Catalytic efficiency of activated carbon functionalized with phosphorus-containing groups in 2-propanol dehydration

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The functionalization of activated carbon (AC) by P-containing groups was conducted, and their thermal desorption was studied. Depending on the used method, the functionalized AC contains 0.5–1.45 mmol/g of acidic groups acting in catalytic 2-propanol dehydration. All catalysts showed 100% conversion of 2-propanol to propylene. The catalytic activity does not change with time under isothermal conditions and during their repeated use in catalysis, for 3 cycles of heating-cooling. In fact, the yield of propylene remains stable; it does not decrease with each cycle. Preliminary oxidation with nitric acid causes a small increase in the catalytic activity.

Introduction

Mineral strong acids are very important for chemical technology. Acid catalysis has always been developed in recent decades. As known, acidic catalysis can be driven by (i) homogeneous and (ii) heterogeneous catalysts. Liquid strong acids are often used to catalyze reactions at rather low temperatures in the homogeneous industrial catalysis. But, there are many problems with their practical adaptation. These include the formation of large amounts of wastes and the corrosive destruction of metal equipment. In fact, such an industrial process is required the laborious separation of the mineral acid catalyst from reaction products. Finally, the sequential implementation of the stages of the chemical process is necessary. On this background, the use of solid acid catalysts based on activated carbon (AC) and related solid acid materials are becoming increasingly popular and developing.

Precursors of AC can be broad materials containing carbon in the form of natural organic compounds. The most commonly used natural precursors are agricultural wastes, wood, and natural coals [1–3]. Because of the growing demand for AC and increased restrictions on environmental protection, new precursors and new technologies for the production of carbons are constantly being sought. From this point of view, the use of post-agricultural and post-production wastes has great economic and environmental advantages. Actually, AC derived from these inexpensive wastes [4] has excellent characteristics to be used as a catalyst carrier. It has a large specific surface area, regulated surface chemistry, and high chemical stability [4–7]. To increase the surface acidity, ACs can be subjected to various additional oxidative treatments. They can generate different surface groups, e.g. acidic carboxylic groups. However, these groups have low thermal stability and decompose at 250 °C [8]. Sulfonation with sulfuric acid results in an insufficient concentration of sulfogroups groups having moderate thermal stability. This does not satisfy the requirement for the effective passage of many catalytic reactions [9]. Corrosion and oxidation are degraded the carbon texture and dropped mechanical characteristics resulting in loss of activity [10]. AC is usually obtained by carbonizing the raw material in an inert atmosphere. To an increase in the adsorption capacity of the materials obtained, carbonized mass is subjected to chemical and physical activation. Phosphoric acid and related compounds containing phosphorus are used as chemical activators [11]. By adding phosphorus compounds, the mechanical and adsorption properties of carbon materials can be improved [12]. However, this activation is corrosive, and the resulted phosphorylated AC has limited application. Factually, the porous structure and the number of acidic sites could not be controlled after carbonation [13–16].

In this work, we functionalized AC having advanced textural parameters with phosphorus-containing functional groups and studied their thermal desorption and catalytic activity in the dehydration of 2-propanol alcohol.

Experimental part

Material and methods

We used, as a starting material, AC obtained from fruit seeds which specific surface area is 1350 cm^3/g, granules of 0.5–1 mm. For the surface functionalization, two groups of treatment methods as used. The first is direct which included the direct interaction with the modifying reagent. The second is indirect which included the pretreatment of the carbon surface before the grafting of acid groups. Preliminary surface treatment was carried out by oxidation with hydrogen peroxide and nitric acid to increase the concentration of polar groups that should be used in the substitution reactions for the formation of acid sites. Alternatively, chlorination with carbon tetrachloride at heating

was used to functionalize carbon surface with chlorine groups to be replaced by phosphoryl groups. Here we considered the influence of the pre-oxidation treatment on the physical and chemical properties of the resulted AC.

Thermal desorption studies were carried out using thermogravimetric analysis (TGA), thermoprogrammed desorption with infrared spectrometric gas products registration (TPD IR) and thermoprogrammed desorption mass spectrometry (TPD MS) [17]. The thermal analysis was carried out in the temperature range of 30–800 °C, at a heating rate of 10 °C/min. When using TGA and TPD IR simultaneously, the concentration of CO and CO_2 desorption products was determined by IR spectrometry.

The chlorine content was determined by inverse Volgard titration for Cl^- using pyrolytic decomposed samples [18]. Phosphorus, tungsten, and sulfur were found by the gravimetric method [19]. The concentration of the surface acidic sites was determined by potentiometric titration (PT) [20]. For this purpose, pre-dried AC (0.1 g) was poured into 25 ml of 0.1N NaOH solution and kept for 24 hours. This solution was titrated, and the total acidic sites concentration was calculated by the difference in NaOH concentrations before and after contact with the sample. The surface morphology was studied on a JEOL JSM 6060LA scanning electron microscope (SEM). Catalytic test for 2-propanol dehydration into

propylene was conducted as reported earlier in [17, 21].

Preparation

Oxidation with nitric acid: AC (2 g) was poured into 30% HNO_3 (60 ml) and was refluxed on a sand bath for 2 h. Resulted AC/HNO_3 was washed with distilled water to a pH of 5.5–6 and air-dried at 120 °C.

Oxidation with hydrogen peroxide: AC (2 g) was added to 50 ml of 30% H_2O_2 for 4 h at 25 °C. Resulted AC/H_2O_2 was washed with water and dried at 120 °C.

Chlorination with tetrachloromethane. Before chlorination, decarboxylation of AC was carried out in dynamic argon at 500 °C for 1.5 h. At typical chlorination, AC was heated in argon diluted CCl_4 vapors at the temperature of 450 °C for 1.5 h. After the reaction, argon flow was passed through the sample for 1 h and then AC/CCl_4 was cooled to 25 °C under argon. The decarboxylation was carried out to remove groups that cannot be substituted for chlorine: carboxylic, anhydride, and a part of lactone groups. As a result of decarboxylation, the carbon surface contains hydroxyl, carbonyl, quinone and an insignificant number of lactone groups.

Phosphorylation with phosphorus oxychloride. 2 g of AC/H_2O_2 was decarboxylated at 450 °C to remove the carboxyl and part of the lactone groups unreactive in further phosphorylation. 1.5 g of decarboxylated AC was added to 10 ml of $POCl_3$ and refluxed for 3 h. This method is

not effective and does not result in the significant grafting of phosphoryl groups according to Scheme 1 **(Figure 1)**. According to the chemical analysis (CA), the phosphorus content in the prepared phosphorylated AC is insignificant, 0.11 mmol/g. Since this sample contains a few acid groups, it was excluded from further studies. Previously, we showed that the sulfonated ACs containing less than 0.2–0.3 mmol/g of S-containing groups are low or even inactive in the dehydration reaction.
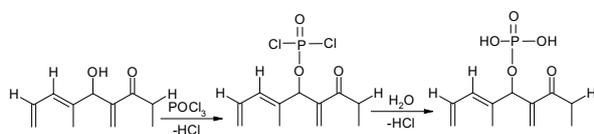
Figure 1. Scheme for functionalization of AC with phosphorus oxychloride.

Phosphorylation with orthophosphoric acid. Since AC phosphorylated with phosphorus oxychloride contains a few phosphoryl groups, 10 ml of 87% H_3PO_4 was added to 1 g of AC/CCl_4 stored in Pyrex beaker. This beaker was capped and gradually heated in an electric oven up to 350 °C for 1.5 h, then maintained under isothermal conditions for 3 h. In the course of the experiments, the release of HCl was registered as a result of the substitution reaction; see Scheme 2 **(Figure 2)**. After cooling the sample of $AC/CCl_4/H_3PO_4$ was washed from unreacted H_3PO_4 with water and dried in air at 120 °C. For the reaction with H_3PO_4, the initial AC and AC/H_2O_2 were also used. Before the AC treatment with H_3PO_4, both them were decarboxylated at 450 °C for 2 h and then degassed by vacuuming for 2 h. According

to the results of CA, the phosphorus content is about 0.5 mmol/g. For the pristine AC and oxidized AC, the content of phosphoryl groups in the resulting samples is low, far below that required for effective catalysis.
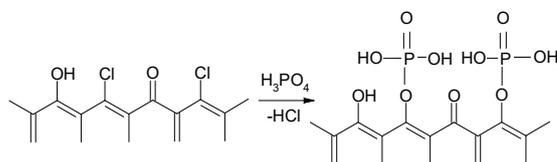
Figure 2. Scheme for AC functionalization with phosphoric acid.

Treatment with phosphorus tungstic acid. 1 g of AC AC/H_2O_2, and AC/HNO_3 was impregnated with a 5% (v/v) water solution of ($H_7(P(W_2O_7)_6 \cdot xH_2O$) at 100 °C for 2 h, and then $AC/H_7[P(W_2O_7)_6]$ and $AC/X/H_7[P(W_2O_7)_6]$ samples, where X = H_2O_2 or HNO_3, were dried in air at 120 °C. According to the CA, the concentration of acid sites with respect to WO_3 was 1.2–1.45 mmol/g.

Results and discussion

According to TPD MS, the TPD spectra of AC showed signals corresponding to H_2O, CO, and CO_2 desorption from the AC surface (m/z 18, 28, and 44, respectively, **Figure 3a**). The water release has a wide temperature maximum at 90 °C sourced from physisorbed water. Water desorption at temperatures of 150–350 °C occurs owing to the decomposition of carboxylic groups, which is confirmed by the simultaneous release of CO_2 peaked at 250 °C. Desorption of H_2O at higher temperatures is due to thermal decomposition of phenolic groups, which is confirmed by significant CO release.
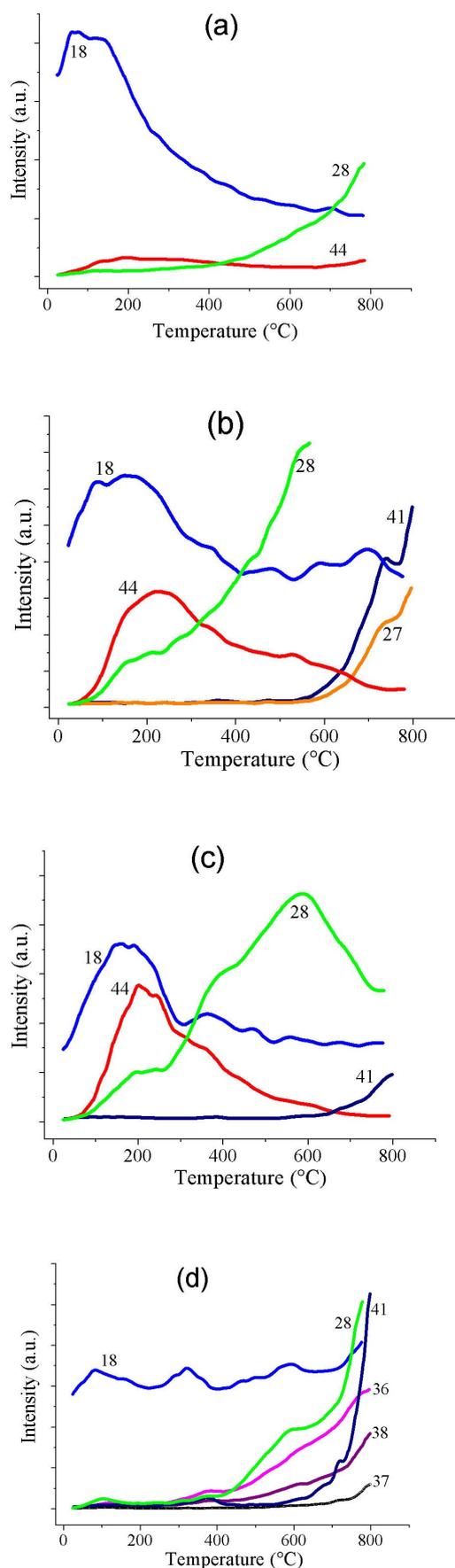
Desorption of other fragments, including parts of the carbon matrix, don't observe in the mass spectra. The relative intensity of CO and CO_2 release is low **(Figure 3a)**. Only some oxygen-containing groups are present on the surface of AC. These observations are confirmed by the TGA and TPD IR data, according to which the concentration of CO and CO_2 that formed during the thermal decomposition of oxygen-containing groups is 0.95 and 0.74 mmol/g, respectively **(Table 1)**. The total mass loss for the pristine AC is negligible, of about 0.06 g/g **(Figure 4a)**.

For AC/H_2O_2 and AC/HNO_3, in comparison with the pristine AC, the mass loss increases by 0.10 and 0.34 g/g, correspondingly, see Table 1. At the oxidation of AC with solutions of H_2O_2 and HNO_3, there is a significant increase in the oxygen-containing groups. We registered the change in the shape and relative intensity of the profile for their thermal desorption products **(Figures 3b and 3c)**.

Depending on the oxidant used, the functional groups are formed at a different intensity. For AC/H_2O_2 and AC/HNO_3, the relative intensity of CO_2 desorption in the entire studied temperature range, for the most between 150 and 350 °C, is significantly increasing. This fact specifies the large amounts of carboxyl groups. They are formed during the oxidative treatment. In the high-temperature region, we found intensive desorption of CO. The

Figure 3. TPDMS profiles of **(a)** AC, **(b)** AC/H_2O_2, **(c)** AC/HNO_3, **(d)** AC/CCl_4 (m/z 18, 28, 41, 36, 37, and 38).

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formation of phenol OH groups could be confirmed by this observation and high-temperature water release.

TPD MS spectra of AC/H_2O_2 and AC/HNO_3 are in contrast to that of AC. In addition to H_2O, CO, and CO_2 desorption, we registered a series of fragments with m/z 55, 42, 41, 40, 39, 27, and 15 at above 600 °C **(Figures 3b and 3c)**. These signals are produced by high-temperature destruction of the carbon matrix. According to CA (Table 1), the oxygen content in AC/H_2O_2 and AC/HNO_3 is increased to 4.56 and 10.6 mmol/g, respectively.

Figure 3d shows TPD mass spectra of AC/CCl_4. The chlorination leads to less intense and nearly constant water release. Because of the decarboxylation, there is a minor CO_2 emission in TPD mass spectra. But CO release is observed at above 450 °C which is the decarboxylation temperature. For AC/CCl_4, the content of the oxygen-containing groups remarkably drops. The concentration of oxygen-containing groups which decomposed to yield CO is somewhat reduced due to the decarboxylation. According to TPD IR data, we registered 2 times increase of CO concentration **(Table 1)**. In our opinion, both CO- and CO_2-bearing sites (phenolic and lactone groups) are formed after chlorination by the mechanism of aging [22]. The concentration of chlorine, according to CA data, is 3.9 mmol/g, and the mass loss increases 3 times compared to that of

AC. Chlorine desorption occurs in the form of HCl (m/z 36 and 38) at above 450 °C.
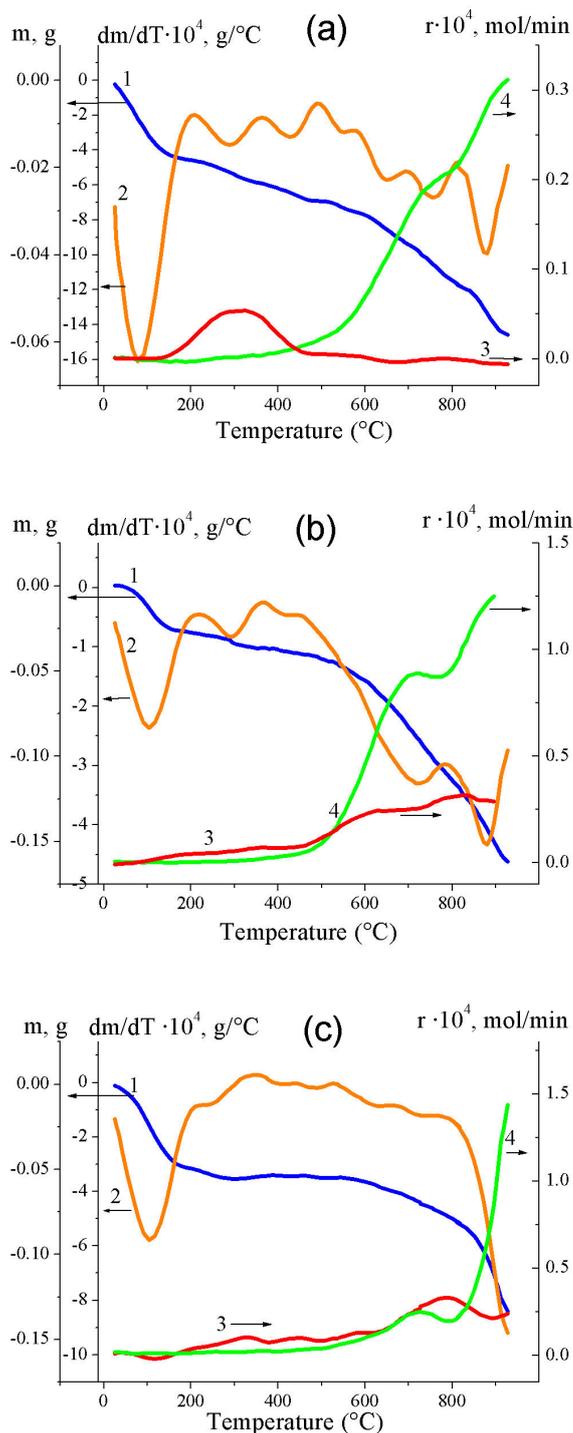
Figure 4. TGA for (a) AC, (b) $AC/CCl_4/H_3PO_4$, and (c) $AC/H_7[P(W_2O_7)_6]$. TG (1), DTG (2), CO_2 (3) and CO (4) evolved gas rate.

For $AC/CCl_4/H_3PO_4$, the mass loss in the temperature range of 180–400 °C is slightly

higher than that of the pristine AC **(Figure 4b)**. This situation means no detectable events of the decomposition of the surface layer in this temperature range **(Table 1)**. For this sample, the formation of small amounts of CO and CO_2, and the absence of desorption of the latter in the region of temperatures up to 450 °C is characteristic, which is the result of preliminary decarboxylation and chlorination at 450-470 °C.

Desorption of water is the only notable process occurring below 500 °C (Figure 4b). This behavior is caused, most likely, the formation of polyphosphoric acids. The main mass loss is registered at above 500 °C. At the same time, we registered a significant amount of CO by TPD IR. This evolved gas is the product of thermal decomposition of carbon fragments of the matrix. It should be noted that in the mass spectra registered at below 850 °C, there are no fragments that could be identified as phosphorus residues, for m/z up to 200. The reason for this is the formation of polyphosphoric acids. They can desorb from the carbon surface as large ions only. Consequently, one can argue that $AC/CCl_4/H_3PO_4$ has a substantially higher thermal stability than samples AC functionalized with sulfur-based acid sites [9]. The reason for the highest thermostability, in our opinion, is the close electronegativity of carbon and phosphorus. Consequently, phosphorous and carbon doesn't participate in redox reactions at below 800–900 °C.

The treatment of the surface of AC with phosphorus-tungsten acid does not lead to significant changes in temperature dependences compared with that of AC/H_2O_2 and AC/HNO_3. This conclusion is logical since phosphorus-tungsten acid **(Figure 4c)** does not undergo significant transformations between 30 and 850 °C. The growth of the mass loss is observed at high temperatures, at above 600 °C. It can be explained by the surface carbon oxidation with oxygen taken from $H_7[P(W_2O_7)_6]$ composition. This is confirmed by the data of mass spectrometry. In fact, the shape of the desorption peak and the temperature range of desorption of H_2O, CO, and CO_2 are in contrast to those for the pristine AC. In the former case, the amount of released desorption products is considerably larger. Another proof of the oxidizing effect of $H_7[P(W_2O_7)_6]$ is the desorption of alkane and alkene fragments (m/z at 40, 29, 27, and 12) from the carbon matrix. We registered them at above 800 °C. Similar trends are observed for oxidized carbons treated with $H_7[P(W_2O_7)_6]$. However, the high-temperature decomposition of $H_7[P(W_2O_7)_6]$ doesn't influence on catalysis, since the reaction temperature is pointedly lower. Significant mass loss observed for $AC/H_2O_2/H_7[P(W_2O_7)_6]$ and $AC/HNO_3/H_7[P(W_2O_7)_6]$ is caused the preliminary oxidation **(Table 1)**. According to the PT data, the total acidity ranged between 0.30 and 4.05 mmol/g of acidic groups. The main contribution to the total composition is made by the oxygen-containing groups, which

content arises for the expanse of the preoxidation.

SEM micrographs of the surface of the pristine AC showed that there are channels of different depths and of the average size of 10–30 microns in section, which are surrounded by smaller channels of 1-2 microns in section **(Figure 5a)**. For AC samples treated with phosphoric acid and $H_7[P(W_2O_7)_6]$, the surface showed prominent changes. The channel entrances become extended. We found sufficiently long cavities which depth and porosity vary to a lesser extent for $AC/H_7[P(W_2O_7)_6]$ and for the most for $AC/CCl_4/H_3PO_4$ **(Figures 5b and 5c)**. For the latter, the deep channels become less porous. They disappear or, to a lesser extent, there are porous openings of deep channels. Besides, shallow channels and cavities became porous **(Figure 5c)**.

We found a low activity of AC and AC/H_2O_2. The yield of propylene over them is less than 25% at 300 °C **(Table 1)**. The yield of propylene drops significantly with each cycle. In fact, AC/HNO_3 showed higher activity and the propylene yield. This slight increase is supplied by many carboxyl groups having a low acidity. The chlorinated AC/CCl_4 is inactive at all, as expected. We registered significant catalytic activity only for AC grafted with phosphoryl groups and treated with $H_7[P(W_2O_7)_6]$. For the $AC/CCl_4/H_3PO_4$, the

temperature of the total conversion of 2-propanol to propylene is 260 °C. Although it is high, it maintains during heating from 25 °C up to the temperature of the total conversion and then under respective cooling, in the heating-cooling cycle, for three times.
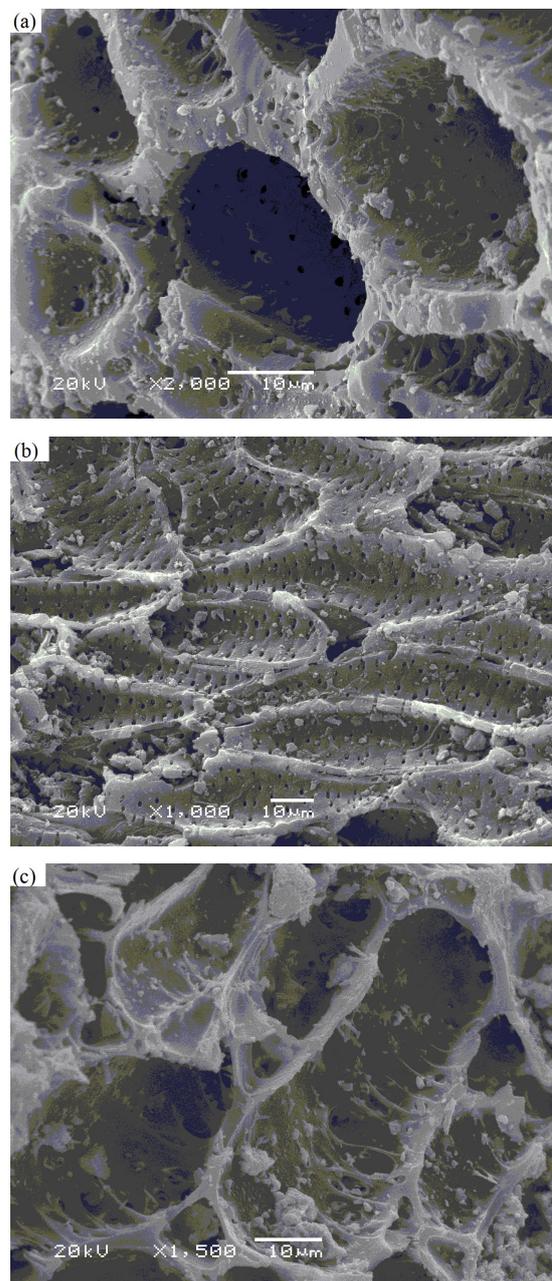
Figure 5. SEM micrographs (a) AC, (b) $AC/CCl_4/H_3PO_4$, (c) $AC/H_7[P(W_2O_7)_6]$.

Table 1. Concentrations of carbon oxides ($C(CO)$ and $C(CO_2)$) from TPD IR, total acidity(C_{PT}), CA for Cl, P, W and reaction temperature/conversion for catalytic 2-propanol dehydration for 1-3 heating-cooling cycle

Sample	Concentration(mmol/g)					Reaction temperature/Conversion (°C/%)		
	$C(CO)$	$C(CO)$	C_{PT}	CA		1 cycle	2 cycle	3 cycle
AC	0.95	0.74	0.30	O	1.37	300/25	330/25	350/10
AC/H$_2$O$_2$	1.87	1.03	1.47	O	4.56	250/11	280/11	300/8
AC/HNO$_3$	4.29	4.73	3.77	O	10.6	320/29	350/23	350/15
AC/CCl$_4$	2.1	0.64	3.9	Cl	3.9	inactive		
AC/CCl$_4$/H$_3$PO$_4$	3.83	1.54	0.98	P	0.5	260/100	260/100	260/100
AC/H$_7$[P(W$_2$O$_7$)$_6$]	1.61	1.46	2.25	WO$_3$	1.31	150/100	150/100	150/100
AC/H$_2$O$_2$/H$_7$[P(W$_2$O$_7$)$_6$]	2.38	1.89	3.03	WO$_3$	1.45	155/100	155/100	155/100
AC/HNO$_3$/H$_7$[P(W$_2$O$_7$)$_6$]	3.65	2.52	4.05	WO$_3$	1.20	140/100	140/100	140/100

The catalyst stability in heating-cooling cycles even at relatively high temperatures showed the phosphoryl groups are grafted strongly enough to be used for industrial acid processes. The most active are AC treated with H$_7$[P(W$_2$O$_7$)$_6$]. They showed the reaction temperature at the total conversion in the range from 140 to 155 °C which is the lowest operating temperature regime. The temperatures at the total conversion do not change with repeated use of catalysts (Table 1). Pre-oxidation with H$_2$O$_2$ caused an increase in the temperature at the total conversion which is 5 °C higher for three cycles of heating-cooling. For AC/HNO$_3$/H$_7$[P(W$_2$O$_7$)$_6$], the oxidation causes a decrease the dehydration reaction temperature by 10 °C as compared with that of AC/H$_7$[P(W$_2$O$_7$)$_6$]. The reason for this observation could be different groups that formed on the surface of oxidized AC [23–24].

Also, we conducted additional catalytic studies to examine their activity with respect to temperature, by holding catalysts from 2 to 3 h under isothermal conditions. Measurements were performed at the reaction temperature that corresponds to the temperature at 50-60% isopropanol conversion. All AC-based catalysts functionalized with phosphorus-containing groups demonstrate reasonable stability of the catalytic action. They showed no events of

deactivation within the selected time periods. Hence, the catalytic activity for other samples gradually decreases. Typically, for the most active catalysts, the temperature at the total conversion of isopropanol alcohol is far below the decomposition temperature of acid groups. Therefore, the most active catalysts exhibit higher thermal stability of phosphoryl groups. They are not subjected to thermal decomposition. No thermodesorption of P_2O_5 was observed in the reaction medium under these conditions. For other, less active catalysts, under the conditions of the dehydration reaction, at and below 300 °C, the most active, acidic carboxyl groups are decomposed partially.

Conclusions

We proposed the functionalization of AC by phosphorus-containing functional groups with direct and indirect methods. Obtained carbon solid acids depending on the used method contain 0.5–1.45 mmol/g of acidic groups. The catalytic properties in the dehydration reaction showed that the conversion temperature depends on the total acidity and, in part, on the oxidation treatment. All phosphorylated AC catalysts and AC treated with $H_7[P(W_2O_7)_6]$ showed 100% selectivity towards propylene at the total conversion of 2-propanol. The yield of propylene does not change at least 3 cycles of heating and cooling.

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