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Catalytic activity of heteropoly tungstate catalysts for ethanol dehydration reaction: Deactivation and regeneration

Orsina Verdes*, Viorel Sasca, Alexandru Popa, Mariana Suba, Silvana Borcanescu

"Coriolan Dragulescu" Institute of Chemistry, Bl. Mihai Viteazul 24, 300223 Timisoara, Romania

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ABSTRACT

The pure and palladium doped 12-tungstophosphoric acid - $H_3PW_{12}O_{40}$ (HPW) and its cesium salts $Cs_xH_{3-x}PW_{12}O_{40}$ (x = 1, 2, 2.25 and 2.5) were prepared and characterized by thermal analysis, FTIR, XRD, BET and XPS methods. In this paper were determined the optimal reaction temperature and the effect of palladium on the coke content during the dehydration of ethanol in the temperature range of 200 − 350 °C. Above 300 °C, a strong deactivation of the catalysts was caused by coke formation. The catalytic tests demonstrate that by supporting the HPW and Pd_yPW (y = 0.15, 0.2 and 0.25) on mesoporous molecular sieve SBA-15 the catalytic activity in ethanol dehydration reaction was improved. Palladium doping of HPW/SBA-15 significantly decreases the formation of coke deposit. The formation of coke during the ethanol dehydration does not affect the Keggin structure which led us to conclude that such catalysts can be regenerated in air and regain their catalytic activity for a short time.

1. Introduction

Heteropoly acids (HPAs) and their metal salts can be used as excellent catalysts for both acid-catalyzed reactions and oxidation reactions due to their acidic and redox properties, which can be controlled at molecular level. The high activity and unique selectivity of these HPAs depends on the bulk type property. One of the most studied reactions is ethanol dehydration over 12-tungstophosphoric acid - $H_3PW_{12}O_{40}$ (abbreviated as HPW). In this case, large amounts of polar molecules reactant are adsorbed into the interstitial spaces of the polyanions (primary structures) and react inside the bulk solid. These HPAs exhibit a so-called "pseudo-liquid" behavior. Unfortunately, their small surface areas (< 10 m^2/g) and low thermal stability lead to a hinder practical utilization [1–3]. These problems can be overcome by two methods: synthesis of water-insoluble acidic salts by substitution of acidic protons with large counter cations (NH_4, Cs, and so on) [4–6] or by immobilizing them onto high surface area supports (oxide supports) to improving the dispersion of the active phase [7–10].

By substitution of H^+ with cesium, important modification takes place on the surface area and pore structure. These salts exhibit microporous/mesoporous structures and high surface area in comparison to the parent acid. The $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (abbreviated as Cs2.5 P W) is usually the most active solid acid for many reactions due to strong acidity and large number of acidic protons on the surface [1,6]. Based on the proposed model for microstructure of $Cs_xH_{3-x}PW_{12}O_{40}$ and $Pd_yCs_xH_{3-x}PW_{12}O_{40}$ have been explained the high activity of Cs2.5 P W, where HPW monolayers have embedded the core of $Cs_3PW_{12}O_{40}$ (abbreviated as Cs3PW) [11,12].

Impregnating the HPAs on the mesoporous silica support such as SBA-15 [7–10] and MCM-41 [13,14] significantly increases the specific surface area which is very important for heterogeneous catalysis reactions. These supports also can influence the acidity and catalytic activity of the catalysts. SBA-15 is the most often used support for HPAs due to his high surface area (up to 1000 m^2/g) and larger pore diameters, which allow easy penetration of the reacting molecules to the active sites.

Several methods have been developed to prepare the HPAs supported onto SBA-15 [7–10]. Among the most used are the sol-gel [7] and impregnation [8–10] methods which lead to a uniform distribution of the active phase in catalysts sample. For HPW supported on silica, ^1H NMR showed that the presence of two heteropolyacids forms deposits on the surface of silica namely bulk crystalline phase and a other resulting from the interaction between SiOH group and acid [15].

A serious problem of the HPA catalysts is their deactivation, i.e. the loss of catalytic activity with time-on-stream (TOS) in industrial processes, due to the poisoning of the active site or/and the pore blockage [16]. By studying the effect of temperature on coke formation were obtained two kinds of coke: non-polyaromatic formed at low

* Corresponding author.
E-mail address: orsinaverdes@yahoo.com (O. Verdes).

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temperatures, below 200 °C and polyaromatic at high temperatures, above 350 °C [17–19].

Doping of solid acid catalyst with palladium enhances catalyst regeneration by coke combustion for propene oligomerization on palladium-doped HPW/SiO_2. The effect of Pd on coke combustion (in air) was observed by TGA/TPO method. In the absence of palladium, the coke burns at approximately 450 °C and by doping with palladium the coke burns at 350 °C (below the temperature of decomposition for HPW). In the case of pure HPW/SiO_2 catalyst a mixture of hard and soft coke was form in contrast with palladium doped catalyst in which only soft coke was detected [18,19].

The amount of total coke can be determined by recording the weight changes by TG-DTA technique [20]. This method involves different heat treatments to remove adsorbed water, as well as adsorbed reactants and volatile products. The coke precursors are removed from the catalyst by increasing the temperature up to 600 °C in N_2 atmosphere, while the hard coke is removed by burning in air.

This work concerns to a study of the optimal temperature reaction and coke formation in the gas phase ethanol dehydration using pure and palladium doped catalysts. The synthesized catalysts were supported on SBA-15 mesoporous molecular sieve in the concentration loading of 30 wt. %. The deactivation and air regeneration of the compounds were also examined. For the clarity of discussion, some data obtained for pure and Pd doped heteropoly tungstate catalysts presented in our previous papers [11,12,21] are also given.

2. Experimental

2.1. Catalysts preparation

The $Cs_xH_{3-x}PW_{12}O_{40}$ salt with Cs contents x = 1, 2, 2.25 and 2.5 (denoted as CsxPW) were prepared by precipitation method from an aqueous solution of the HPW (purchased from Merck) by adding a required stoichiometric quantity of counter-ion salts as $CsNO_3$ under stirring as it was described in detail earlier [21].

The HPW doped with 0.15, 0.20 and 0.25 at Pd/Keggin Unit (KU) namely $Pd_{0.15}H_{2.7}PW_{12}O_{40}$ (Pd0.15 P W), $Pd_{0.20}H_{2.6}PW_{12}O_{40}$ (Pd0.2 P W) and $Pd_{0.25}H_{2.5}PW_{12}O_{40}$ (Pd0.25 P W) were prepared through the reaction between $Pd(NO_3)_2$ and HPW 0.1 M aqueous solutions in the proper ratio. The samples were stirring at 60–70 °C, until a paste was obtained.

The $Cs_xH_{3-x}PW$ salts doped with 0.25 at Pd/KU (denoted as Pd0.25CsxPW) were prepared by adding an amount of $Pd(NO_3)_2$ as aqueous solution 0.1 M into the HPW aqueous solution 0.1 M and after, the required stoichiometric quantity of $CsNO_3$ (aqueous solution) was poured drop by drop under continues stirring. The pH was kept under 1.5 during all syntheses. The suspensions of precipitate were heated at 60 − 70 °C under stirring until a paste was obtained.

The synthesized compounds were: $Pd_{0.25}Cs_1H_{1.5}PW_{12}O_{40}$ (Pd0.25Cs1PW), $Pd_{0.25}Cs_2H_{0.5}PW_{12}O_{40}$ (Pd0.25Cs2 P W), $Pd_{0.25}Cs_{2.25}H_{0.25}PW_{12}O_{40}$ (Pd0.25Cs2.25 P W) and $Pd_{0.25}Cs_{2.5}$ $PW_{12}O_{40}$ (Pd0.25Cs2.5 P W). Finally, all the catalysts were heated at 250 °C, 1 h in air, for nitrate anion total decomposition.

SBA-15 was synthesized according to Zhao et al. [22] by the hydrolysis of tetraethyl orthosilicate (TEOS) using Pluronic P123 block copolymer as surfactant. The HPW and PdyPW (y = 0.15, 0.20 and 0.25) were impregnated by aqueous incipient wetness onto SBA-15 mesoporous molecular sieve as loading of 30 wt. % concentration. To obtain a monolayer array of HPC on SBA-15 the size of Keggin unit was considered. According to the literature data, the size of the Keggin unit has been reported as 10 Å [23], 12.5 Å by X-ray crystallography [24] and 11.7 Å by STM [25]. In our calculation, the diameter value of the Keggin-type molecule was 12 Å.

2.2. Characterization methods

The thermal analyses were carried out using a thermo analyzer system Mettler TGA/SDTA 851/LF/1100. The measurements were conducted in dynamic atmosphere of air (50 ml/min), using the alumina plates crucibles of 150 µl. Heating rate was of 10 °C /min in the range of temperature 25 − 600 °C and the mass samples were about 30 mg.

The FTIR absorption spectra were recorded with a Jasco 430 spectrometer (spectral range $4000 - 400\ cm^{-1}$ range, 256 scans, and resolution $2\ cm^{-1}$) using KBr pellets for the all synthesized heteropoly compounds after their keeping in air at room temperature until to constant mass.

Powder X-ray diffraction data were obtained with X'Pert PRO MPD PANalytical diffractometer with the following measurement parameters: Theta/Theta PW3050/60 Goniometer, PixCEL detector, zero background sample holder (Si), Ni-filtered CuK_α radiation, 45 kV/30 mA, continuous scanning, step size 0.0130 [2θ] in the 2θ range 2–60°.

The specific surface areas of samples were calculated from the nitrogen adsorption-desorption isotherms using a Quantachrome instrument, Nova 2000 series. Prior to the measurements the samples were preheated and degassed at 250 °C for 2 h.

The Brunauer-Emmet-Teller (BET) surface area and pore diameters calculated by Barrett-Joyner-Halenda (BJH) method applied to the desorption branches of the isotherms were determined [26]. From X-ray peak broadening is possible to calculate the crystallite size (D) using Scherrer equation:

$$D = 0.9\lambda/(\beta-\beta_o)\cos\theta \quad (1)$$

where: λ is X-ray wavelength (CuK_α) in angstroms (1.54 Å), θ the diffraction angle, β the line width (in radians) and β_o the instrumental line width (in radians). The crystallite size was estimated from the full width at half maximum of diffraction peak. It is well known that the cesium salts of Keggin type heteropoly acids possess a porous structure and a partial substitution of H^+ from HPW with Cs^+ will lead to an increase in surface area and pore structure [4,5,26].

For XPS studies the samples were pressed into tablets with a few tenth of mm thickness and 1 cm diameter. Sample treatments were performed in a high pressure cell directly attached to the analysing chamber. SPECS instrument was equipped with a PHOIBOS 150 MCD-9 hemispherical electron energy analyser operated in the FAT mode. K_α radiation of a magnesium anode (h_ν = 1252.6 eV) was used as excitation source. X-ray gun was operated at 180 W power and the pass energy was set to 20 eV. The binding energies were calibrated with respect to the position of C 1s to compensate for possible charging effect. Commonly five scans were added to get a single spectrum.

2.3. Catalytic reaction

The ethanol dehydration was performed in a flow microreactor (stainless steel tubular reactor of 10 mm inner diameter), which was placed into an electric furnace. The microreactor temperature was adjusted by a temperature controller within ± 1 % in the temperature range of 200 − 350 °C. The catalysts sample was placed in the middle of the reactor and supported by quartz packing at both ends. The amounts of unsupported and silica-supported catalysts introduced in reactor were 100 and 330 mg, respectively.

Liquid ethanol (99.8 % Riedel de Haën) was introduced by a Hamilton syringe pump at a flow rate of 1.2 ml/h into an evaporator heated at 150 °C. The nitrogen flow was kept constant at 30 ml/min.

The composition of the reactor effluent stream was analysed by gas chromatograph equipment with a flame ionization detector (FID). For separation of the products were used a stainless steel packed columns of 3 m long and 1.5 inner diameter packed with Porapak QS 80–100 mesh.

A temperature program (hold the temperature at 50 °C for 5 min, increase the temperature up to 200 °C with a heating rate of 20 °C /min. and maintain the temperature for 12 min at 200 °C) was used in GC analysis. The methane, C_2 (ethane, ethylene), C_3 (propane, propene), C_4 (butane, butane), C_5 (pentane, pentene), C_6 (hexane, hexane) and diethyl ether (DEE) compounds have been detected. The main reaction products have the following retention times: ethylene at 5.6, ethanol at 14.8 and diethyl ether at 18.8 min. The formation of aromatic compounds, such as benzene, toluene and xylene cannot be excluded, but their amounts are below the detection limit. All the connection lines were heated at 150 °C to prevent condensation. Prior to the reaction catalysts were pre-treated "in situ" under the nitrogen flow at 250 °C for 1 h.

The ethanol conversion and ethylene selectivity were calculated based on the carbon balance as follows:

$$\text{Ethanol conversion} = \text{moles of ethanol reacted} \times 100/\text{moles of ethanol in the feed} \quad (2)$$

$$\text{Selectivity} = \text{moles of product} \times 100/\text{moles of reacted ethanol} \quad (3)$$

2.4. Thermal analysis of spent catalysts

Coking was analyzed by temperature-programmed oxidation (TGA/TPO) method on the same thermo analyzer system, Mettler TGA/SDTA 851/LF/1100. Experiments were carried out using about 20 mg samples into alumina crucibles of 150 µl. The heating rate was 10 °C /min in the range of temperature 25 − 650 °C with an isothermal step at 300 °C for 30 min. The measurements were conducted in dynamic atmosphere of nitrogen (50 ml/min) and finally under flow of air for 30 min to oxidize the catalysts. By switching from N_2 to air at the same flow rate, the remaining coke deposited on the catalysts was burnt out.

The amount of coke precursor present in the catalysts was calculated as difference between the initial mass of spent catalyst sample after isothermal heating at 300 °C (temperature of reaction test) and the sample mass heated in nitrogen at 650 °C. Soft coke is removed from the samples through volatilization in inert nitrogen and refers to high molecular weight aliphatic oligomers. The amount of hard coke present in the catalysts was calculated as difference between samples mass heated in nitrogen at 650 °C and mass loss of sample at 650 °C in air, when the coke was burnt out. Hard coke refers to heavy polynuclear aromatics. The sum of coke precursor and hard coke represent the total coke.

3. Results and discussion

3.1. Thermal stability and water content

The thermal decomposition of pure and palladium doped HPW and its cesium salts takes place between 25 and 650 °C and was studied in detail in our previous papers [12,21,31]. For easier tracking of subsequent experiments, some considerations from the previous papers are given below.

The TG-DTA profile for these HPCs exhibits three main peaks: (1) a peak at a temperature below 110 °C, corresponding to the loss of physisorbed water (the amount depending on the number of hydration waters in the sample); (2) a peak in the temperature range of 110 − 300 °C corresponds to the loss of water molecule, in which the waters are hydrogen-bonded to the acidic protons to form the $[H_2O\ldots H^+\ldots OH_2]$; and (3) a peak over 300 °C due to the loss of constitutional water and decomposition of Keggin structure with formation of corresponding oxides (WO_3 and P_2O_5). The tungsten oxide crystallizes between 570 and 590 °C with exothermic effect on the DTA curves.

The number of protons, respectively Brönsted acidity were determined by thermal analysis from TG curve and calculated from constitutional water (the water formed from the protons and the oxygen of the $[PW_{12}O_{40}]^{-3}$). All values are identical to those obtained from TPD of n-butyl amine method [21]. For all synthesized heteropoly compounds the results are summarized in Table 1.

Table 1
Protons number per KU, surface area, pore volume, average pore diameter and crystallites size of catalysts.

Catalyst	H^+/KU	Surface area (m^2/g)	Pore volume BJH_{Des} (cc/g)	Average pore diameter BJH_{Des} (nm)	Size of nano-crystallites (D) from the Scherrer equation (nm)
SBA-15	–	725	1.100	6.2	–
HPW	2.87	3	0.002	2.4	57.5
HPW/SBA-15	–	194	0.175	6.6	–
Cs1PW	1.93	5	0.012	3.6	17.5
Cs2 P W	1.02	17	0.022	3.4	14.5
Cs2.25 P W	0.73	54	0.048	3.2	14.5
Cs2.5 P W	0.50	130	0.119	2.4	11.7
Pd0.25 P W	2.46	5	0.001	3.8	53.2
Pd0.25 P W/SBA-15	–	323	0.644	7.8	–
Pd0.25Cs1PW	1.52	4	0.011	3.8	28.4
Pd0.25Cs2 P W	0.51	15	0.021	3.8	18.9
Pd0.25Cs2.25 P W	0.43	49	0.043	3.7	18.8
Pd0.25Cs2.5 P W	0.31	98	0.057	3.4	18.6

On the other hand, in the case of pure and palladium doped HPW supported on SBA-15 (Figs. 1 and 2) appear the same endothermic peak around 70 °C but the amount of the removed hydrated water is higher than for unsupported composites. This phenomenon occurs due to thermal overlap effects of the desorbed water from the silica surface and to the loss of HPC physisorbed water.

In the temperature range 110–300 °C a continuous loss of sample mass is proceeding owing to the departure of water molecules which are linked by hydrogen bonds with acidic protons and probably due to removing of some traces of the surfactants used for synthesis of mesoporous molecular sieve SBA-15. The mass loss removed between 300 and 650 °C corresponds to the constitution water (dehydroxylation) and water molecules present on the silica surface.

For both supported catalysts an exothermic peak appears on DTA curves at 590.5 and 599.5 °C and could be assigned to the decomposition of active phase and crystallization of WO_3 resulted after decomposition.

It can be noted that the supported HPW and Pd0.25 P W may be considered slightly more stable than pure catalysts, probably due to the interaction of catalyst with silanols on the surface.

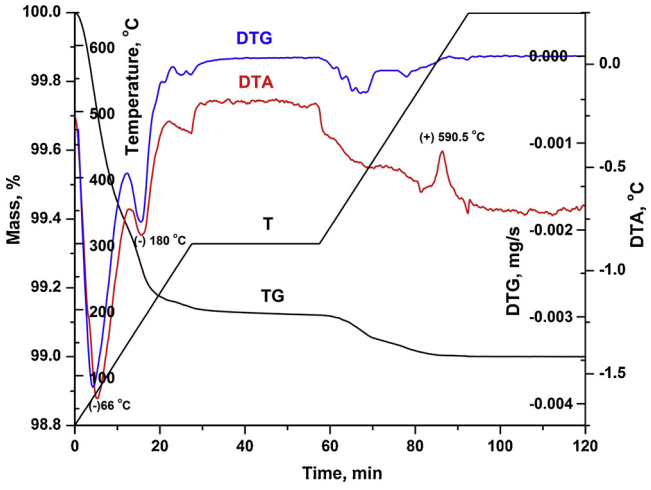


Fig. 1. TG-DTG and DTA curves of HPW/SBA-15 catalyst.

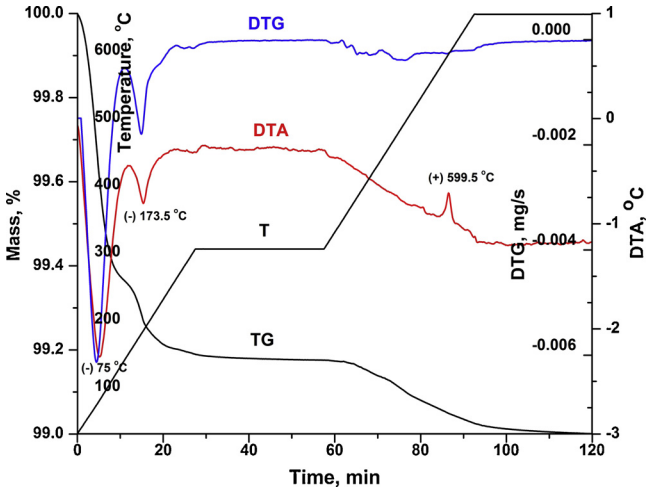


Fig. 2. TG-DTG and DTA curves of Pd0.25 P W/SBA-15 catalyst.

3.2. FTIR

The pure and palladium doped HPW and its cesium salts were characterized by FTIR and the results were briefly reported before [12,21].

FTIR spectra represent a real fingerprint of the Keggin structure for these heteropoly compounds. The Keggin anion has four types of oxygen, which give four characteristic bands in the range $700-1200\ cm^{-1}$. These bands could be assigned to the typical vibrations of Keggin unit ($PW_{12}O_{40}^{3-}$) at 1080, 986, 890, 789 and 576 cm^{-1} which were assignable to the vibrations of ν_{as}(P-O_i), ν_{as}(W = O_t), corner-sharing ν_{as}(W-O_c-W), edge-sharing ν_{as}(W-O_e-W) and δ(O-P-O), similar to the literature data [27–29].

In the case of cesium salts the intensity of the adsorption bands increase with the increasing of Cs content, more precisely due to high content of neutral cesium salt according of $Cs_xH_3PW_{12}O_{40}$ model microstructure [11,12]. The position of these bands may also change due to the interaction between cesium cation and host lattice [6].

In order to determine the state of the HPW and Pd0.25 P W species impregnated into the mesoporous siliceous matrix, the FTIR spectra were recorded (Fig. 3). It is well known [30] that SBA-15 shows the characteristic four major bands as follows: at 1100 cm^{-1} and 807 cm^{-1} (the asymmetrical stretching of the siloxane bonds Si—O—Si), 950 cm^{-1} (the stretching of the hydroxyl group in Si—OH) and 450 cm^{-1} δ(Si—O—Si) bonds. The appearance of the absorption band at 1630 cm^{-1} (adsorbed H_2O) indicates that the surface of SBA-15 contains a larger amount of water and —OH groups than HPW and Pd0.25 P W.

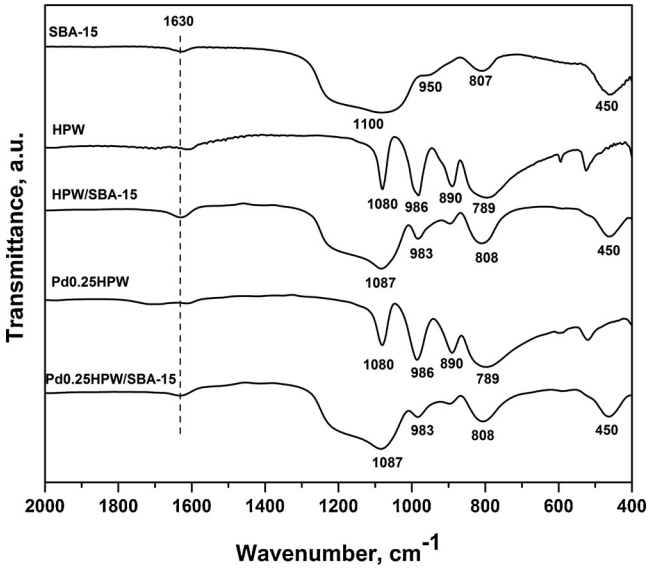


Fig. 3. FTIR spectra of HPW/SBA-15 and Pd0.25 P W/SBA-15 composites.

It should be noted that all the bands of supported HPW and Pd0.25 P W in the 1200-400 cm^{-1} range are formed by overlapping between the HPW and Pd0.25 P W with SBA-15 band. Weak bands corresponding to the primary structure of supported catalysts is due to the low concentration of acid caused by its dispersion in the silica matrix after impregnation. The slightly changes in positions of these peaks indicates that the primary structure of HPCs is retained on the surface of mesoporous SBA-15 silica.

Finally, the IR results suggest that primary Keggin structure of HPW and Pd0.25 P W was preserved after impregnation on the SBA-15, as evidenced by the agreement between the IR bands of parent and supported catalysts.

3.3. X-ray diffraction

The X-ray diffraction spectra of cesium salts of HPW exhibit all reflections corresponding to a cubic crystalline structure, similar with other literature data [4,5,21,29]. The secondary structure for those catalysts was described in [24] as belonging to the space group *Pn3m*.

However, all compounds containing cesium show a shift to higher 2θ positions with the increasing of cesium content [12]. By adding palladium, the diffraction maxima at 2θ = 10.3 and 14.6° angles are significantly reduced as shown in the insert of Fig. 4 for wide angle X-ray diffraction of HPW and Pd0.25 P W.

In the case of supported catalysts from small-angle X-ray diffraction were obtained data about mesostructure and long range ordering of silica framework. The SBA-15 patterns which correspond to hexagonal mesophase structure (space group *p6mm*) show a strong peak at 0.96° and two low-intensity peaks at 1.62° and 1.82° indicating a significant degree of long range ordering in the structure and a well-ordered two-dimensional mesostructure (Fig. 4). These diffraction peaks were indexed as the (100), (110) and (200) reflections in the 2θ = 0.5-2° associated with a hexagonal ordered structure [22].

The HPW/SBA-15 and Pd0.25 P W/SBA-15 samples showed a decrease in (100) peak intensity, the (110) and (200) peaks almost disappeared. This indicates that the mesostructure ordering is modified by the impregnation of the catalysts. Decreasing the intensities of

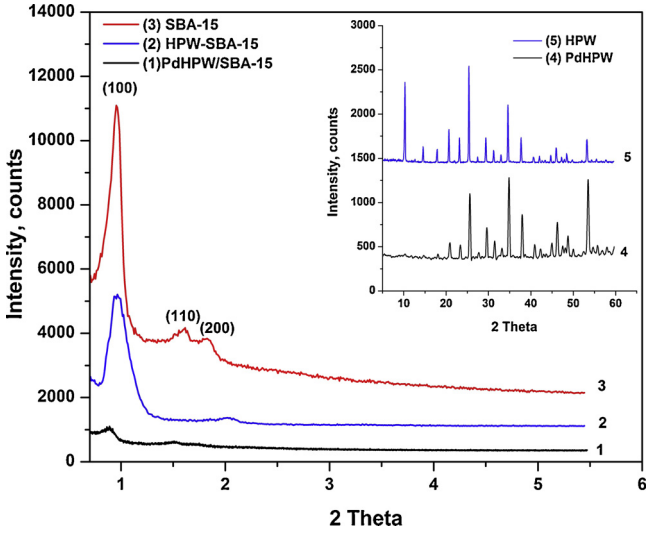


Fig. 4. The small-angle X-ray pattern of HPW/SBA-15 and Pd0.25 P W/SBA-15 composites. The inset shows the wide-angle X-ray pattern of HPW and Pd0.25 P W.

aforementioned peaks can be attributed to the inclusion of phosphotungstate anions inside the SBA-15 that could fill the silica pores.

The X-ray diffraction patterns of supported catalysts do not show any bulk HPW and Pd0.25 P W crystal phases at 30 wt. % loading, indicating that the active phase is finely dispersed on the SBA-15 support.

3.4. Porosity and surface area

The results of textural characteristics analysis (specific surface area, pore volume, average pore diameter and crystallites size) for heteropoly compounds are summarized in Table 1.

It has been observed that the specific surface area of the unsupported catalysts increases with cesium content and decreases with crystallites size. In the case of Pd0.25Cs_xPW the surface areas were less than 10 m^2/g for x = 0 and x = 1. When the Cs content (x) exceeds to 2, the surface area increases steeply, similarly as in case of pure CsxPW. These results can be explained by microstructural model [11] according to which the Cs3PW crystallites are formed at first, and then HPW is adsorbed epitaxially on the surface of Cs3PW during the synthesis.

Pore size distribution of pure and Pd doped HPW and Cs1PW exhibited Type II isotherm according to the International Union of Pure and Applied Chemistry (IUPAC) classification [32], which are ordinarily observed for nonporous catalysts. A Type IV (a) isotherms usually observed for mesoporous material (pore width between 2 and 50 nm) were found for pure and Pd doped Cs2 P W, Cs2.25 P W and Cs2.5 P W (not shown). For these catalysts an increase in the adsorption at low-pressure range ($p/p_0 < 0.1$) is observed suggesting the presence of micropores. On the other way the hysteresis loop at a relative pressure of p/p_o = 0.4-0.9 indicate the formation of mesopores [32].

By supporting the catalysts on SBA-15 appears a sharply increase in surface area from 3 m^2/g (HPW) to 194 m^2/g (HPW/SBA-15) and from 5 m^2/g (Pd0.25 P W) to 137 m^2/g (Pd0.25 P W/SBA-15), respectively. The pore volume and average pore diameter show an increase trend with the increasing of the surface area.

From nitrogen adsorption-desorption isotherms of HPW/SBA-15 and Pd0.25 P W/SBA-15 some changes of porous structure was observed (Fig. 5). The insert in Fig. 5 shows that all catalysts have narrow pore size distribution within mesopores range. The pore size distribution has a maximum of 8.5 nm for SBA-15 (not shown) and slightly decreases to 6.6 and 7.8 nm for HPW and Pd0.25 P W supported catalysts.

All catalysts exhibited a Type IV (a) isotherm with a hysteresis loop

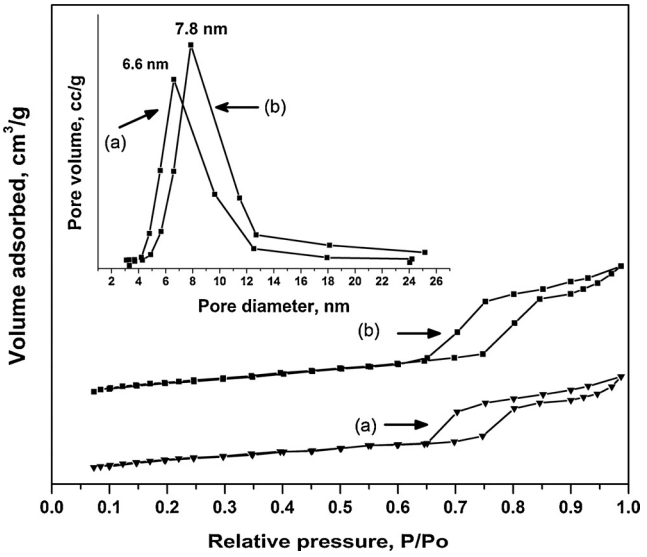


Fig. 5. N_2 adsorption-desorption isotherm and pore size distribution (insert) of (a) HPW/SBA-15 and (b) Pd0.25 P W/SBA-15.

H1 type and a sharp increase in volume adsorbed at relative pressure of p/p0 = 0.5-0.9, characteristic of highly ordered mesoporous silica. The shape of hysteresis loops are specific for pore structures and associated with agglomerates or compacts of approximately uniform spheres in fairly regular array [32].

A significant loss of surface area by supporting the catalysts on SBA-15 from 725 m^2/g (SBA-15) to 194 m^2/g (HPW/SBA-15) and 137 m^2/g (Pd025 P W/SBA-15) respectively indicates a partial blockage of particles on external surface of molecular sieve.

3.5. XPS

The XPS measurements were performed to investigate the changes in surface composition by adding Pd for all unsupported synthesized catalysts. XPS collects data from the few top layers on the sample and the Pd, Cs, W, P and O atomic concentration were determined.

The spectra were acquired in the electron binding energy (BE) regions corresponding to Pd 3d, Cs 3d, W 4f, P 2p and O 1s core excitation. The XPS measurements gave characteristic peaks for W^{+6} (4f), P (2p), O (1 s), Cs (3d) and Pd (3d) at 36.3, 134.6, 531.4, 724.2 and 338 eV respectively (Fig. 6).

The binding energy of 36.3 eV for W (4f) core excitation is close to the value given by literature data which confirm the oxidation state of W^{6+} for activated carbon-tungstophosphoric acid catalysts [33]. The O (1 s) spectrum of synthesis catalysts is characterized by one component, the main peak at 531.4 eV being attributed to the lattice oxygen in the primary structure - UK (W-O-W). A close value (530.4 eV) was obtained for the lattice oxygen in the Keggin structure (Mo-O-Mo). A peak at 134.6 eV was attributed to the PO_4 tetrahedron from the center of Keggin unit $[(PO_4)W_{12}O_{36}]^{3-}$ which remain stable regardless of the changes taking place in the surrounding WO_6 octahedrons [34]. The main peaks for Pd 3d and Cs 3d are at 338 and 724.2 eV, respectively. The intensity of cesium peaks increased with the increase of the Cs/KU ratio, being zero for Pd0.25 P W.

Theoretical and experimental concentration (Table 2) for oxygen and tungsten are almost similar which means that their concentration does not vary on the catalysts surface. The value of oxygen concentration is slightly smaller than theoretical one due to undergoing thermal treatments (heated at 250 °C after synthesis). The experimental concentration for cesium gives a value of zero for 1 Cs/KU because the number of acid layers is too high and cesium could not be determined.

The phosphorus concentration does not change in any way being almost identical for all samples. The atomic concentration of experimental Pd from Pd0.25 P W is about six times larger than theoretical concentration. This result indicates that the palladium could not penetrate inside the bulk of the acid maybe due to water molecules which are linked to the protons from inside the acid. Therefore, Pd is found mainly on the external layers of HPW.

For cesium salts (x = 1 and 2) the experimental concentration of Pd is higher than theoretical one which means that palladium is not uniformly distributed on the catalyst surface. This happens because Pd $(NO_3)_2$ precipitates in the presence of large amounts of HPW after the acid crystallites have been previously formed.

The similarity of the theoretical and experimental concentration for palladium in the case of cesium salts (x = 2.25, 2.5 and 3) show that palladium is uniformly distributed on the surface of the catalyst. Therefore, it can be assumed that Pd^+ is found inside the structure of cesium structure due to the large space between Cs3PW molecules.

These results indicate that the atomic concentrations of Cs, O, P and W correspond to the proposed model of Pd0.25$Cs_xH_{3-x}PW_{12}O_{40}$ microstructure [11,12] which consists of Cs3PW crystallites core coated with Pd0.25 P W layers.

3.6. Catalytic conversion of ethanol

Ethanol conversion over the bulk heteropoly compounds was found

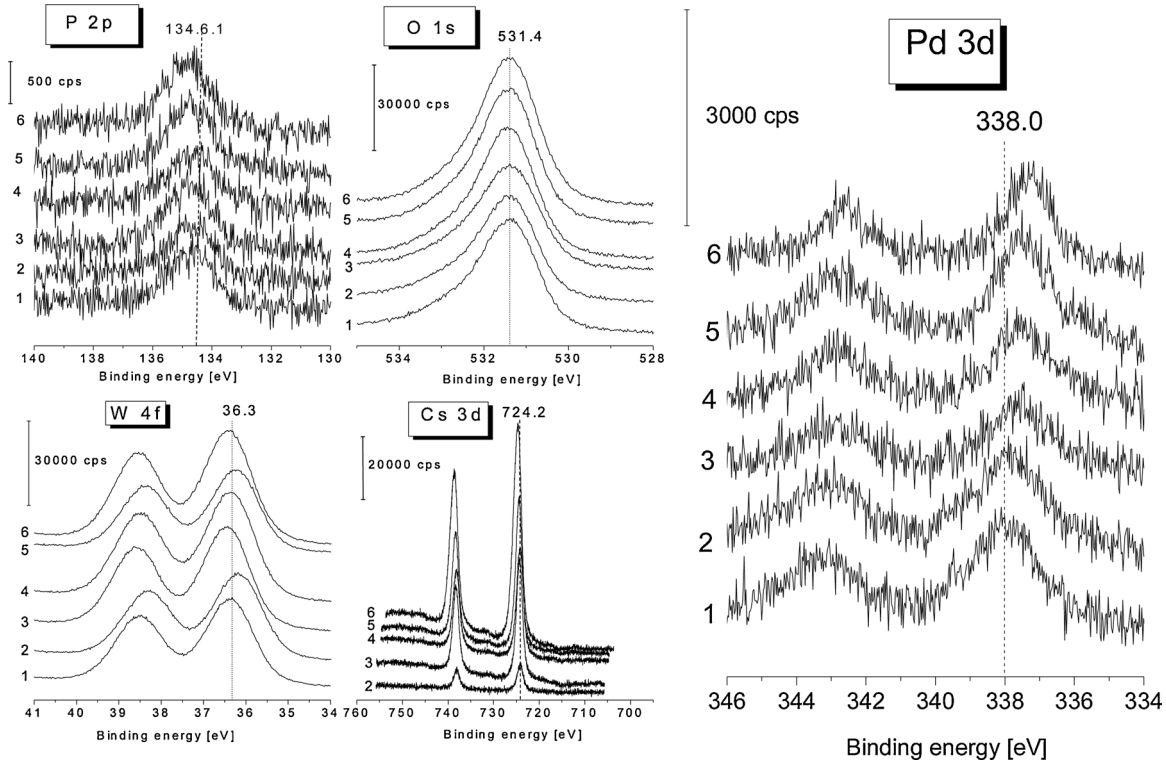


Fig. 6. The XPS peaks of P, O, W, Cs and Pd for Pd0.25 P W (1), Pd0.25Cs1PW (2), Pd0.25Cs2 P W (3), Pd0.25Cs2.25 P W (4), Pd0.25Cs2.5 P W (5) and Pd0.25Cs3PW (6).

to yield a range of products, ethylene (ET) and diethyl ether (DEE) being the main products, together with small amounts of hydrocarbons [6,10,11,13,35,36].

The mechanism of ethanol dehydration in gas phase over different heteropoly acid catalysts suggest that the ethylene (ET) is formed by the decomposition of chemosorbed ethanol (EtOH) molecules through a unimolecular mechanism and diethyl ether (DEE) by the reaction between chemisorbed and physisorbed ethanol molecules through a bimolecular mechanism. Both reactions occur in the bulk phase of the heteropoly acids [35,36]. These results were supported by mechanism proposed of D. Varisli et al. [37] according to the formation of ET and DEE are taking place in parallel pathways rather than following a consecutive reaction. It was generally observed that ET was the main product at higher temperature, while DEE was produce in significant amount at lower temperature.

The catalytic activity of the synthesized pure and Pd doped catalysts in ethanol conversion were studied in a tubular flow reactor described in the experimental section. Because the temperature plays a very significant role in any catalytic system, the catalysts were tested in a temperature range between 200–350 °C.

For each catalyst were made three experimental measurements to obtain a good reproducibility. Finally, data points which were reported in the ethanol conversion and ethylene selectivity figures correspond to the average of these three measurements. The main reaction products obtained were ET and DEE, the dehydration reaction taking place on the acidic sites of the catalyst.

The effect of temperature on catalytic performances in ethanol conversion over pure and Pd doped HPW, Cs2.25 P W and Cs2.5 P W catalysts was tested by continuous flow method. Fig. 7 represents the average of the first four ethanol injections introduced within 35 min of reactant. This average was used because the quantities of some catalysts are changing after 140 min due to their deactivation and to prevent some errors resulting from the introduction of the ethanol. The catalyst activity increased monotonically with the reaction temperature in the range of 200 − 300 °C and started to decrease after 300 °C due to catalytic deactivation. It can be clearly seen that an optimal reaction temperature for these catalysts was obtained within the range from 275 to 300 °C.

Fig. 8a and b show the variation of the ethanol conversion and ethylene selectivity as a time on stream at 300 °C. The HPW and Pd0.25 P W has the lower catalytic activity in ethanol conversion which is in agreement with literature date [6,11], attributed to low specific surface area, in the range from 3 to 5 m^2/g.

Cs2.5 P W exhibiting the highest activity due to higher surface area

Table 2
The XPS theoretical (Theor.) and experimental (Exp.) atomic concentration (%) for oxygen, tungsten, cesium, phosphorus and palladium.

Catalysts	Pd		Cs		W		P		O	
	Theor. conc. (%)	Exp. conc. (%)	Theor. conc. (%)	Exp. conc. (%)	Theor. conc. (%)	Exp. conc. (%)	Theor. conc. (%)	Exp. conc. (%)	Theor. conc. (%)	Exp. conc. (%)
Pd0.25 P W	0.92	6.32	–	–	75.98	74.54	1.07	1.25	22.04	17.89
Pd0.25Cs1PW	0.87	1.87	4.37	0.13	72.56	77.54	1.02	1.39	21.18	17.20
Pd0.25Cs2 P W	0.84	1.37	8.38	5.27	69.52	73.57	0.98	1.47	20.29	16.19
Pd0.25Cs2.25 P W	0.83	0.77	9.33	6.17	68.80	74.01	0.97	1.52	20.08	15.28
Pd0.25Cs2.5 P W	0.82	0.76	10.27	6.92	68.09	72.17	0.96	1.39	19.88	15.90
Pd0.25Cs3PW	0.80	0.78	12.07	12.07	66.08	67.58	0.93	1.34	20.25	15.64

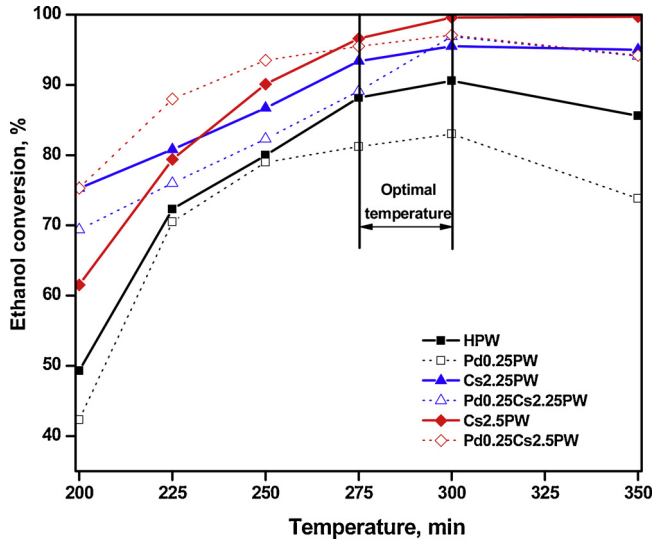


Fig. 7. The influence of temperature on the ethanol conversion in the present of pure and Pd doped HPW, Cs2.25 P W and Cs2.5 P W.

(130 m^2/g) and accessibility of the acid sites from the catalysts surface to the reactants. This is not a surprise because Cs2.5 P W is well known to be an excellent acid catalyst in various gas-phase reactions being the most investigated cesium salt of 12-tungstophosphoric acid [1,6]. The highest ET selectivity was also obtained for the same catalyst and the lowest selectivity for Pd0.25 P W around of 65 %.

For all the studied catalysts, the ethanol conversion decreases with time on stream due to the cokes formation which is leading to blocking the acidic centers responsible for ethylene formation at temperature above 300 °C.

3.7. Deactivated catalysts analysis

In the ethanol conversion reaction, the formation of coke during the time on stream is very important, because in most cases the catalytic activity decreases with the increasing of the coke content. In order to study the deactivation/activation of catalysts the experiments were conducted at 300 °C. The amounts of coke precursors and hard coke produced during ethanol conversion were determined by temperature-programmed oxidation (TGA/TPO) method. It can be clearly observed an increase in total amount of coke in case of Pd doped $Cs_xH_{3-x}PW_{12}O_{40}$ compared to pure catalysts. Also a simultaneously increase of the amount of hard coke with increasing of the cesium content (Fig. 9), can be seen.

On previous work, the Brönsted acidity was determined by TG curves [12] and TPD of n-butyl amine on the same heteropoly compounds [21]. It is notice that a decreasing of Brönsted acidity leads to an increase of total coke quantity which can be explain by reducing of the necessary acidic centers for the reaction.

In this regard, the smallest amount of coke is formed on the acid and the higher quantity that includes both types of coke (coke precursor and hard coke) is formed on Pd0.25Cs2.5 P W. In the case of bulk catalysts with low surface area the deactivation process is fast due to blocking of the reactant access to the acidic sites with coke deposit. This may be the reason why only precursor coke (aliphatic compounds) is formed.

By increasing the specific surface area as a result of increasing the cesium content, the reaction take place on the catalysts surface, leading to accessibility increase of reactants to the acidic sites. For these compounds both types of coke are formed (aliphatic and aromatic).

Using FTIR (Fig. 10), it has been shown that formation of coke during the ethanol conversion, as well as a rapidly deactivation of these compounds, does not affect the Keggin structure (primary structure). The intensity of the IR bands is the same for both fresh and spent catalysts. All characteristic IR bands for the main vibration bonds of KU are evidenced in spectrum. It means that the Keggin structure is stable and the preserving of primary structure of these heteropoly compounds could lead to a possible regeneration of the catalysts.

3.8. Regeneration in air

For the improvement of the catalytic activity, the HPW and PdyPW (y = 0.15, 0.20 and 0.25) were impregnated on mesoporous silica SBA-15 and then regenerated with air. From the literature data is known that by supporting of HPAs on mesoporous SBA-15 the acidity and thermal stability increases in comparison with unsupported catalysts, leading to a significant increase in catalytic activity [9].

Since the formation of coke during dehydration of ethanol did not affect the Keggin structure of the catalyst, the regeneration with air of the compounds was attempted. The ethanol dehydration was studied as a test reaction for the deactivation and regeneration with air of the catalysts at 275 and 300 °C (Fig. 11). Regeneration was done in the same flow reactor where the ethanol dehydration reaction was performed. The reaction products are similar with those resulting on unsupported catalysts, which have been previously reported. For all reactions the ethanol feed was stopped when the ethanol conversion dropped to about 85 % and then the catalysts were regenerated in flowing air (30 ml/min) for 20 min. The air regeneration procedure was repeated several times for each catalyst.

HPW/SBA-15 and Pd0.25 P W/SBA-15 start to deactivate after 10 h on stream for catalysts tested at 275 °C, respectively after 20 h for catalysts tested at 300 °C (Fig. 11). It can be observed a significant increase of catalytic activity after impregnation on mesoporous silica SBA-15.

After regeneration with air the catalytic activity increases for o short time and then decreases again. It is notice that both catalysts show better regeneration at 300 °C. The catalysts regain for a short time its catalytic activity without significant loss in activity after regeneration under above conditions.

In the case of tested samples after 60 h on stream, the coke deposit was determined using TGA method (Fig. 12). With increasing the reaction temperature an increase in the amounts of total coke was observed for both supported samples. On the other hand, by doping with Pd the quantities of total coke decreases, especially hard polyaromatic coke, which is more difficult to be eliminated. The effect of palladium concentration (0.15, 0.20 and 0.25 at. Pd/KU) on the ethanol conversion values as a function of TOS is shown in Fig. 13.

All supported catalysts present a high catalytic activity, the most stable being the HPW/SBA-15 which starts to be deactivated after 30 h on stream. Among Pd doped catalysts the best catalytic activity was observed for Pd0.15 P W/SBA-15 which according to the thermal analysis (Fig. 14) shows the lowest amount of coke formation.

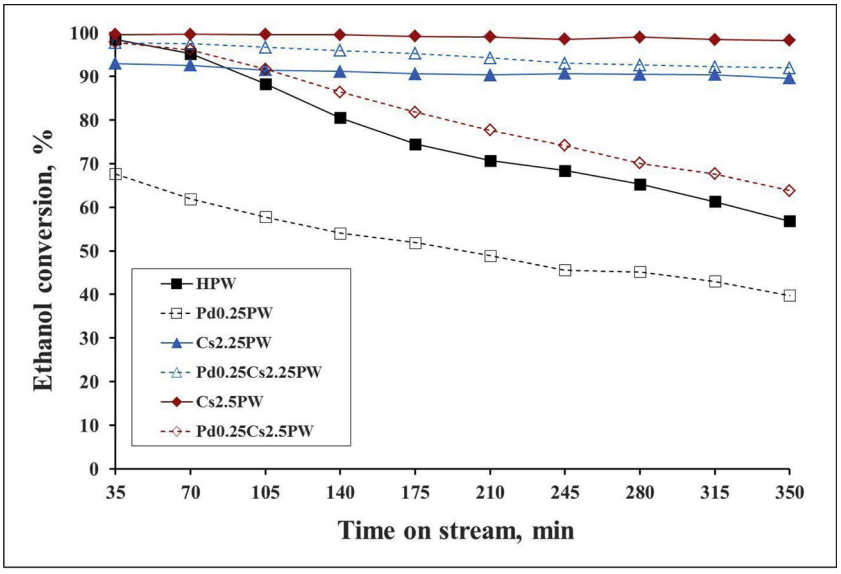
A decrease in the amount of palladium leads to a reduction of coke formation. An optimal balance between Brönsted acidity and palladium is obtained at a concentration of 0.15 at. Pd/KU. The presence of both palladium and SBA-15 improved the catalytic activity of the samples leading to a slowly deactivation.

Based on the results previously described, it is possible to affirm that by doping the HPW/SBA-15 with different quantities of Pd, the coke deposit has decreased significantly, especially the hard coke. It is well known that the hard coke is eliminated more difficult at high temperatures.

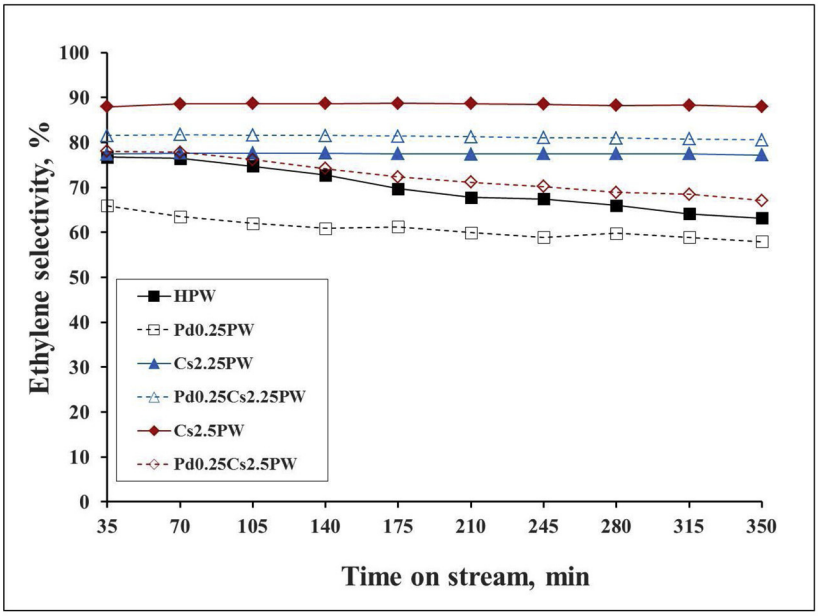
4. Conclusions

In this study, a series of pure and Pd doped catalysts were prepared and investigated in ethanol dehydration reaction. Mesoporous molecular sieves SBA-15 containing HPW and PdyPW with various amount of Pd/KU were synthesized by impregnation method.

The XPS measurements were performed to investigate the changes



a.



b.

Fig. 8. Conversion of ethanol (a) and ethylene selectivity (b) over pure and Pd doped HPW, Cs2.25 P W and Cs2.5 P W as a function of TOS at 300 °C.

in surface composition by adding Pd for all synthesized catalysts. The similarity of the theoretical and experimental concentration for palladium in the case of cesium salts (x = 2.25, 2.5 and 3) show that palladium is uniformly distributed on the surface of the catalyst. Therefore, it can be assumed that Pd is found inside the structure of cesium structure due to the large space between Cs3PW molecules. These results indicate that the atomic concentrations of Cs, O, P and W correspond to a $PdyCs_xH_{3-x}PW_{12}O_{40}$ microstructure model which consists of Cs3PW crystallites core coated with PdyPW layers.

The optimal temperature of ethanol dehydration reaction was determined in the range of 275 − 300 °C. After 300 °C a deactivation process occurs as a result of blocking the reactant molecules access to the acidic centers during the ethanol dehydration reaction. Thus, unsupported catalysts with low surface area have undergone a fast deactivation as a small amount of coke is enough to block the access of reactants to the acidic sites. The high catalytic activity in ethanol conversion over Cs salts $Cs_xH_{3-x}PW_{12}O_{40}$, comparing to Pd doped catalysts can be explained by the higher number of acid sites and a better reactants accessibility on the surface of the Cs salts (surface acidity).

By supporting the catalysts as a monolayer on SBA-15, the catalysts deactivation process is more slowly due to the palladium which partially inhibits the coke deposit, especially hard coke. Their catalytic performance was significantly improved and the catalysts could remained stable for more than 10 h of reaction, even 30 h in the case of HPW/SBA-15.

Using regeneration with air, the catalytic activity was regained for a short time, as the amount of total coke deposition was partially removed by this regeneration treatment. By doping the catalysts with Pd,

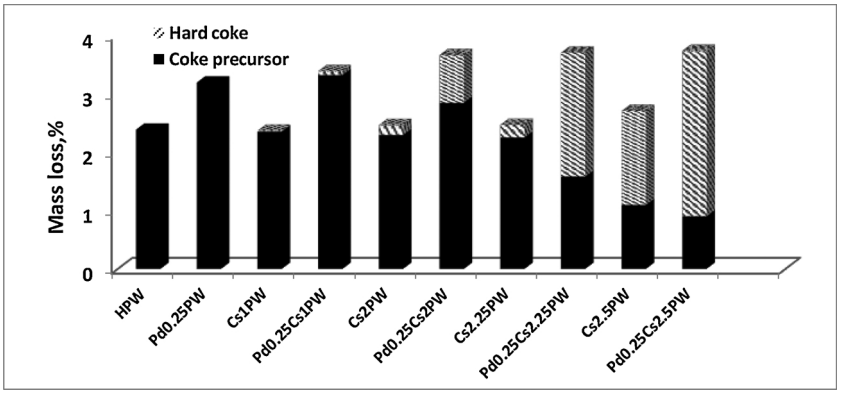


Fig. 9. Coke precursors and hard coke content for pure and Pd doped HPW and cesium salts formed by ethanol conversion in a fixed-bed flow reactor at 300 °C.

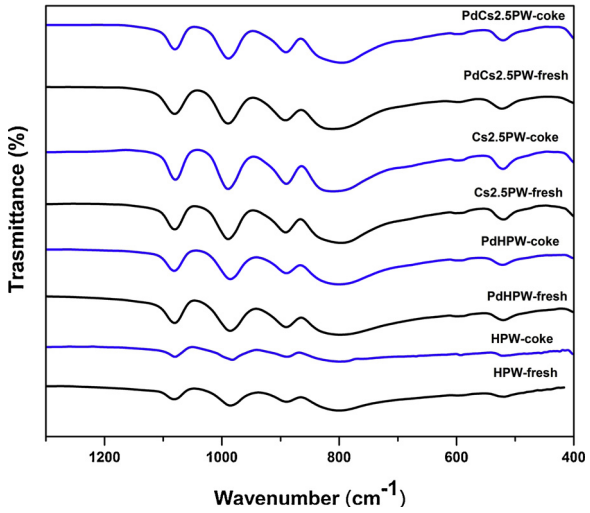


Fig. 10. Infrared spectra for pure and Pd doped HPW and cesium salts formed by ethanol conversion in a fixed-bed flow reactor at 300 °C.

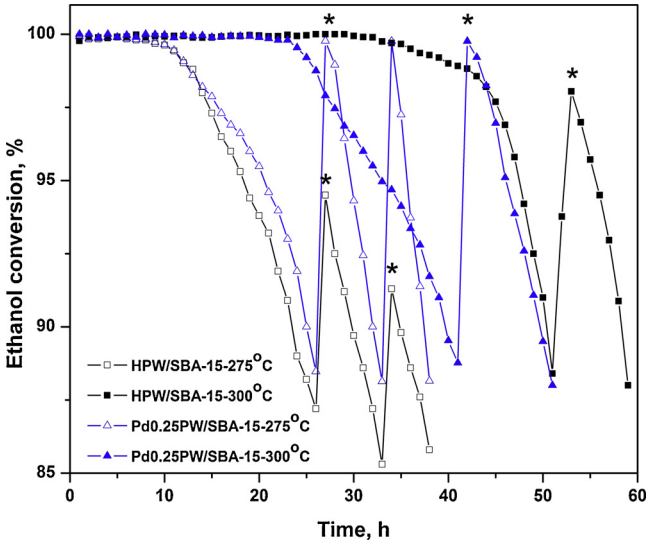


Fig. 11. Ethanol dehydration and regeneration (*-starting to add air within 20 min.) over HPW/SBA-15 and Pd0.25 P W/SBA-15 at 275 and 300 °C.

the ratio between coke precursor and hard coke can be change. Concentration of 0.15 Pd/KU was the optimal balance between suitable concentration of Brönsted acid sites and Pd ions which are favourable to obtain a lower amount of coke deposition. The results obtained in this

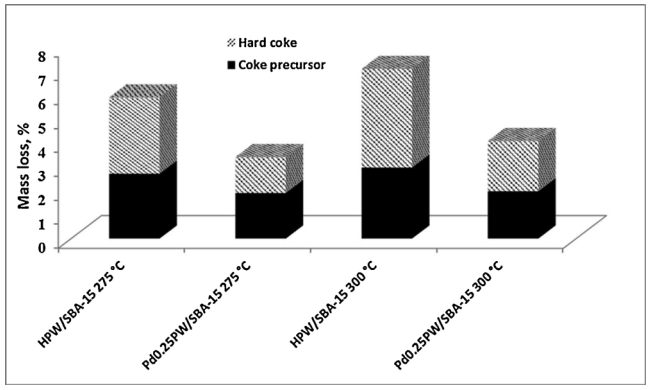


Fig. 12. Coke precursors and hard coke formed after dehydration over HPW/SBA-15 and Pd0.25 P W/SBA-15 at 275 and 300 °C.

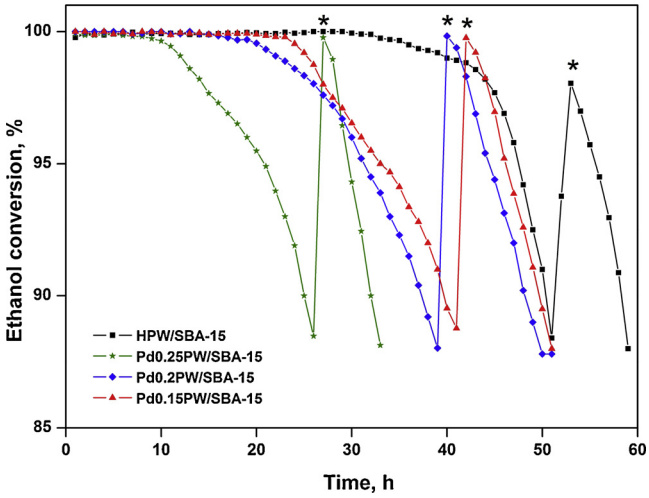


Fig. 13. Ethanol dehydration and regeneration (*-starting to add air within 20 min.) over HPW/SBA-15 and PdxPW/SBA-15 (x = 0.15, 0.2 and 0.25) at 300 °C.

work, proved that the HPCs impregnated on silica mesoporous materials were highly promising solid acid catalysts which could prevent the coke formation during dehydration reaction of alcohols.j

CRediT authorship contribution statement

Orsina Verdes: Methodology, Writing - original draft, Investigation. **Viorel Sasca:** Conceptualization. **Alexandru Popa:** Visualization, Writing - review & editing. **Mariana Suba:** Validation.

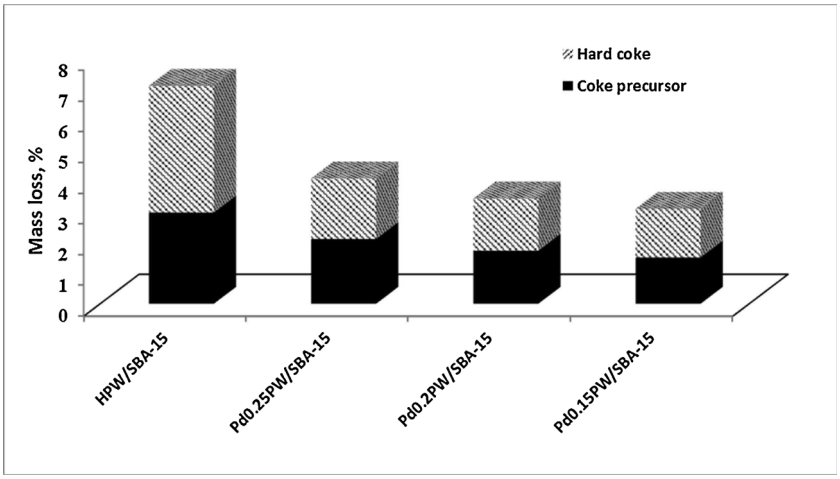


Fig. 14. Coke precursors and hard coke formed after ethanol dehydration over HPW/SBA-15 and PdxPW/SBA-15 (x = 0.15, 0.2 and 0.25) at 300 °C.

Silvana Borcanescu: Software.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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