Article

Thermogravimetry Applied for Investigation of Coke Formation in Ethanol Conversion over Heteropoly Tungstate Catalysts

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Abstract: Thermogravimetric analysis (TGA) was used to evaluate the thermal stability and the amount of coke deposition resulting from the deactivation of catalysts during ethanol dehydration reaction in a fixed bed continuous flow reactor. In this study, a series of catalysts containing 30% of Pd doped and pure 12-tungstophosphoric acid and its insoluble $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ salt supported on SBA-15 were prepared. The catalytic efficiency of ethanol dehydration reaction was also evaluated. Two types of coke are identified from the TPO (Temperature programmed oxidation) profiles and assigned to the coke precursor and hard coke, respectively. The results indicate that cesium salts reduced the formation of hard coke. The amount of total coke formed was significantly reduced by supporting the catalysts on mesoporous SBA-15 molecular sieves.

Keywords: heteropoly acid; thermogravimetric analysis; ethanol conversion; coke formation; catalyst stability; cesium salts

1. Introduction

The catalytic conversion of ethanol over bulk and supported Brönsted solid acid catalysts based on tungsten Keggin heteropoly acids (HPAs) is an alternative route for the production of ethylene (ET) and diethyl ether (DEE) [1–5]. From an economic point of view, ethylene is an interesting starting material in the chemical industry. Currently, special attention is directed toward green alternatives for the manufacture of ethylene, namely, the catalytic dehydration of bioethanol would lead to the reduction of greenhouse gas emissions and a decrease in dependence on fossil fuels. Diethyl ether (DEE) is a valuable renewable fuel that can be used as a fuel additive for diesel engines. Dehydration of ethanol on supported and unsupported heteropoly compounds (HPCs) indicates that at temperatures lower than 180 °C, the main product formed is diethyl ether. At high temperatures, ethylene is obtained in large quantities and is the main reaction product [3–5].

At the same time, heteropolyacids (HPA) as a green solid catalyst have become attractive due to their low toxicity, being environmentally friendly, and being easy to recover and recycle [6–8]. According to literature data [9,10], the most active heteropoly acids (HPAs) catalysts are $H_3PW_{12}O_{40}$ (HPW) and its bulk heteropoly salt $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (Cs2.5PW). Cs2.5PW catalyst was shown by Misono and co-workers [9] to be more efficient than its parent acid due to high surface acidity. Until now, numerous studies have been conducted on the Cs2.5PW salt due to its remarkable activity in a large number of reactions. In comparison with basic heteropolyacids, which have a low specific surface area below $10 \ m^2/g$, Cs2.5PW salt has a higher specific surface area ($130 \ m^2/g$) due to its micro- and mesoporous structure that allows very efficient use of protons. In order to increase the specific surface area of heteropoly acids, it, therefore, becomes necessary to disperse HPAs on supports that possess a large surface area. Highly ordered mesoporous materials with a two-dimensional porous structure such as SBA-15 can be incorporated as a support in the catalyst leading to good dispersion of the active phase during the synthesis of the catalysts. SBA-15 is a mesoporous silica molecular sieve with uniform tubular channels whose

pore diameter is variable from 50 to 300 Å. Compared with other supports, for instance, MCM-41, SBA-15 has a larger pore diameter, thicker pore wall, and higher hydrothermal stability [11–13].

During organic reactions catalyzed by heteropoly compounds (HPCs), a deactivation process occurs due to the formation of carbonaceous deposits (coke), which cause pore blockage and/or poisoning of active sites [14–17]. Generally, the formation and deposition of coke take place on the external surface of the catalysts. Coke consists of aliphatic molecules (precursor coke) as well as polyaromatic molecules (hard coke).

Ultrastable Y (US-Y) zeolite was studied quantitatively by thermogravimetric method during catalytic cracking of normal n-hexane and 1-hexene in order to identify the coke formation and the role of coke precursors in catalytic cracking reaction. The amount of coke was estimated by weight loss during coke burning and composition by coke extraction after the dissolution of the US-Y in HF [18,19].

The ^{13}C MAS NMR and TGA/TPO measurements are shown that modification of heteropoly acid catalysts, e.g., $H_3PW_{12}O_{40}$, by doping with Pt or Pd, significantly decreases the temperature of coke gasification with oxygen. In the case of propene oligomerization reaction on PW/SiO_2 catalyst by adding Pd, only the soft coke is observed [16]. The undoped catalyst forms two types of coke: soft coke (high molecular weight aliphatic oligomers) and hard coke (polynuclear aromatics). At the same time, the addition of palladium increases the regeneration of catalysts without loss of catalytic activity [16,17].

The aim of this paper is to examine the thermal stability and quantity of coke formed during ethanol conversion at different temperatures using the thermal analysis method. Thermogravimetry (TG/DTG) is regarded as an essential method to determine the mass loss of coke precursor and hard coke.

2. Results and Discussion

2.1. Characterization of the Catalyst

2.1.1. Structure and Thermal Stability of Heteropoly Compounds

The high angles XRD patterns (2θ = 5–60°) of pure and Pd doped HPW and Cs2.5PW salt exhibit all reflections corresponding to a cubic crystalline structure (*Pn3m* phase), similar to other literature data [20]. In the case of silica-supported catalysts, the characteristic peaks for HPCs are not detected (not shown). This indicated that HPW, PdPW, Cs2.5PW, and PdCs2.5PW were finely dispersed on the surface, incorporated in the pore walls, or inside the hexagonal channels of SBA-15 [2,20]. The highly ordered hexagonal SBA-15 structure was confirmed by the presence of three main diffraction peaks below 2.0° (2θ) corresponding to the Miller indices (100), (110), and (200) [20].

Figure 1 showed the low angle XRD patterns of SBA-15, HPW/SBA-15, PdHPW/SBA-15, Cs2.5PW/SBA-15 and PdCs2.5PW/SBA-15 catalysts. All supported samples exhibited one intense diffraction peak at 0.92 indexed to (100) and two peaks at 1.59 and 1.83 indexed to (110) and (200) that almost disappeared in the case of HPAs supported SBA-15. The results indicated that the mesostructured ordering is slightly modified by the impregnation of the catalysts into SBA-15.

The presence of Keggin anion in organized mesoporous silica-HPCs composites was identified by Fourier transform infrared spectroscopy (FTIR) in the range of 400–1200 cm^{-1} (Figure 2).

FTIR spectra represent a real fingerprint of the Keggin unit for these compounds, and the results were briefly reported before [2]. The four principal bands of Keggin anion vibration appear at 1080 cm^{-1} due to $\nu_{as}(PO_i)$ vibration, 980 cm^{-1} due to the terminal $\nu_{as}(W = O_t)$ vibration, 890 and 789 cm^{-1} assigned to corner-sharing $\nu_{as}(W\text{-}O_c\text{-}W)$ and edge-sharing $\nu_{as}(W\text{-}O_e\text{-}W)$, respectively. In addition, a weaker adsorption band appeared at 520 cm^{-1}, which was attributed to $\nu_s(W\text{-}O\text{-}W)$. All characteristic infrared adsorption bands are similar to the literature data [21–23]. The IR spectrum of Cs2.5PW salt was identical to that of the acid, but it has narrower vibration bands due to a weaker interaction between cesium and the Keggin anion. No significant difference between pure and Pd-

doped HPW and Cs2.5 PW was observed. It could be concluded that by adding cesium and palladium to the heteropoly compounds, the structure of the primary structure is not changed. In the case of supported catalysts, all bands are preserved, but they are broadened and partially overlapped because of the strong absorption bands of mesoporous silica from SBA-15 (1100, 950, 807, and 450 cm^{-1}). When comparing the IR spectra of catalysts within the structural vibration region, it was observed that the primary Keggin structure of HPW, Cs2.5PW, PdPW, and PdCs2.5PW were preserved after impregnation on the SBA-15 molecular mesoporous sieve.
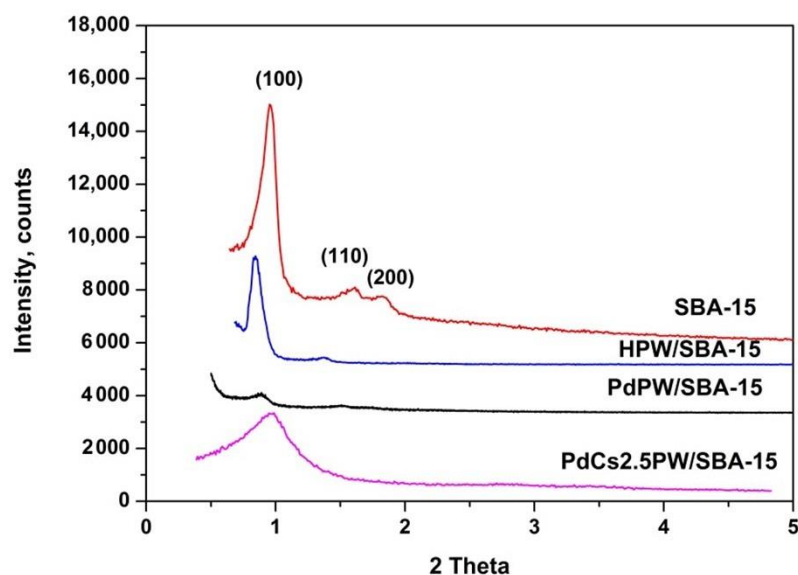

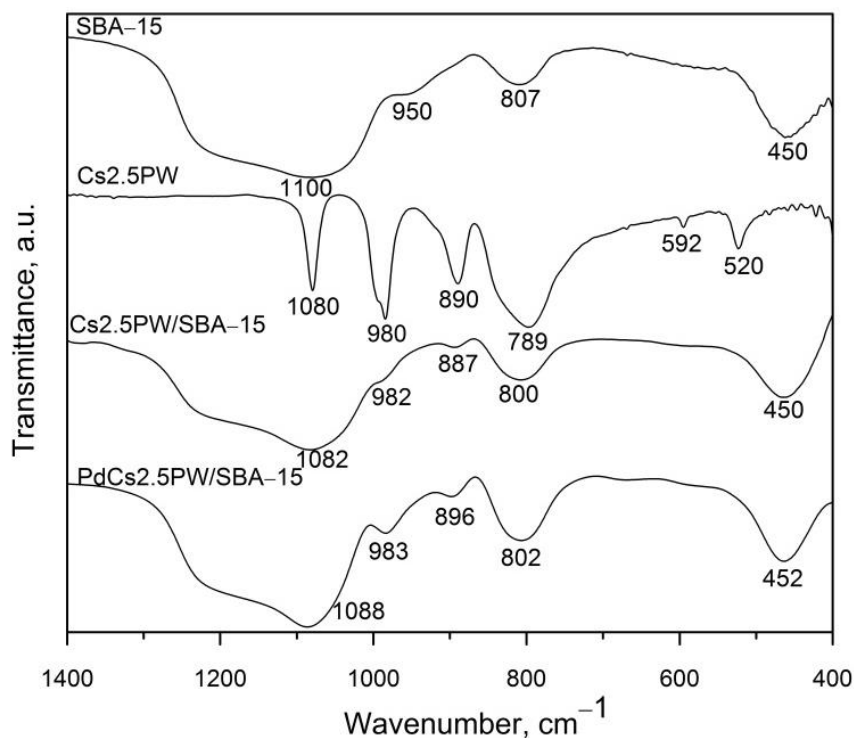**Figure 1.** Low-angle XRD patterns of the catalysts.

Figure 2. FTIR spectra of synthesized catalysts.

The thermal decomposition of catalysts was determined by thermal analysis and studied in detail in our previous papers between 25 and 650 °C [2,23]. Some considera-

tions from the previous papers are given below. According to TG curves, the stage until 110 °C indicated the removal of the physically adsorbed water. The stage between $110-300$ °C corresponds to the loss of water molecules, in which the waters are hydrogen-bonded to the acidic protons to form the $[H_2O \ldots H+ \ldots OH_2]$. At the last stage, over 300 °C corresponds to the loss of constitutional water and decomposition of Keggin structure with the formation of corresponding oxides (WO_3 and P_2O_5). The oxides crystallize between 570 and 590 °C with an exothermic effect on the DTA curves.

On the other hand, in the case of supported catalysts, the removed hydrated water is higher than for unsupported ones due to the thermal overlap effects of the desorbed water from the silica surface and the loss of HPCs physisorbed water. The departure of water molecules which are linked by hydrogen bonds with acidic protons due to removing some traces of the surfactants used for the synthesis of mesoporous sieve SBA-15, takes place in the second step. An exothermic peak that appears on DTA curves around 590 °C could be assigned to the decomposition of the active phase.

It can be noted that the HPW/SBA-15, PdPW/SBA-15, Cs2.5PW/SBA-15, and PdCs2.5PW/SBA-15 catalysts may be considered slightly more stable than pure catalysts, probably due to the interaction of catalyst with silanols on the surface.

2.1.2. Textural Properties of Heteropoly Compounds

The results of textural characteristics analysis (specific surface area, pore volume, and average pore diameter for catalysts are summarized in Table 1. In our previous articles [2,23] was reported that upon Cs incorporation, the surface area increases significantly, from $3 \text{ m}^2 \text{ g}^{-1}$ for HPW to $130 \text{ m}^2 \text{ g}^{-1}$ for Cs2.5PW. By adding palladium, the surface area of Cs2.5PW decreases from $130 \text{ m}^2 \text{ g}^{-1}$ to $98 \text{ m}^2 \text{ g}^{-1}$, which explains the microstructural model [23] according to the Cs3PW crystallites are formed at first, and then HPW is adsorbed epitaxially on the surface of Cs3PW during the synthesis.

Table 1. Specific surface area, pore volume and average pore diameter of catalysts.

Catalyst	Surface Area (m^2/g)	Pore Volume BJH$_{Des}$ (cm^3/g)	Average Pore Diameter BJH$_{Des}$ (nm)
SBA-15	725	1.100	6.2
HPW/SBA-15	194	0.191	6.0
PdPW/SBA-15	137	0.211	5.8
Cs2.5PW/SBA-15	303	0.830	6.1
PdCs2.5PW/SBA-15	298	0.790	5.9

The significant decrease in surface area from $725 \text{ m}^2/\text{g}$ (SBA-15) to $194 \text{ m}^2/\text{g}$ (HPW/SBA-15) is due to the dispersion of the acid on the large surface of the SBA-15 molecular sieve. For supported cesium compounds, a slight decrease is taking place from $725 \text{ m}^2/\text{g}$ (SBA-15) to $303 \text{ m}^2/\text{g}$ (Cs2.5PW/SBA-15) and $298 \text{ m}^2/\text{g}$ (PdCs2.5PW/SBA-15) respectively which indicates a partial blockage of particles on the external surface of the mesoporous SBA-15 sieve. For all catalysts, the average pore diameter tends to increase with the increased surface area.

The N_2 adsorption–desorption isotherms of HPW/SBA-15, PdPW/SBA-15, Cs2.5PW/SBA-15 and PdCs2.5PW/SBA-15 catalysts were depicted in Figure 3. All catalysts exhibited a Type IV (a–e) isotherm according to the IUPAC classification [24] with a hysteresis loop H1 type and a sharp increase in volume adsorbed at a relative pressure of p/p0 = 0.6–0.9, characteristic of highly ordered mesoporous silica.
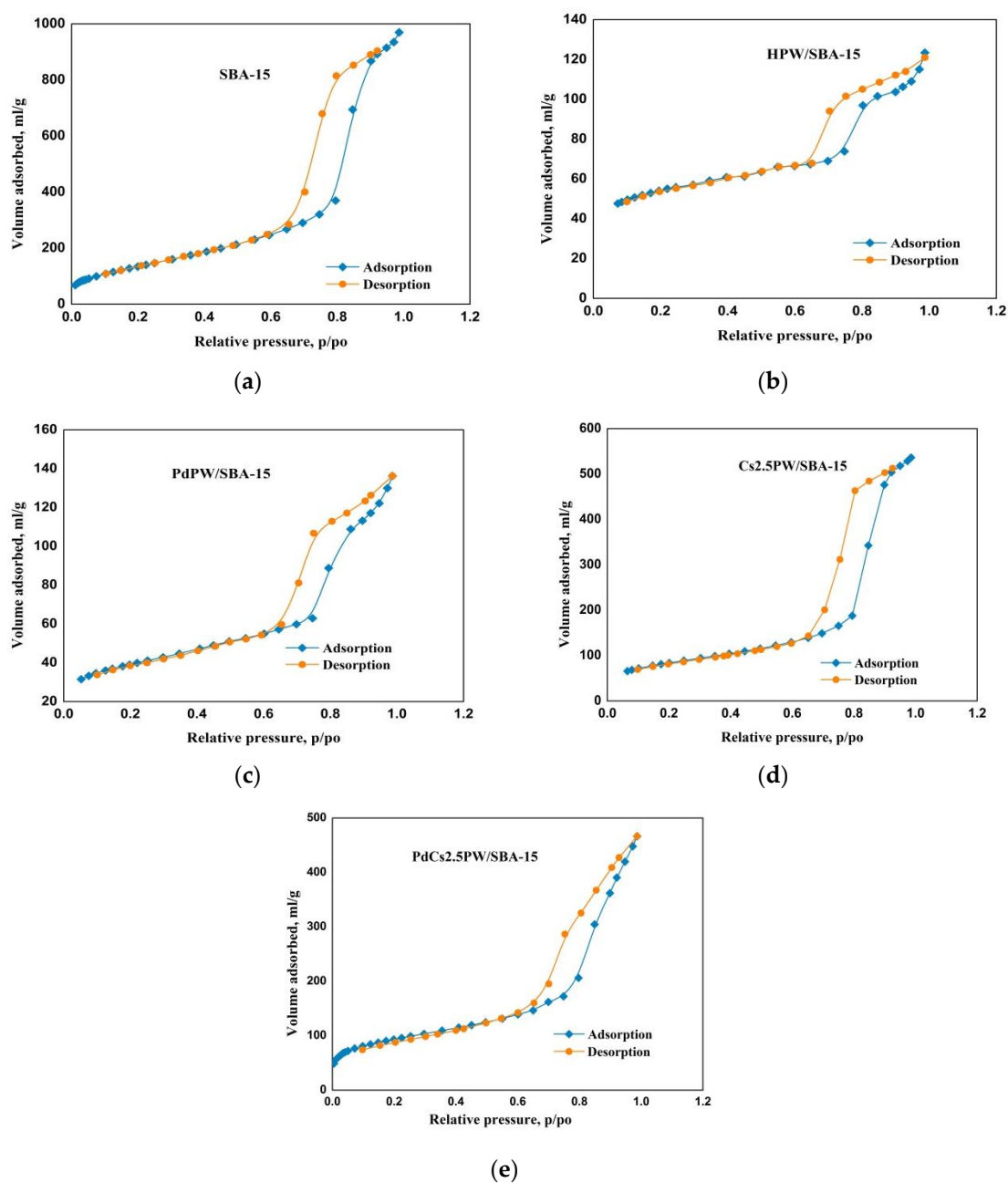
Figure 3. Nitrogen adsorption–desorption isotherms of SBA-15 (**a**), HPW/SBA-15 (**b**), PdPW/SBA-15 (**c**), Cs2.5PW/SBA-15 (**d**) and PdCs2.5PW/SBA-15 (**e**).

Comparing adsorption–desorption isotherms, it was observed that all catalysts have a hysteresis loop similar to the parent support. This indicates that the 2D hexagonal structure of SBA-15 is preserved after Pd doping and Cs2.5 impregnation.

2.2. Catalytic Ethanol Transformation

Ethanol conversion over catalysts was found to produce a range of products, with ethylene and diethyl ether being the main products. It should be noted that, during ethanol dehydration, by products such as small amounts of hydrocarbons were also obtained [1,2,4,5].

In a previous work, we show that the conversion and selectivity of synthesized catalysts in ethanol conversion, are strongly influenced by temperature. Catalyst activity

increases with temperature and the optimum reaction temperature is between 275 and 300 °C. The catalysts begin to deactivate above 300 °C [2].

For pure compounds, significant quantities of DEE (around 20%) were produced via dehydration of ethanol at 200 °C. For silica supported catalysts DEE was obtained in very small amount due to its decomposition to ethylene (Table 2). A comparison of ethanol conversion of catalysts shows that the supported catalysts have significantly higher conversion than the unsupported ones.

Table 2. Ethanol conversion, ethylene and diethyl ether selectivity for pure and supported catalysts as a function of TOS at 200 °C.

Sample	Ethanol Conversion (%)		Ethylene Selectivity (%)		Diethyl Ether Selectivity (%)	
	Time on Stream (TOS)					
	35 min	*350 min*	*35 min*	*350 min*	*35 min*	*350 min*
HPW	51.2	45.5	43.2	39.0	18.1	19.2
PdPW	43.2	39.0	38.8	36.0	19.2	19.9
Cs2.5PW	78.6	76.1	28.4	25.2	26.3	23.2
PdCs2.5PW	84.2	79.2	50.9	42.6	18.3	19.7
HPW/SBA-15	93.4	89.6	90.1	80.1	0.3	0.5
PdPW/SBA-15	94.7	84.7	88.4	80.6	0.2	0.1
Cs2.5PW/SBA-15	98.9	90.1	93.2	89.4	0.3	0.4
PdCs2.5PW/SBA-15	94.9	87.2	91.2	86.4	0.1	0.3

Deactivation of the catalysts has been examined for ethanol conversion at 300 °C under atmospheric pressure. The results obtained for unsupported catalysts are shown in Figure 4. As can be seen a temperature increase causes an increase in ethanol conversion especially for Cs2.5PW which exhibiting the highest activity. Cs2.5 PW is well known to be an excellent acid catalyst in various gas-phase reactions exhibiting the highest activity in ethanol conversion due to its larger surface area (130 m^2/g). It is regarded as the most active catalyst in the gaseous phase reaction. The other catalysts begin to deactivate after 1 h of TOS due to the cokes formation which is leading to blocking the acidic centers responsible for ethylene formation. The lower catalytic activity of HPW and PdPW in ethanol conversion reaction is due to a very low specific area, 3 and 5 m^2/g, respectively which are in agreements with literature date [9,10]. In the same conditions the highest ET selectivity values were obtained for Cs2.5PW salt catalysts (Figure 5).

A significant increase in catalytic activity on the same catalysts but supported on an SBA-15 molecular sieve as a function of TOS at 300 °C was observed (Figure 6). This could be explained by the fact that a large specific area and a good dispersion of active sites on support leads to high catalytic activities.

The highest ethanol conversion was obtained for Cs2.5PW/SBA-15 salt. By adding palladium, the catalytic activity slowly decreases for both pure and supported HPW/SBA-15 and Cs2.5/SBA-15 catalysts. I.V. Kozhevnikov et al. studied the coking during propene oligomerization over silica-supported HPAs, namely, HPW and its Pd-doped form (1.6–2.5 wt.% Pd), and subsequent catalyst regeneration. It has revealed that the Keggin structure of the catalyst was unaffected by coke deposition in both unmodified PW/SiO2 and Pd-modified form, but it should be noted that under the conditions studied, the Pd-modified HPW deactivated a bit faster than the unmodified HPW [16,17].
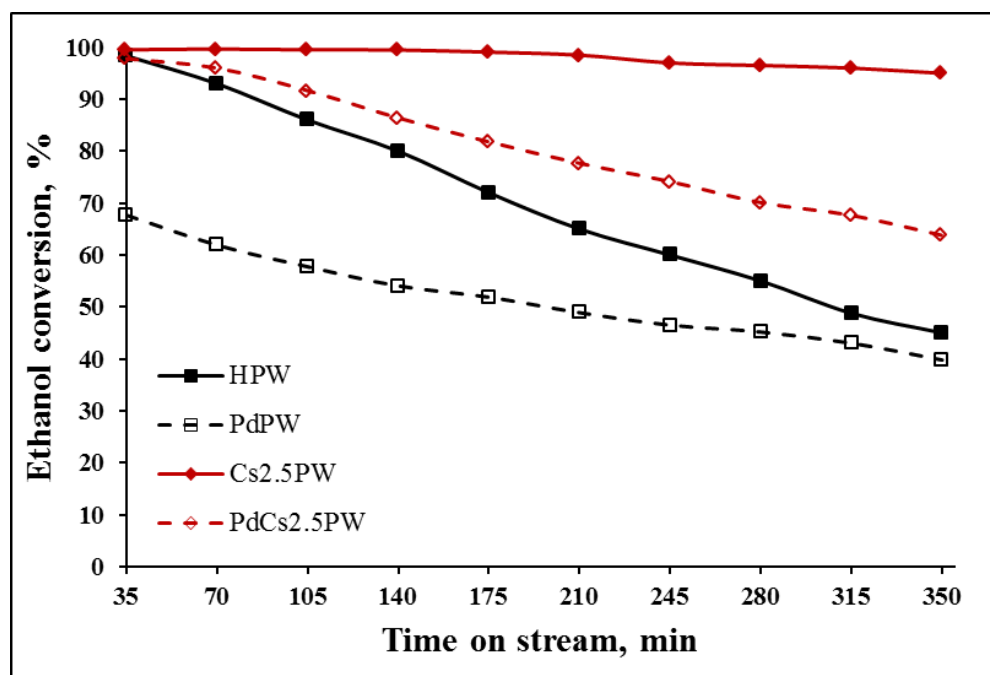
Figure 4. Conversion of ethanol over pure and Pd doped HPW and Cs2.5 PW as a function of TOS at 300 °C.
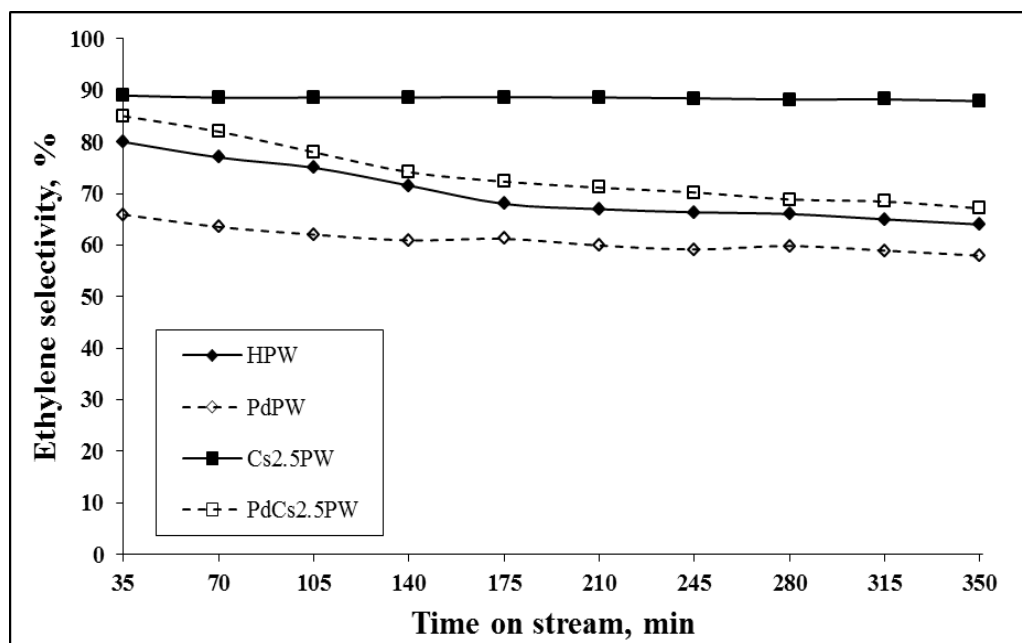

Figure 5. Ethylene selectivity over pure and Pd doped HPW and Cs2.5 PW as a function of TOS at 300 °C.
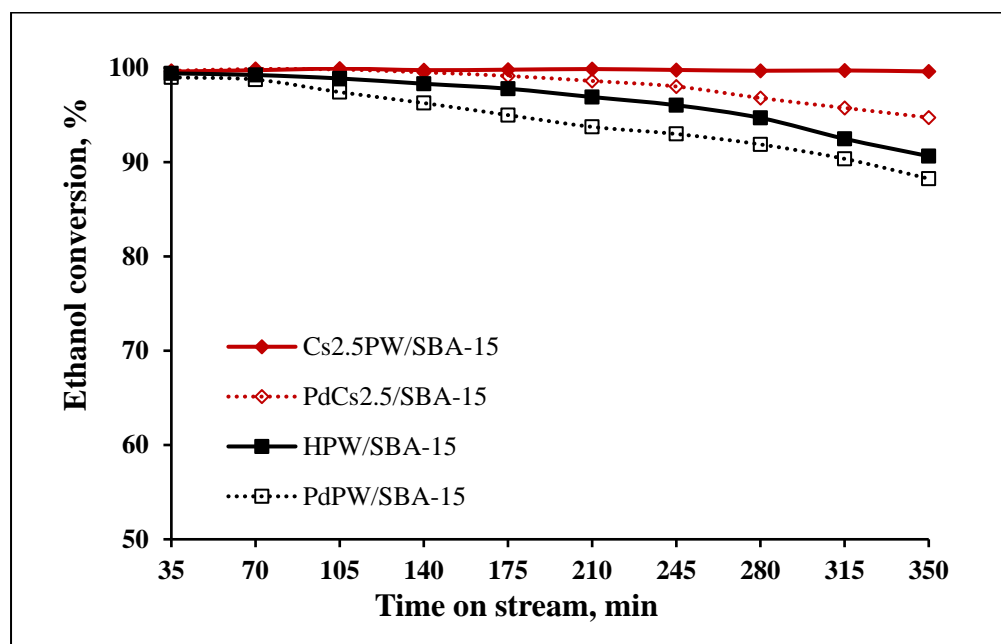
Figure 6. Conversion of ethanol over pure and Pd doped HPW/SBA-15 and Cs2.5 PW/SBA-15 as a function of TOS at 300 °C.

For all catalysts, the ethanol conversion has increasing values during the temperature increase from 200 to 300 °C, but the conversion values are higher for the supported ones. The ethylene selectivity rises with increasing temperature from 200 °C to 300 °C for both pure and supported catalysts. Anyway, as in the case of ethanol conversion, the values of ethylene selectivity decrease slowly with time on stream (Figure 7). Generally, the catalytic activity of supported mesoporous SBA-15 catalysts was higher than that of bulk catalysts.
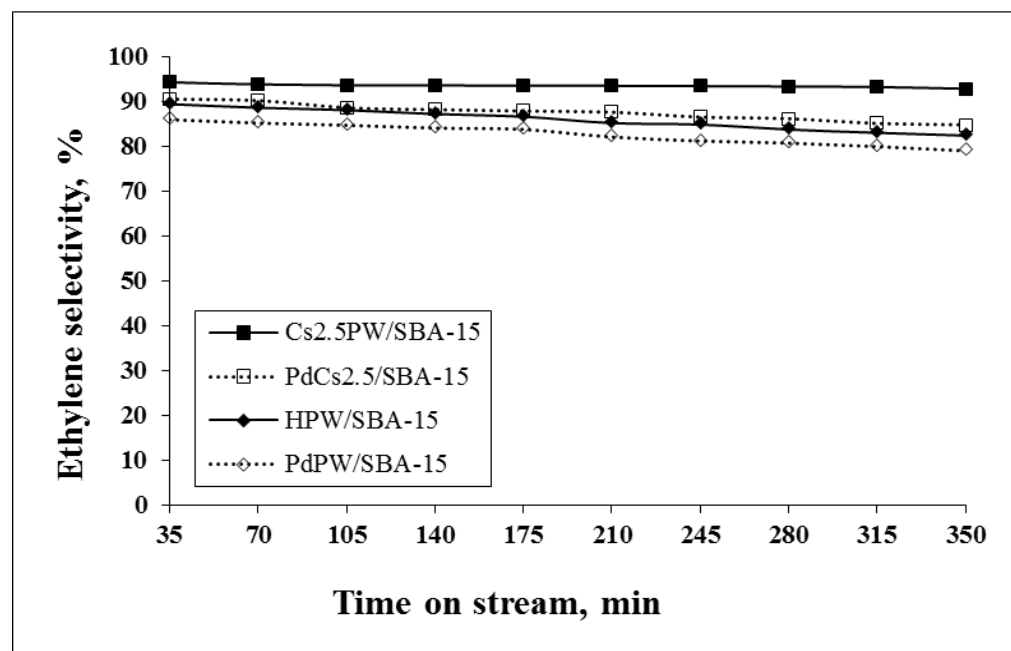

Figure 7. Ethylene selectivity over pure and Pd doped HPW/SBA-15 and Cs2.5 PW/SBA-15 as a function of TOS at 300 °C.

2.3. Temperature Programmed Oxidation (TPO) of Spent Catalysts

As we mentioned before, heteropoly compounds have a high catalytic activity for ethanol conversion but undergo a deactivation process due to the formation of coke [15–18]. Coke deposition of spent catalysts was studied by the temperature-programmed oxidation (TGA/TPO) method. The quantities of coke precursor and hard coke were determined from TG curves. The measurements were conducted in the range of 25–650 °C in a nitrogen atmosphere with an isothermal step at 300 °C. Finally, the catalysts were oxidized under air flow. TGA/TPO data for coke precursors and hard coke of spent catalysis are presented in Figures 8–11.
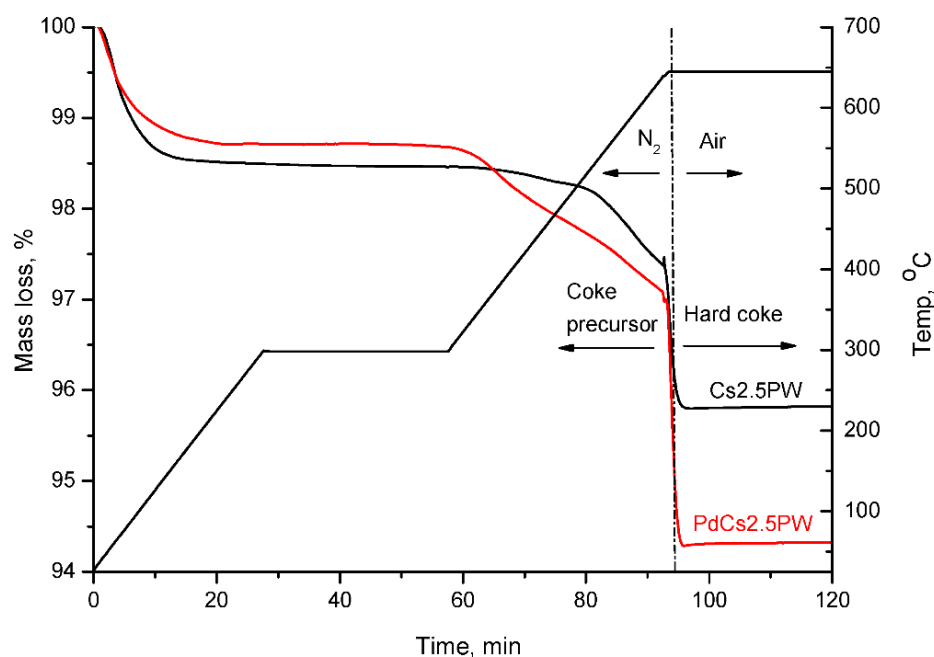

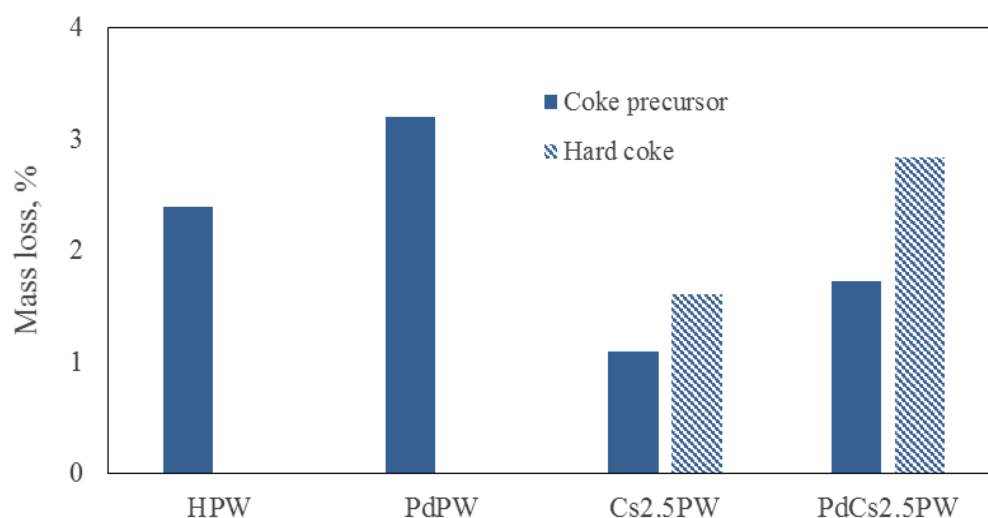**Figure 8.** Coke precursors and hard coke of Cs2.5PW and PdCs2.5PW at 300 °C.

Figure 9. Quantities of coke precursor and hard coke for unsupported catalysts formed by ethanol conversion at 300 °C.
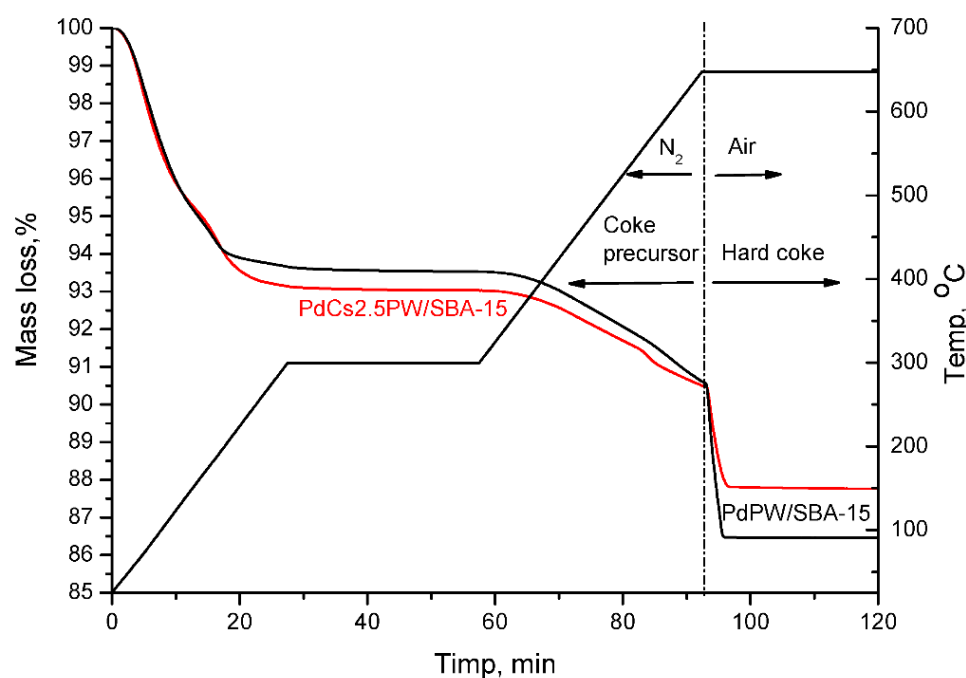
Figure 10. Coke precursors and hard coke of PdCs2.5PW/SBA-15 and PdPW/SBA-15 at 300 °C.
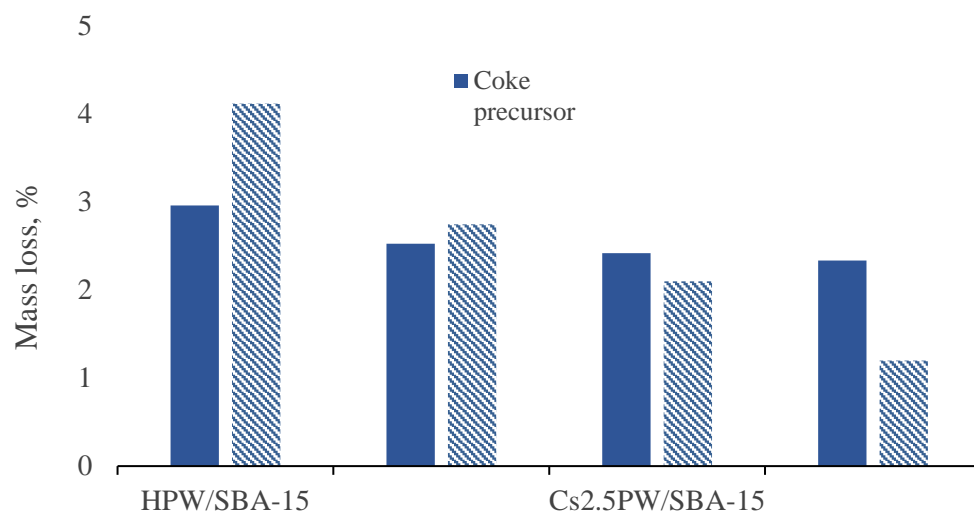

Figure 11. Quantities of coke precursor and hard coke for supported catalysts formed by ethanol conversion at 300 °C.

An increase in the total amount of coke can be clearly observed in the case of unsupported PdCs2.5PW compared to the pure Cs2.5PW catalyst (Figure 8). However, the quantities of coke decrease significantly when PdCs2.5PW is supported on a mesoporous SBA-15 sieve (Figure 10).

Also, there is a significant decrease in hard coke formation for pure and Pd-doped Cs2.5PW (Figure 9). By adding cesium, the Brönsted acidity increases (the number of acid centers increases), which explains the decrease in coke formation. In previous work, the Brönsted acidity of these compounds was determined by TG curves [2].

The number of total coke decreases for Cs2.5PW/SBA-15 and PdCs2.5PW/SBA-15, especially hard coke (Figure 11). As the supported Cs2.5PW and PdCs2.5PW salts contain a mesoporous sieve with an SBA 15 two-dimensional structure, deactivation is slower, resulting in a reduction in the quantity of coke. In the case of supported compounds, the interaction between the heteropoly acid and hydroxyl groups (-OH) present in the meso-

porous silica SBA-15 is important; the degree of dispersion influences the acid concentration of these sites [11,13,25].

The IR frequencies of catalysts were studied after the formation of coke during ethanol conversion in a fixed-bed flow reactor at 300 °C. All characteristic bands of the Keggin unit (primary structure) are preserved after depositing the coke on the catalysts. Deactivation of these compounds does not affect the primary structure, as is evident in Figure 12.
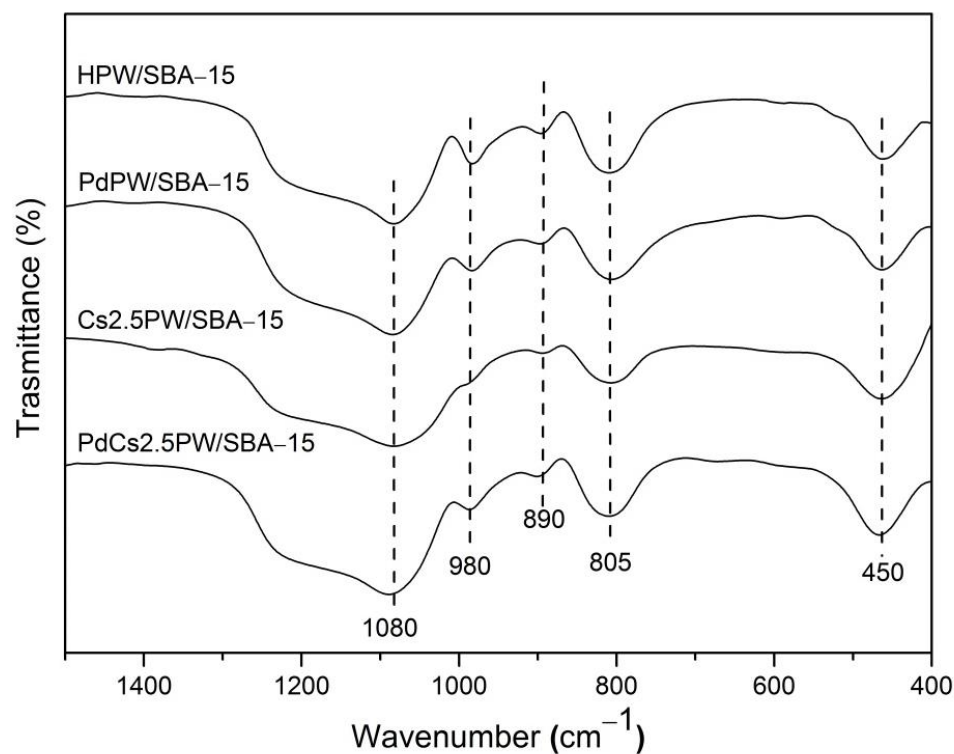

Figure 12. Infrared spectra for spent supported catalysts after ethanol conversion in a fixed-bed flow reactor at 300 °C.

3. Experimental

3.1. Chemicals and Materials

Tungstophosphoric acid ($H_3PW_{12}O_{40}xH_2O$), abbreviated as HPW, was prepared from sodium phosphate dibasic ($NaHPO_4 \cdot H_2O$, ACS reagent, $\geq$99%, Merck, Darmstadt, Germany) and sodium tungstate dehydrates ($Na_2WO_4 \cdot H_2O$, ACS reagent, $\geq$99%, Merck, Darmstadt, Germany). The $CsNO_3$ and $Pd(NO_3)_2 \cdot 2H_2O$ salts were purchased from Sigma-Aldrich (St. Louis, MI, USA). Tetraethyl orthosilicate (TEOS) reagent grade, 98% and *Pluronic P123* (EO20PO70EO20) Poly (ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol)-PEG-PPG-PEG used for preparation of SBA-15 mesoporous silica were purchased from Merck (Darmstadt, Germany). All chemicals were used directly without further purification.

3.2. Measurement

The thermal analyses (TGA and DTA) of both bulk and supported catalysts were carried out by using a thermoanalyzer system Mettler TGA/SDTA 851/LF/1100 (Columbus, OH, USA). The measurements were conducted in a dynamic atmosphere of air (50 mL/min) in alumina crucibles of 150 µL. The mass samples were about 20–30 mg. The heating rate was about 10 °C/min in the temperature range of 25–650 °C.

Fourier transform infrared spectroscopy (FT-IR) was performed on a Jasco 430 spectrometer (Tokio, Japan) for all prepared compounds using KBr pellets at ambient temperature. The IR spectra were obtained in the region from 4000 to 400 cm^{-1} range with 256 scans at 2 cm^{-1} resolution.

Powder X-ray diffraction data were collected using an XD 8 Advanced Bruker automated diffractometer (Karlsruhe, Germany) using the Cu Kα radiation at small angles (2θ = 0.5–5°) and wide angles (2θ = 5–60°), respectively.

A Quantachrome instrument Nova 2000 series (Boynton Beach, FL, USA) was applied to measure the nitrogen adsorption–desorption isotherms. The samples were preheated and degassed at 250 °C for 2 h under vacuum. The specific surface areas of samples were calculated based on Brunauer–Emmet–Teller (BET) equation according to a linear part of the adsorption curves. The pore diameters were calculated by Barrett–Joyner–Halenda (BJH) method applied to the desorption branches of the isotherms.

3.3. Catalyst Preparation

Tungstophosphoric acid $H_3PW_{12}O_{40}$ (HPW) was synthesized according to the J. C. Bailar method [25,26]. The $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (Cs2.5PW) salt was prepared by precipitation from the aqueous solution of acid after adding the stoichiometric amount of $CsNO_3$ under continuous stirring according to our previous report [2]. The HPW doped with 0.25 Pd/Keggin unit (KU), namely $Pd_{0.25}H_{2.5}PW$ (PdPW), was prepared through the reaction between $Pd(NO_3)_2$ and HPW 0.1 M aqueous solutions in the proper ratio. The Cs2.5H0.5PW salt doped with 0.25 at Pd/KU (denoted as PdCs2.5PW) was 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. For all catalysts, the pH was lower than 1.5 during all steps of the synthesis. All samples were dried at 50–60 °C under stirring and heated up to 250 °C in air for nitrate anion total decomposition. *SBA-15 mesoporous* silica was prepared by the hydrolysis of tetraethyl orthosilicate (TEOS) using Pluronic P123 block copolymer as surfactant, according to Zhao et al. [27]. The HPW, PdPW, and PdCs2.5 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 final products obtained were denoted as HPW/SBA-15, PdPW/SBA-15 and PdCs2.5/SBA-15.

3.4. Catalytic Activity Measurement

The catalytic activities of the as-prepared catalysts for ethanol conversion were carried out in a homemade flow microreactor (10 mm inner diameter) placed into an electric furnace. The experimental conditions are presented in Table 3. The catalyst sample was placed in the middle of the reactor and supported by quartz packing at both ends. The reactor temperature was adjusted by a temperature controller within ± 1% in the temperature range of 200−350 °C.

Table 3. Summary of experimental conditions.

Variable	Values
Amount catalyst unsupported (mg)	100
Amount catalysts supported (mg)	330
Catalyst loading (wt.%)	30
Operating temperature (°C)	200, 250, 300, 350
Ethanol flow rate (mL/h)	1.2
Nitrogen flow rate (mL/min)	30
TOS (min)	350

Liquid ethanol was introduced by a Hamilton syringe pump into an evaporator heated at 150 °C. The composition of the reactor effluent stream was analyzed by a gas chromatograph equipped with two detectors: thermal conductivity detector (TCD) and flame ionization detector (FID). In order to separate the products, GC-packed columns filled with Porapak QS 80–100 mesh were used. A temperature program (keep 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 technique. The main

reaction products have the following retention times: ethylene at 5.6, ethanol at 14.8, and diethyl ether at 18.8 min. Secondary products such as methane, C2 (ethane, ethylene), C3 (propane, propene), C4 (butane, butane), C5 (pentane, pentene), C6 (hexane, hexane), and diethyl ether (DEE) have been detected. 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:

$$\text{EtOH conversion}\% = (\text{moles of EtOH reacted}/\text{moles of EtOH total}) \times 100 \quad (1)$$

$$\text{Product selectivity}\% = (\text{moles of product}/\text{moles of reacted EtOH}) \times 100 \quad (2)$$

3.5. Thermal Analysis of Coke

The amount of coke 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 the 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, as shown in Figure 13.
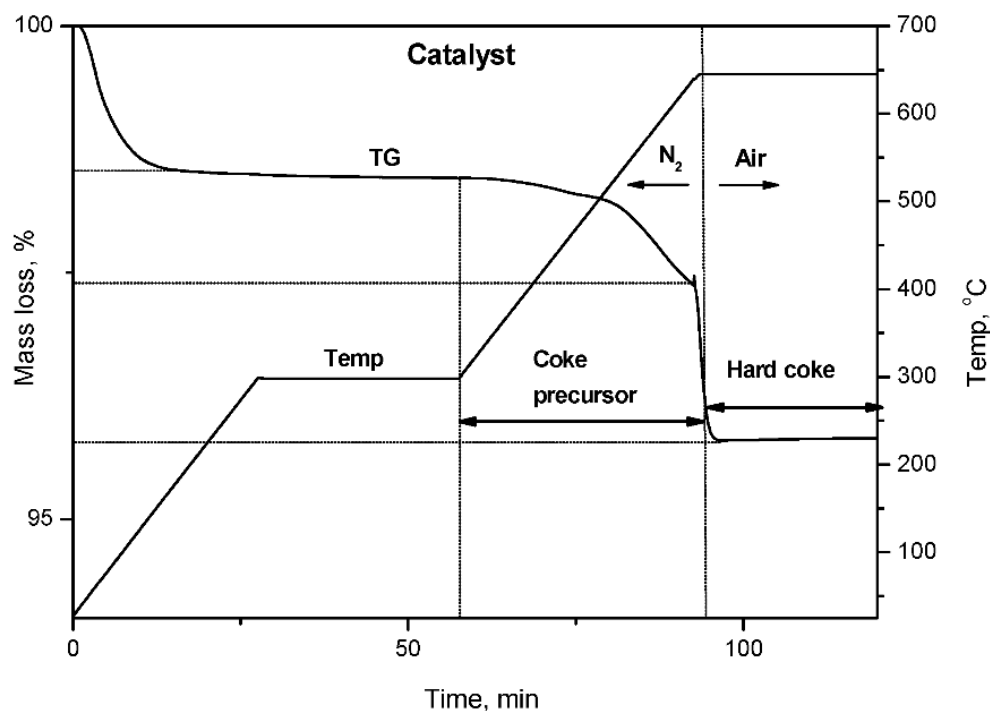

Figure 13. Coke precursor and hard coke catalyst during TGA-TPO method.

The quantities of coke precursor present in the catalysts were calculated as difference between the initial mass of spent catalyst sample after isothermal heating at 300 °C 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 aromatic.

4. Conclusions

A series of pure and Pd-doped HPW/SBA-15 and Cs2.5PW/SBA-15 catalysts have been prepared, and their catalytic performance and coke formation in ethanol conversion have been investigated.

The XRD results indicated that the mesostructured ordering is slightly modified by the impregnation of the catalysts into SBA-15.

By comparing adsorption–desorption isotherms, it was observed that all catalysts have a hysteresis loop similar to the parent support, which indicates that the hexagonal structure of SBA-15 is preserved after Pd doping and Cs2.5PW impregnation.

In the case of supported samples, the effect of the support leads to higher values of ethanol conversion and ethylene selectivity. As a result, during the time on stream (TOS), the amount of coke decreases significantly. The effect of palladium doping on the coke formation was studied; thus, it can be concluded that Pd increases the coke formation for pure catalysts while Cs decrease it. However, in the case of catalysts supported on SBA-15, Pd decreases significantly the quantities of coke, especially hard coke.

FTIR studies show that the formation of coke deposits during the ethanol conversion, although the deactivation occurs, it does not affect the Keggin structure of catalysts supported on SBA-15.

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