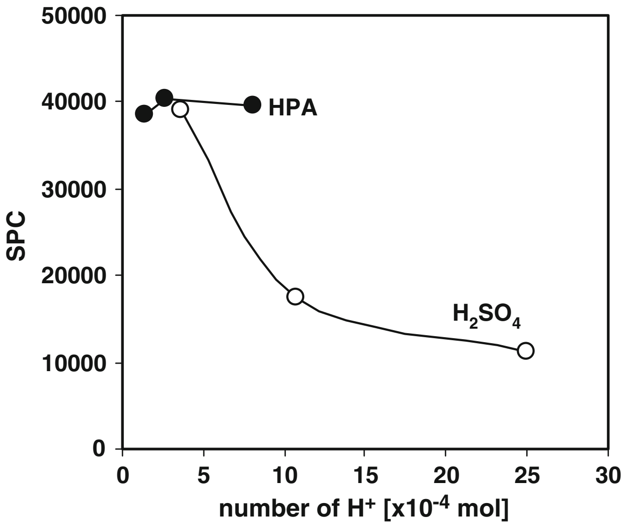


Fig. 2 The comparison of HPW and H_2SO_4 activity. Specific activity (SPC) defined as the yield to bio-ester after 30 min of reaction, related to one stoichiometric H^+ in acids

obtained after drying the salts precipitates at 313 K the heteropolyacid is deposited in the bulk form on the neutral K3 core. Aging of the salts at room temperature brings the spreading of HPW over the surface of the K3-core with the formation of epitaxial surface layer evidenced by the XRD, XPS and ^{31}P MAS NMR techniques. The transformation of the bulk HPW into a surface layer covering the K3-core took place between 2 and 7 days of samples aging at room temperature. Moreover, drying of salts at higher temperature i.e. 353–363 K accelerated the process of HPW spreading. This resulted in the increase of specific surface area of the K2 and K2.5 salts. DTA-TG experiments revealed that HPW existed on the surface of K3-core in the form of at least partially dehydrated phase [28]. Such a dehydrated HPW is not stable as a separate phase and can exist only because it is stabilized by the K3-core support. The coverage of the K3-core by HPW in the K2-salt was estimated to be equal to one monolayer while in K2.5 this coverage was much lower than 1 monolayer [28]. To the best of our knowledge, no information concerning the role of aging in the morphology of Cs-salts has been reported. However, taking into account literature suggestion concerning an analogy between the structure of acidic cesium and potassium salts of $H_3PW_{12}O_{40}$, in the present work, freshly prepared and aged Cs and K salts of $H_3PW_{12}O_{40}$ were studied in the methanolysis of castor oil. Moreover, the salts obtained by drying freshly precipitated samples at higher temperature i.e. at 353 K were also investigated.

3.3 Cs-salts of $H_3PW_{12}O_{40}$

Literature data showed that the surface area of Cs-salts prepared from Cs_2CO_3 changed with the extent of Cs substitution (x) for proton in $H_3PW_{12}O_{40}$ [11, 31]. The surface area of pure HPW 5 m^2/g decreased as x increased to 2 and for Cs2 the surface area as low as only 0.5–1 m^2/g was observed by number of authors [11, 31]. However, the surface area greatly increased as x exceeded 2 and become as high as ca. 130 m^2/g when $x > 2.5$, i.e. for Cs2.5 sample [11]. The same relationship between the Cs content and surface area is observed for our Cs–CO_3 catalysts (Table 1). The specific surface area of HPW is determined to be 5 m^2/g, the one of Cs2–CO_3 is lower and equal to 1 m^2/g, whereas Cs2.5–CO_3 salts exhibits the surface area as high as 136.7 m^2/g.

In the present work the Cs-salts were also precipitated using CsCl reagent. This reagent was used because it produced Cs2 salt of remarkably larger specific surface

Table 1 Cesium salts of HPW, physicochemical properties and activity in the transesterification of castor oil Activity data for 1 year storage samples

Sample	Specific surface area [m^2/g]	Colloidal particles size[a] [nm]	Yield to bio-ester after 180 min [%]
Cs3–CO_3	119.8		0.62
Cs3–Cl			
Cs2.5–CO_3	136.7	135	3.1
Cs2.5–Cl	135.0		2.6
Cs2–CO_3	1	125	19.2
Cs2–Cl	78.2	120	19.4

[a] Determined by laser diffraction technique

area than that prepared from Cs_2CO_3 solution [10, 32]. This effect is observed for our Cs2 salts. As shown in Table 1, the specific surface area of Cs2–Cl sample is amounted to 78.2 m^2/g whereas that of Cs2–CO_3 is equal to 1 m^2/g. No difference in specific surface areas is observed for differently prepared Cs2.5 samples, as for both samples they are similar and equal to 136.7 and 135 m^2/g.

The morphology of both Cs2–CO_3 and Cs2–Cl salts was studied by scanning electron microscopy and the obtained images are reported in Fig. 3. Literature survey shows that the particles of Cs-salts obtained by the precipitation from aqueous solutions are in the form of irregular aggregates of size within wide range [33, 34]. This shape is also observed for our Cs2–CO_3 and Cs2–Cl samples.

The catalytic activities of Cs-salts in methanolysis of castor oil are collected in Table 1. As the measure of activity the yield to methyl-esters (Y %) determined after 3 h of reaction was assumed. In these experiments the samples dried at 313 K and aged for 1 year are studied.

As shown in Table 1, the Cs3 sample exhibits only trace activity in methanolysis of castor oil. The yield to bio-ester determined after 3 h of reaction is very low, below 1%. The activities of both Cs2.5 catalysts are only somewhat higher. Distinctly higher activities are obtained for both Cs2–CO_3 and Cs2–Cl catalysts. It can be seen that although the specific surface areas of the latter Cs2–CO3 and Cs2–Cl catalysts strongly differ, (1 m^2/g and 78.2 m^2/g, respectively) their activities are practically the same. This may indicate that their specific surface area determined by N_2-sorption (BET) for solid samples is not a crucial variable for their activity in methanolysis of castor oil.

For the most active Cs2–CO_3 catalyst the influence of catalyst concentration in solution on the yield to bio-ester was studied and the obtained results are plotted in Fig. 4a, b. As Fig. 4a shows the yield to bio-ester [Y, %] increases when the content of Cs2–CO_3 salt in solution grows. In Fig. 4b the yield to bio-ester obtained after 30 min of reaction as a function of Cs2–CO_3 catalyst concentration is plotted. The observed linear increase of Y against the

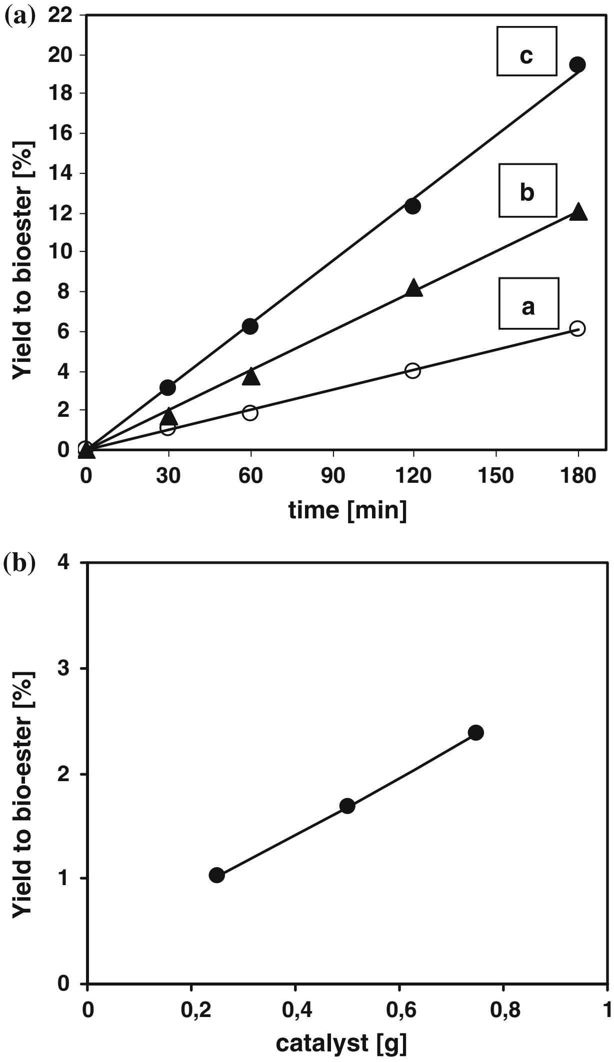
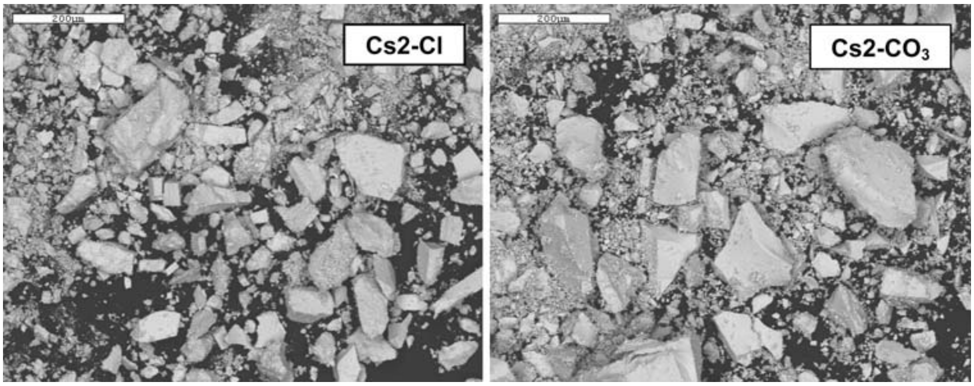


Fig. 4 Formation of methyl esters (percentage yield) in the methanolysis of castor oil in the presence of Cs2–CO_3 catalyst. The reaction conditions were: molar proportion of MeOH/oil = 29:1 temperature 60 °C. (**a**) the effect of catalyst concentration (**a**) 7.95×10^{-5}, (**b**) 15.9×10^{-5}, (**c**) 23.8×10^{-5} mol per 6.5×10^{-3} mol of oil n the reactor. (**b**) The yield to bio-ester after 30 min of reaction as a function of catalyst amount [g] in the reactor

Fig. 3 Scanning electron micrographs of Cs2–CO_3 and Cs2–Cl salts (freshly prepared samples, dried at 313 K)



catalyst amount indicates that mass-transport of reactants to external surface of catalyst particles does not affect activity.

In methanolysis of castor oil the activity of freshly prepared Cs2–CO_3 salts was also evaluated. The catalysts were obtained by drying the precipitate of Cs2–CO_3 salt at standard temperature 313 K as well as at higher temperature 353 K. Moreover, the Cs2–CO_3 sample was additionally annealed at 573 K (for 18 h). The obtained yields to bio-ester against reaction time are displayed in Fig. 5. It can be seen that in the presence of all three freshly prepared Cs2 salts the yield to bio-esters (ca. 10–14%) is lower than that obtained in the presence of aged Cs2 catalysts (ca. 20%) (Table 1); (Fig. 5). Freshly prepared Cs2 sample dried at 353 K exhibits higher activity than the Cs2 sample dried at standard temperature 313 K. Moreover, annealing of Cs2 sample (dried at 313 K) at 573 K leads to further increase in activity. Thus, temperature treatment of freshly precipitated Cs2 salt influences its transesterification activity. This effect may be explained assuming that temperature of drying influences the secondary structure and morphology of Cs2 particles. Moreover, the size of catalyst particles, irregular aggregates (Fig. 3), may be influenced by the method of drying. However, it can not be excluded that similarly as in the case of potassium salts, treatment of samples at higher temperature facilitated spreading of $H_3PW_{12}O_{40}$ onto the surface of Cs3-core.

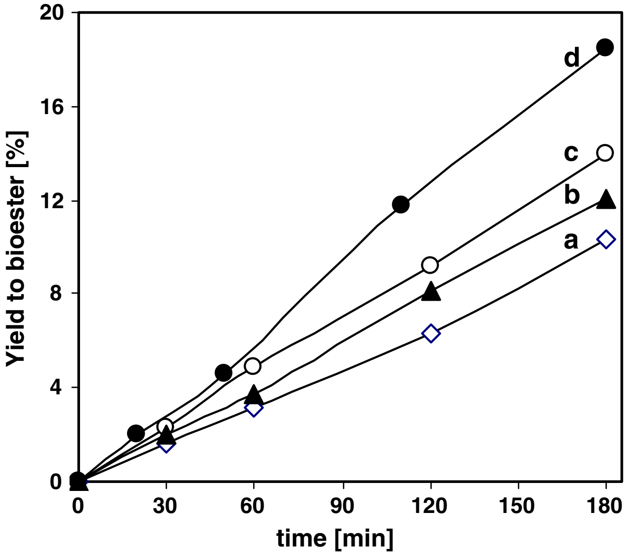


Fig. 5 Formation of methyl esters (percentage yield) in the methanolysis of castor oil performed in the presence of Cs2–CO_3 salts, (**a**) freshly prepared sample dried at 313 K, (**b**) freshly prepared sample dried at 353 K, (**c**) sample dried at 313 K and subsequently annealed at 573 K, (**d**) aged sample. The reaction conditions were: molar proportion of MeOH/oil/catalyst = 29:1:0.025, temperature 60 °C

3.4 K-salts of $H_3PW_{12}O_{40}$

Literature data showed that in the case of K salts, the change of the surface area with the content of K^+ cation in $H_3PW_{12}O_{40}$ was rather loose, not so much evident as for Cs-salts [9]. A relatively small change in surface area is also observed for our K-salts differing in the potassium content (Table 2). The specific surface area of K-salts increases only slightly from 100.4 m^2/g for K2–CO_3 to 114.5 m^2/g for fully neutralized K3–CO_3 salt. The SEM micrographs registered for these salts are shown in Fig. 6. It can be seen that all three, K2, K2.5 and K3-salts are in the form of spherical particles. However, the size of spherical particles strongly decreases when the content of potassium in the $H_3PW_{12}O_{40}$ increases. From the SEM images the size of spherical particles of K2 salt is estimated to be within the range 1.9–2.2 µm. The particles of K2.5 salt are smaller, 1–1.5 µm in size. Complete substitution of protons in HPW by potassium in K3-salts brings the smallest particles of sizes within the range 0.4–0.6 µm.

Methanolysis of castor oil was studied in the presence of freshly prepared and 1 year aged K-salts.

The activities (yield to bio-ester determined after 180 min of reaction) of aged K-salts are collected in Table 2. In the presence of fully exchange K3-salt the yield to bio-ester after 3 h of reaction is very low, below 1%, similarly to that of C3-salt. On the other hand, both K2.5 and K2 salts are very active. The most active is K2–CO_3 salt and its activity is ca. 3.8 times higher than that of

Table 2 Potassium salts of HPW, physicochemical properties and activity in the transesterification of castor oil. Activity data for 1 year aged salts

Sample	Specific surface area [m^2/g]	Particle size Powdered sample[b] [µm]	Colloidal particles size[a] [nm]	Yield to bio-ester after 180 min [%]
K3–CO_3	114.5	0.4–0.6		0.69
K2.5–CO_3	105.8	1–1.5	110	10.3
K2–CO_3	100.4	1.9–2.2	50	37.8

[a] Determined by laser diffraction technique

[b] Evaluated from the scanning electron microscope images

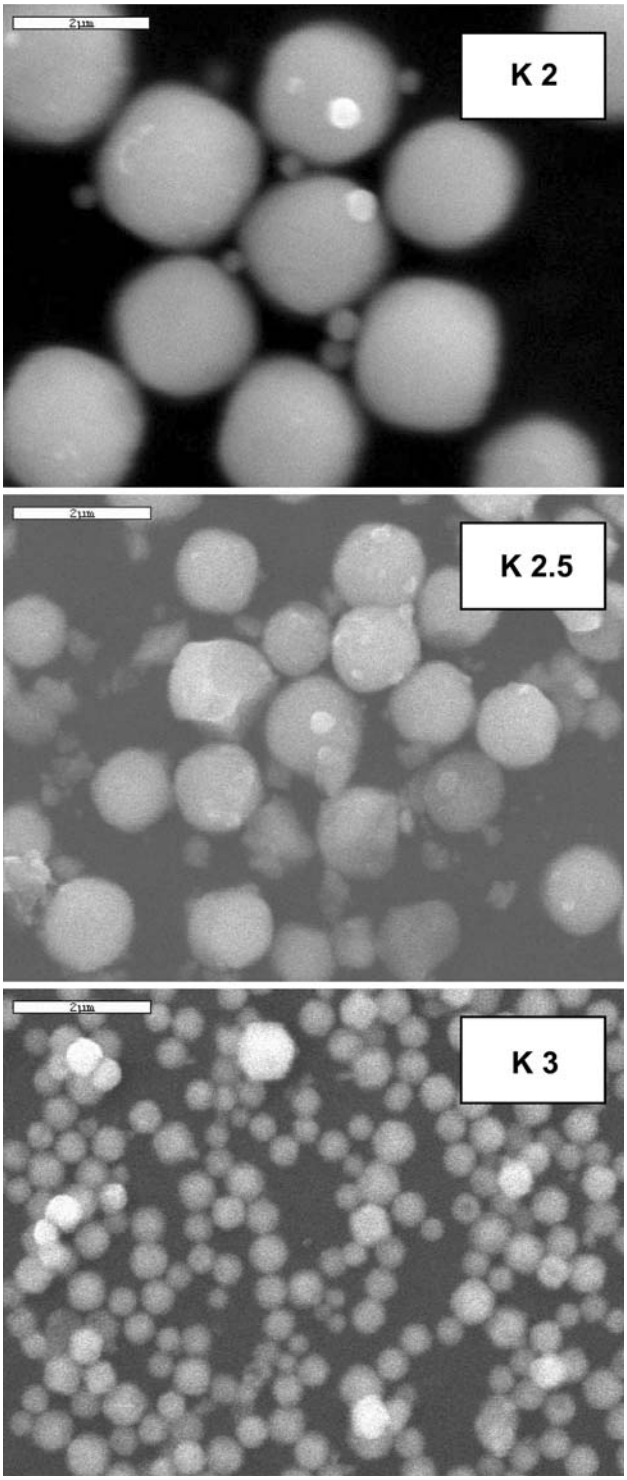


Fig. 6 Scanning electron micrographs of K2, K2.5 and K3 salts (freshly prepared samples, dried at 313 K)

K2.5–CO_3 salt. Thus, the activity of K-salts increases when the content of potassium in $H_3PW_{12}O_{40}$ decreases.

It can be seen from the data in Tables 1 and 2 that both K2 and K2.5 salts are more active than their Cs-analogues. Detailed comparison of activities for potassium and cesium doped HPW shows that the activity of both K-salts, K2 and K2.5, are about 2 times higher than the activities of their Cs-analogues.

For the most active K2-salt the effect of sample aging is examined. It should be noted that aging of the samples resulted in the increase in their surface areas. The surface area of freshly prepared K2 and K-2.5 samples amounted to 79.2 m^2/g and 98.7 m^2/g increased to 100.4 m^2/g and 105.8 m^2/g, respectively. No change was observed for K3–CO_3 sample. As described before, these changes in surface areas were related to the change in secondary structure of K-salts identified as enhanced spreading of HPA onto the K3-core [28].

The yields to bio-ester against reaction time for methanolysis performed in the presence of freshly prepared (dried at 313 K and 353 K) and aged K2-salts are compared in Fig. 7. Similarly to the Cs2–CO_3 salt, the activity of aged K2-salt is higher than those of two freshly prepared K2-salts. The aging affect is also checked for the K2.5-salt. However, in contrary to the K2-salt, freshly prepared and aged K2.5 salts exhibit practically the same activity (Fig. 7).

Owing to attractive performance of Cs and K salts of HPW, it seems interesting to perform leaching studies to determine whether HPW present in the salt was released into the reaction. As described before, it is assumed that the K2 and Cs2 salts are composed of the K3/Cs3-core coated by less or more-spreading amorphous HPW.

The acidic K, Cs salts, however, formed colloidal suspension in reaction mixture. Therefore the separation of catalyst by means of simple filtration and recovering of the catalysts was not easy. For microscopic studies, the catalysts were separated from the reagent solution by centrifugation. The samples of K2 and Cs2 salts, before and after the methanolysis were studied by the EDS technique. X-ray microprobe analysis for W, K and Cs elements was performed in several points for the samples of catalyst before and after methanolysis reaction. The values of W/K or W/Cs ratios calculated from the data of EDS analysis (wt%) are taken into consideration. One can expect that removing of HPW from the catalyst under the catalytic reaction would lead to lower content of W in the reused catalyst. As a consequence in the case of reused catalyst, the ratio of tungsten to potassium or cesium (W/K or W/Cs) would increase. The EDS analysis shows the value of W/K ratio equal to 22.86 for our K2-salt before reaction and 21.17 for the reused catalyst. Similarly, the W/Cs ratios obtained for initial and reused Cs-2 salts are close, equal to 11.3 and 9.5, respectively. Thus, both K2 and Cs2 salts are stable catalysts under the conditions used in the transesterification of castor oil confirming previously observed heterogeneous mode of their action.

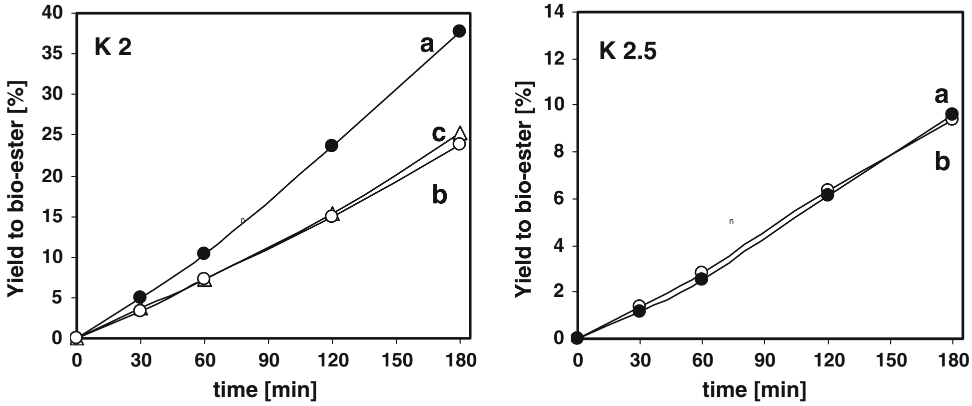


Fig. 7 Formation of methyl esters (percentage yield) in the methanolysis of castor oil performed in the presence of K2 and K2.5 salts (**a**) aged sample, (**b**) freshly prepared sample dried at 313 K, (**c**) freshly prepared sample dried at 353 K. The reaction conditions: molar proportion of MeOH/oil/catalyst = 29:1:0.025, temperature 60 °C

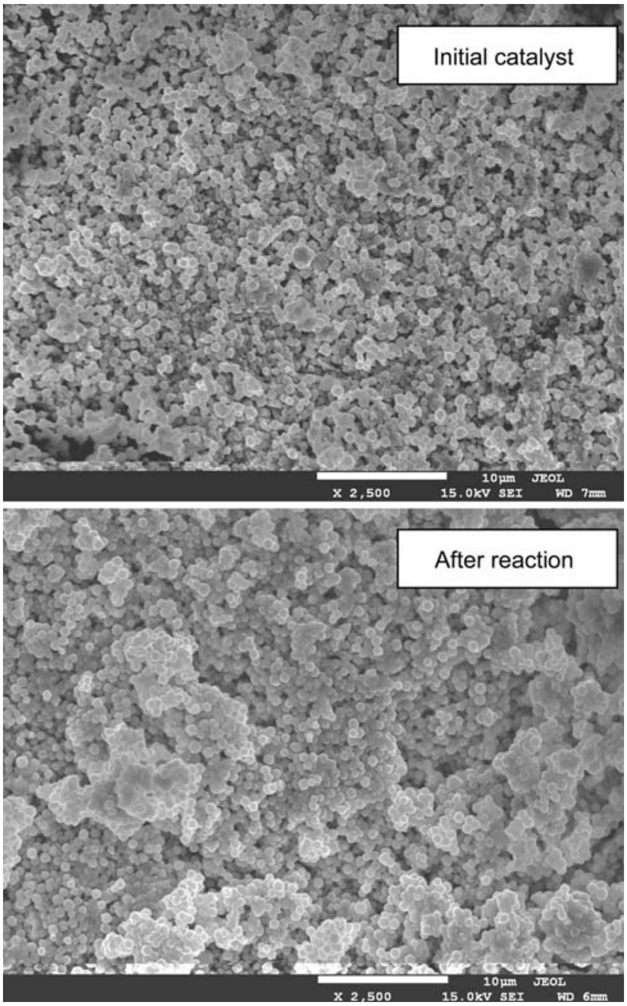


Fig. 8 Scanning electron micrographs of K2 salt before and after methanolysis reaction (freshly prepared samples, dried at 313 K)

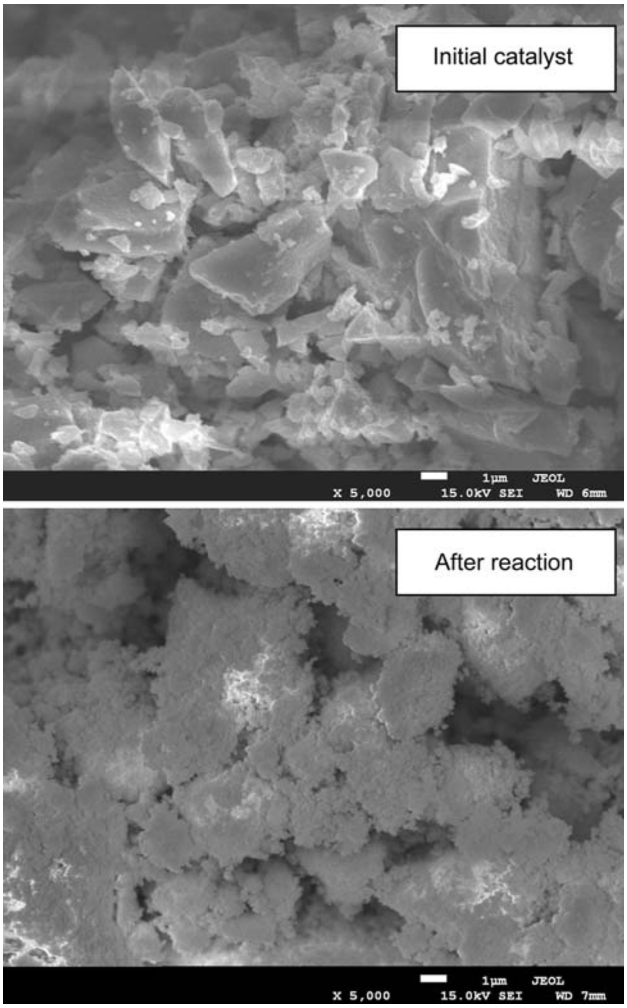


Fig. 9 Scanning electron micrographs of Cs2 salt before and after methanolysis reaction (freshly prepared samples, dried at 313 K)

Interesting effects concerning the morphology of initial and reused catalysts are also provided by the SEM studies. The micrographs of initial and reused catalysts are displayed in Figs. 8 and 9 for K2 and Cs2 salts, respectively. It can be seen that the morphologies of initial and reused salts remarkably differ and the change in morphology during the methanolysis reaction is especially distinct in the case of Cs2–CO_3 salt (Fig. 9). The irregularly shaped particles of starting Cs2–CO_3 catalyst (Fig. 3) are rearranged after the reaction to irregularly shaped aggregates composed of spherical particles of very uniform diameters (Fig. 9). This may indicate that Cs2–CO_3 salt is in colloidal state under the catalytic reaction and colloidal particles are formed in contact with reaction medium. The latter observation seems to be important as it indicates a high complexity of the catalytic system during the methanolysis of castor oil catalysed by the K and Cs salts of $H_3PW_{12}O_{40}$.

Literature data showed that the Cs salt of HPW readily dispersed in highly polar medium such as water or alcohol forming a colloidal suspension because they consist of very fine crystal particles (ca. 10 nm in average) [35–37]. For the Cs2.5 dispersed in water laser diffraction technique afforded the size of the particles distributed from 40 to 200 nm with predomination of the particles of ca. 90 nm in size. This size was about 10-times larger than the size of primary particles—crystallites (the Keggin anions arranged in a body-centered cubic manner with countercations, Cs, H, K) of salts [35, 36].

In order to obtain more information concerning the "colloidal state" of our Cs2 and K2 salts, the particle size measurements were performed in the colloidal solutions of the Cs2–CO_3 and K2 salts. At first, the measurements were performed in water solutions after the precipitation of the K2 and Cs2–CO_3 salts (Figs. 10a and 11a). After evaporation of these colloidal solutions in the oven at 313 K to dryness, the obtained white powders of Cs and K2 salts were again dispersed in water and the measurements of particles size distribution were subsequently performed (Figs. 10b and 11b). The obtained distribution profiles demonstrate that the size of colloidal particles and the contributions profiles strongly depend on the type of cation, Cs^+ or K^+ but especially on the "history" of sample.

It is observed that the Cs-salts formed larger colloidal particles than the K-salts. Furthermore, in the colloidal solutions of Cs2–CO_3 and Cs2–Cl the particles of similar diameter ca. 120–125 nm dominate and they are slightly smaller than the particles dominating in solution of Cs2.5 salt, 135 nm. The particles of the smallest size ca. 50 nm appear in the solution of K2 salt (Fig. 10b). They are about 2 times smaller compared to those of K2.5 salt, ca. 110 nm in size (Tables 1 and 2).

From the colloidal particles size distribution profiles (Figs. 10 and 11) one can conclude that the role of samples "history", drying and aging, in the transesterification activity may be related not only to effect of $H_3PW_{12}O_{40}$ spreading. This role may be to some extent a consequence of the change in the size of colloidal particles formed in reaction medium.

To summarize, catalytic data obtained in methanolysis of castor oil show that the activity of K-salts is higher than those of Cs-salts. Moreover, for both K and Cs-salts, the activity decreases when the content of K^+ or Cs^+ in the $H_3PW_{12}O_{40}$ increases and the most active is K2 catalyst.

Acidic salts (K^+, Cs^+, Ag^+, $NH_4{}^+$) of $H_3PW_{12}O_{40}$ with various contents of cations are known to be effective catalysts for various kinds of acid-catalysed reaction. Among the acidic salts, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was found to be an excellent solid acid catalyst exhibiting the activity comparable or even higher than pure HPW.

The excellent activity of Cs2.5 has been inferred to be due to very high "surface acidity" and an appropriate porosity [17, 35]. The acid amount on the surface which is called 'surface acidity" was estimated by Okuhara [17]

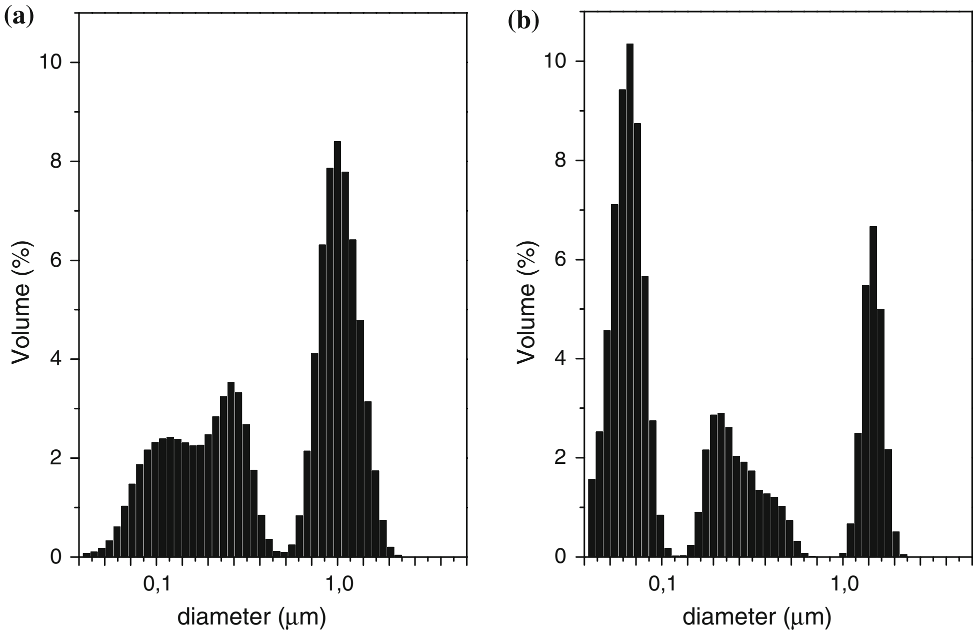


Fig. 10 The distribution diagram of particle size for K2 salt, (**a**) colloidal solution after precipitation of salt, (**b**) colloidal solution obtained after re-dispersion of salts dried at 313 K

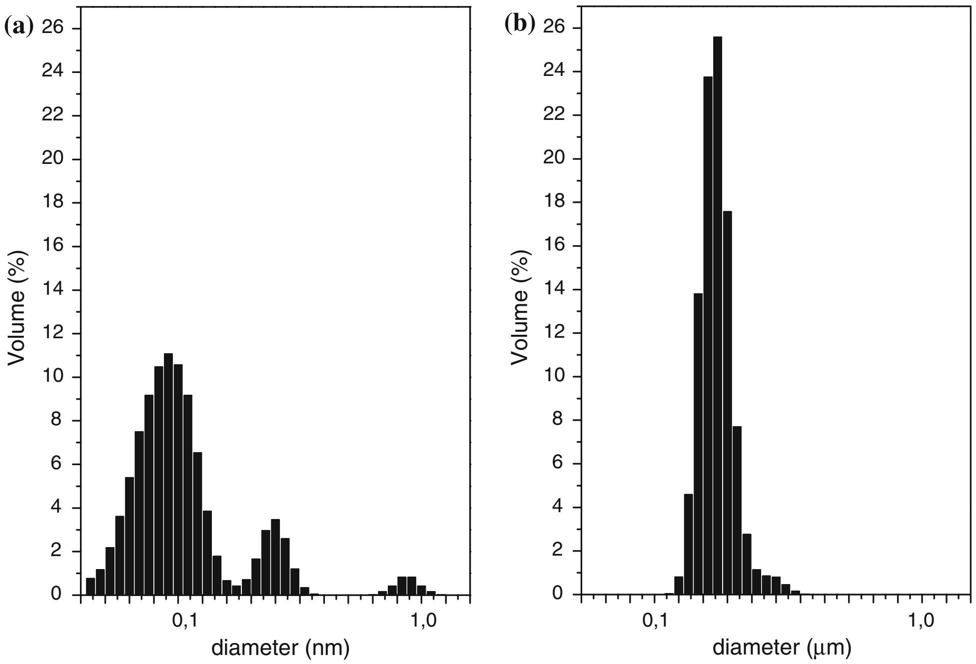


Fig. 11 The distribution diagram of particle size for Cs2–CO_3 salt, (**a**) colloidal solution after precipitation of salt, (**b**) colloidal solution obtained after re-dispersion of salts dried at 313 K

form the surface area and the formal concentration of proton attached to the polyanion. These calculations show that the surface acidity decreases at first with the Cs content, but sharply increases when x exceeds 2. The maximum appeared at $x = 2.5$ (Cs2.5) and indeed in numerous reactions the Cs2.5 salts exhibited much higher activity than the Cs-salts of lower and/or higher Cs content. The "surface acidity" parallels very well the catalytic activity of Cs-salts in reactions classified as "surface type". These reactions are the ones involving nonpolar molecules such as hydrocarbons (butene isomerization, butane cracking, propene oligomerization, n-butane isomerization, cracking of C_6–C_8 alkenes and aromatics alkylation [13]) which are unable to penetrate the bulk of a heteropoly compounds. It implies that the reaction occurs mostly on the surface acids of the heteropoly compounds [13, 38]. In these reactions the activity of acidic salts of HPA does not correlate with the total proton content of the catalyst, but with the "surface acidity". This correlation was observed for alkylation of 1,3,5-trimethylene with cyclohexene [11] and alkylation of isobutane with 2-butene [13].

On the other hand, polar molecules such as water, alcohols and esters can easily penetrate the bulk structure between the anion and the counterions (H^+) accessing to all the protons. The reactions may proceed in the bulk of heteropoly compounds at the state called the "pseudo-liquid phase" [38]. For example, the activity of K-salts of HPW in dehydratation of ethanol and hydration of ethylene decreases stepwise when the number of K^+ cations in HPW increased going from the $K_{0.5}$ to the K_2 salt, parallel as the acidity of catalyst originating from the presence of $H_3PW_{12}O_{40}$ decreases [39]. Similarly, in the esterification of acetic acid and isoamyl alcohol a straight correlation of activity with the acidic characteristics of $H_3PW_{12}O_{40}$ and its partially substituted Cs and K salts was observed [10].

Narasimharao et al. studied tributyrin transesterification to methyl butyrate and palmitic acid esterification in the presence of $Cs_xH_{3-x}PW_{12}O_{40}$ salts of various Cs contents, ranging from $x = 0.9$ to $x = 3$ [27]. At Cs content below $x = 2$ and above $x = 2.3$ the activity of catalysts was low. The optimum performance was reached at the Cs content corresponding to $x = 2.0$–2.3 [27]. The activity relations were consistent with the acidity measurement showing the greatest number of accessible surface acid sites at Cs loading of $x = 2$–2.3. Similarly, in methanolysis of castor oil the activity of Cs2 catalyst is much higher than that of Cs2.5 and K2 catalyst is much more active than the K2.5 sample.

On the other hand, as described before, the Cs salt of HPW readily dispersed in highly polar medium such as water or alcohol forming a colloidal suspension [35–37]. When acidic salts Cs_xH_{3-x} $PW_{12}O_{40}$ of various Cs contents (ranging from $x = 0.9$ to $x = 3$) were studied in the hydrolysis of ethyl acetate performed in an excess of water the salts particles formed a colloidal solution [37]. In these conditions their activity decreased monotonously with increasing Cs content or decreasing acidity, whereas the surface area increased abruptly from less than 10 m^2/g (Cs1, Cs2) to 130 m^2/g at $x > 2$ (Cs2.5). This activity change was related to the bulk (formal) acidity of the Cs salts [37].

Similar effects are observed in our reaction mixture composed of castor oil and methanol in which the particles of K and Cs salts are in colloidal states. It can be expected that their activity will be determined by the accessibility of the reactants to acid sites which is facilitated by the high surface area and open structure of the colloidal form. This may lead to better utilization of acid sites and higher activity of samples with lower content of K^+ or Cs^+ cations in the HPW. The observed highest activity of K2 salt may be therefore related to the smallest size of colloidal particles in its solution. Moreover, in the colloidal suspensions of Cs2–CO_3 and Cs2–Cl salts the particles of similar sizes appear and this may explain practically the same activity of these two catalysts.

Although the Cs and especially K salts of HPW prove to be very active in the methanolysis of castor oil they formed colloidal suspension in reaction medium and recovering of the catalysts was not easy. This problem can be solved by immobilization the salts on support like silica and such studies are under progress.

4 Conclusions

Potassium and cesium salts of various level of HPW proton exchange $M_xH_{3-x}PW_{12}O_{40,}$ where $M = K$ or Cs and $x = 2$, 2.5 and 3 (K2, K2.5, K3 and Cs2, Cs2.5 Cs3) were prepared using K_2CO_3,Cs_2CO_3 and/or CsCl reagents, respectively. The obtained salts were tested in the transesterification of castor oil with methanol.

Microscopic studies evidenced colloidal form of Cs and K salts particles under the catalytic reaction. The size of colloidal particles was found to depend on the type of cation Cs^+ or K^+ as well as the "history" of catalysts preparation (temperature of drying). The potassium doped HPW samples, K2 and K2.5 prove to be much more active catalysts (ca. 2 times) than their Cs-containing analogues The relationship between the activity of K-salts and the level of K doping was identical to that for Cs-doped HPW. The activity of K2 and Cs2 salts was higher than those of K2.5 and Cs2.5 and the K2 salt was the most active catalyst. Based on the results obtained in this work, it can be concluded that activity is determined by the accessibility of the reactants to acid sites which is facilitated by the high surface area and open structure of the colloidal form. This may lead to better utilization of acid sites and higher activity of samples with lower content of K^+ or Cs^+ cations in the HPW.

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