



Dehydration of Fructose into 5-Hydroxymethylfurfural Catalyzed by Phosphorylated Activated Carbon Catalyst

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Surface functionalized activated carbon catalysts with phosphate group were synthesized and used to catalyze dehydration of fructose into 5-hydroxymethylfurfural. The surface oxygen-containing functional groups of phosphorylated activated carbon were characterized and analyzed by XPS, infrared spectroscopy and Boehm titration techniques. The catalysts exhibit high dehydration activity of fructose but low 5-hydroxymethylfurfural selectivity using water as the solvent. Organic solvent can effectively improve the 5-hydroxymethylfurfural selectivity and yield. The highest 5-hydroxymethylfurfural yield of 66.6 % was achieved using DMSO as the solvent at 160 °C for 30 min. It was found that the amount of phosphate group is correlated with the fructose conversion, but higher concentration of phosphate group leads to the decrease of 5-hydroxymethylfurfural selectivity.

Keywords: Phosphorylated activated carbon, Fructose dehydration, 5-Hydroxymethylfurfural, Phosphate.

INTRODUCTION

In recent years, much effort has been taken to the development of alternatives to the fossil-based industry of today. The development of a new, long term, environmentally friendly and sustainable chemical source has received wide attention. 5-Hydroxymethylfurfural, a versatile and key renewable platform chemical produced from biomass feedstock, can be transformed into fuels and various valuable chemicals through catalytic conversion, such as the gasoline additives-2,5-dimethylfuran (DMF), an alternative polymer precursor-2,5-furandicarboxylic acid (FDCA) and levulinic acid¹⁻¹⁶.

In past years, the production of 5-hydroxymethylfurfural was performed by mineral acid-catalyzed hydration of biomass, such as glucose, fructose and inulin^{1,17,18}. The drawback of mineral acid is that it leads to the severe environmental pollution. In recent years, some novel and green methods have been developed. Ionic liquid system is a hot topic due to excellent catalytic performance of producing high yield of 5-hydroxymethylfurfural yield through catalytic hydrolysis of biomass feedstock¹⁹⁻²³. In addition, heterogeneous solid acid catalysts, such as sulfated zirconia²⁴ and acid zeolite²⁵⁻²⁸, have been also attracted wide attention. Among all the solid acid catalyst suitable for aqueous reactions, sulfonated carbon materials have received much attention since its surface acidity and the hydrophilic/hydrophobic character are easily tuned and it has more stable at hydrothermal reaction condition²⁹⁻³¹.

In this work, we use a novel phosphate group functionalized activated carbon, phosphorylated activated carbon, to catalyze dehydration of fructose to produce 5-hydroxymethylfurfural. The surface properties of the functionalized activated carbon were tailored through the incorporation of different concentration of phosphate group. The catalytic activities of these materials were evaluated by the fructose dehydration using H₂O and DMSO as the solvents. The relationship of the activity and selectivity of these samples with the amount of surface oxygen-containing functional groups is discussed.

EXPERIMENTAL

Preparation of catalysts: The preparation of phosphorylated activated carbon is similar to the method reported in the literature³². Coconut activated carbon was used as support. The support was impregnated with aqueous solution of H₃PO₄ at room temperature and then the mixture was stirred for 2 h. Subsequently, water was removed from the mixture through heating it at 90 °C. The dry samples were activated under N₂ flow in a quartz reactor heated by tubular furnace. Different activation temperatures [350, 450 and 550 °C and impregnation ratios (1 and 0.5)], defined as H₃PO₄/AC weight ratio, were used to synthesize the samples with different amount of phosphate group. The calcined samples were cooled under N₂ flow and then washed with distilled water until neutral pH and dried at 120 °C overnight. The activated carbon obtained are denoted

by the letter AC-x-T, where x and T correspond to the impregnation ratio and the activation temperature in degree celsius, respectively.

Catalyst characterization: X-Ray photoelectron spectroscopy (XPS) was carried out on an AXIS ULTRA DLD instrument (SHIMADZU company) using Al K α radiation to determine the oxygen-containing functional groups and the valence state of phosphorus elements. The samples were pressed into a sample holder and then were evacuated to 10⁻⁶ Pa. The spectra were analyzed and processed with the use of XPSpeak software.

Boehm titrations was used to quantify surface oxygen-containing functional groups on activated carbon³³. Surface oxygen-containing functional groups including carboxyl (R-COOH), lactone (R-OCO), phenol (Ar-OH) and carbonyl groups were determined using different reactants. The procedure was described as follows: 0.10 g of each sample was mixed in a closed flask with 50 mL of a 0.1 mol/L aqueous reactant solution (NaOH, Na₂CO₃ or NaHCO₃). The mixtures were shaken for 24 h at room temperature and then filtered off. Back-titrations of the filtrate were then carried out with standard HCl (0.01 mol/L) to determine the oxygenated functional group contents.

Catalytic reaction: Reactions were conducted in a 100 mL autoclave equipped with a thermostat and an electronically controlled magnetic stirrer charged with N₂ (5 bar). The fructose concentration of 2 wt % was used as the feedstock and the catalyst (substrate/catalyst = 4/1 wt/wt) were mixed in solvent (total volume 50 mL). The reactor was pressurized at 5 bar of N₂ and ramped to desired temperature. Once the reaction temperature was reached, the monitoring of the reaction started. The catalysts were removed periodically and analyzed by high-performance liquid chromatography (HPLC) using a column (Zorbax SB-C18) with UV detector to analyze 5-hydroxymethylfurfural yield. Aqueous solution was used as a flow phase. The quantitative analysis of 5-hydroxymethylfurfural was performed by external standard method. The reducing sugar was detected by DNS method according to the reference³⁴.

RESULTS AND DISCUSSION

Table-1 shows effect of reaction temperature, water and solvent on the dehydration reaction of fructose catalyzed by AC-0.5-450. It can be seen that phosphorylated activated carbon could effectively catalyze the dehydration of fructose into 5-hydroxymethylfurfural. The fructose conversion increases with the reaction temperature, but the 5-hydroxymethylfurfural yield does not always increase and its highest yield of 29.6 %

is achieved using water as the solvent at 140 °C for 30 min. When H₃PO₄ is used as the catalyst at 140 °C, the fructose conversion is about 96.8 % and the 5-hydroxymethylfurfural yield is 38.9 %. The reason is that the acid strength of phosphate group anchored activated carbon is weaker than H₃PO₄, resulting in a decrease in the activity of phosphorylated activated carbon sample. The influence of the reaction time on fructose conversion as well as 5-hydroxymethylfurfural yield and selectivity was also analyzed. As can be seen from Table 1, the fructose conversion increases but the 5-hydroxymethylfurfural yield and selectivity decrease with increasing the reaction temperature. This is because 5-hydroxymethylfurfural can be further rehydrated to produce levulinic acid and polymerized into humin, leading to a decrease of 5-hydroxymethylfurfural yield and selectivity. It was reported that DMSO can effectively inhibit the degradation of 5-hydroxymethylfurfural to by-products, thus DMSO was selected as the reaction solvent^{9,35,36}. As DMSO was used as the solvent, the 5-hydroxymethylfurfural yield and selectivity achieve about 60.1 and 68.2 % at 140 °C and the highest 5-hydroxymethylfurfural yield and selectivity achieve 66.6 % and 79.1 % at 160 °C, respectively.

XPS has been shown to be a useful tool for analyzing the surface oxygenated functional groups of carbon materials. It allows for semi-quantitative analysis of surface oxygenated functional groups by measuring the shift in binding energy and thus the local chemical state. Fig. 1a presents the XPS results of C1s excitation of AC-0.5-450. The spectra were deconvoluted into five components according to the literature results³⁷. The components are assigned to carbide, graphitic carbon, carbon species in ether groups and alcohol, carbon in carbonyl groups, carboxyl and/or ester groups³⁷, their corresponding binding energies and area percentages as illustrated in Table-2. It can be seen that the amounts of carboxyl group and R-OH+C-O-C or C-O-P of AC-0.5-450 are greater than three other samples. Fig. 1b indicates the XPS results of P 2p excitation of AC-0.5-450. The phosphorous spectra can be convoluted into two peaks at 132.9 and 133.8 eV attributed to tetra coordinated phosphorus (PO₄ tetrahedra)³². It is noted that XPS results of three other samples are similar to that of AC-0.5-450 (not shown), suggesting that the samples contain mainly phosphate groups.

To further identify the nature of the oxygen-containing functional groups over phosphorylated activated carbon, IR spectroscopy was conducted (Fig. 2). As can be seen from Fig. 2, two weak bands at 3435 and 1146 cm⁻¹ are observed for the activated carbon catalyst (Fig. 2a), while four IR peaks

TABLE-1
FRUCTOSE CONVERSION, YIELD OF 5-HYDROXYMETHYLFURFURAL, AND 5-HYDROXYMETHYLFURFURAL SELECTIVITY IN THE DEHYDRATION OF FRUCTOSE CATALYZED BY AC-0.5-450 USING WATER AND DMSO AS SOLVENTS

Catalyst	Temperature (°C)	Time (min)	Solvent	Conversion (%)	5-HMF yield (%)	5-HMF selectivity (%)
AC-0.5-450	120	30	H ₂ O	47.4	18.2	38.4
AC-0.5-450	140	30	H ₂ O	84.5	29.6	35.0
AC-0.5-450	160	30	H ₂ O	92.8	28.5	30.7
AC-0.5-450	140	60	H ₂ O	86.1	28.1	32.6
AC-0.5-450	140	90	H ₂ O	91.6	21.9	23.9
AC-0.5-450	140	30	DMSO	88.1	60.1	68.2
AC-0.5-450	160	30	DMSO	84.2	66.6	79.1
H ₃ PO ₄	140	30	H ₂ O	97.4	43.7	44.8

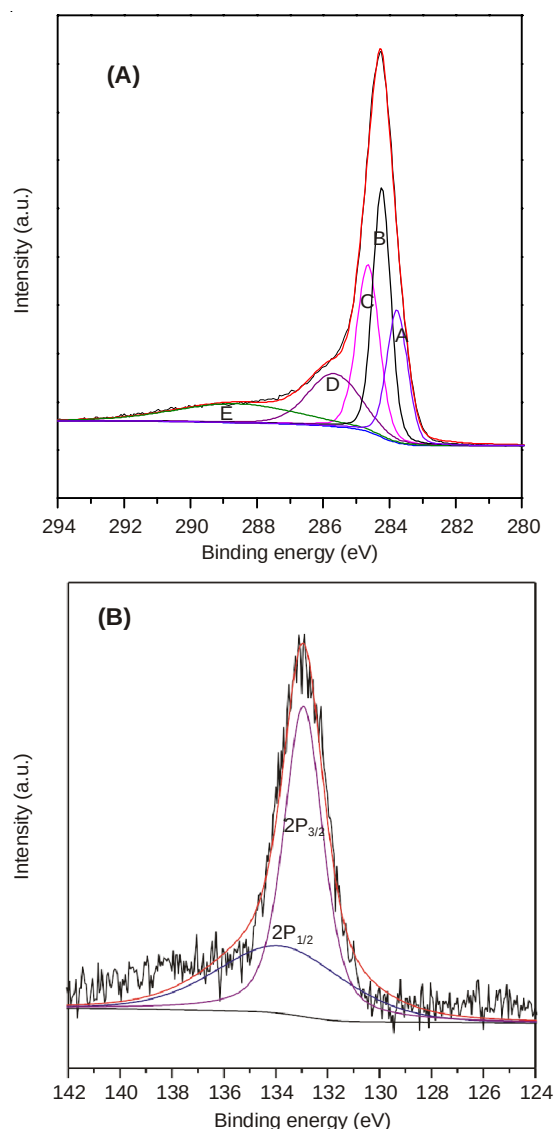


Fig. 1. X-Ray photoelectron spectrum of (A) C1s and (B) P 2p peaks of AC-0.5-450. For details see Table-2

appear at 3435, 1588, 1175 and 1066 cm^{-1} after the treatment by H_3PO_4 . The band at 3435 cm^{-1} is assigned to the stretching vibration of hydrogen-bond $\text{P}=\text{O}$ groups from phosphates and polyphosphates of $\text{O}-\text{C}$ stretching vibrations in the $\text{P}-\text{O}-\text{C}$ linkage and of $\text{O}=\text{P}-\text{OH}$ groups³². This result support the results discussed in the XPS analysis. Moreover, it is observed that the intensity of the band at 1175 cm^{-1} increases with the phosphorous content. The band at 1066 cm^{-1} is ascribed to $\text{P}-\text{O}-$ in acid phosphate esters and the symmetrical vibration in polyphosphate chain $\text{P}-\text{O}-\text{P}$ ³². Thus, IR spectral result further demonstrates

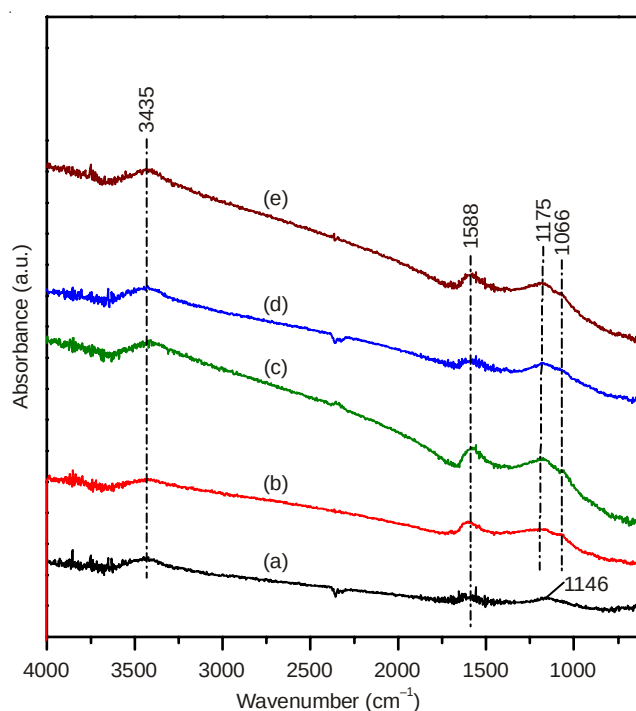


Fig. 2. IR spectra of (a) AC and phosphorylated activated carbon: (b) AC-0.5-450; (c) AC-1-350; (d) AC-1-450; (e) AC-1-550

that the samples contain phosphate group and polyphosphates after H_3PO_4 treatment.

To further explore the impact of surface oxygenated groups of the catalysts on the fructose conversion, 5-hydroxymethylfurfural yield and 5-hydroxymethylfurfural selectivity, Boehm titration method was utilized to quantitatively analyze the amounts of surface oxygenated functional groups.

Table-3 represents the concentration of the surface oxygenated functional groups of these samples. Boehm titration results show that AC-0.5-450 has more strong acid sites in comparison with three other samples, which is good agreement with XPS results (Table-2). The phosphorus content increases with increasing the calcination temperature, suggesting high temperature activation favors the formation of $\text{C}-\text{O}-\text{P}$ bond.

Fig. 3 shows the correlation of fructose conversion, 5-hydroxymethylfurfural yield and selectivity with the surface oxygenated functional groups. It seems that the activity of the sample is correlated with the phosphorous content, while 5-hydroxymethylfurfural selectivity is not associated with the phosphorous content. It should be noted that no remarkable correlation is observed between the fructose conversion and the amount of carboxyl, lactonic and phenolic acid groups measured by Boehm titrations (Table-3). As well known, the

TABLE-2
DEVOLUTION RESULTS OF XPS SPECTRA OF THE SAMPLES

Assignment	AC-0.5-450		AC-1-350		AC-1-450		AC-1-550	
	P (eV)	A (%)	P (eV)	A (%)	P (eV)	A (%)	P (eV)	A (%)
Carbide	283.8	16.9	283.7	6.4	283.7	12.02	283.7	15.5
Graphite	284.2	27.9	284.2	34.1	284.3	52.1	284.2	41.0
R-OH+C-O-C or C-O-P	284.6	23.5	284.6	23.4	285.0	12.8	284.7	15.5
C=O + >C=O	285.7	17.1	285.8	16.4	286.1	10.4	285.7	13.1
COOH+ C-O-C	288.6	14.5	288.7	13.2	288.9	12.6	288.5	12.3

P-Position; A-Area percent

TABLE-3
SURFACE ACIDIC GROUPS EVALUATED BY
BOEHM TITRATIONS AND PHOSPHORUS
CONTENT MEASURED BY XPS

Catalysts	AC-0.5-450	AC-1-350	AC-1-450	AC-1-550
Carboxylic (10^{-4} mol/g) ^a	2.28	1.43	1.12	1.13
Lactonic (10^{-4} mol/g) ^a	0	0	0	0.05
Phenolic (10^{-4} mol/g) ^a	0	1.48	1.95	0.02
P content (wt.%) ^b	1.03	1.16	1.26	1.98

^aConcentration of acid is determined by Boehm titration method;

^bPhosphorus content is measured by XPS method

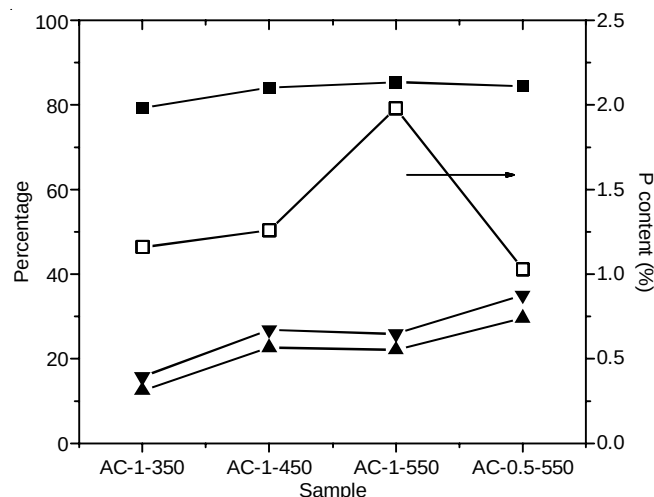


Fig. 3. Fructose conversion, 5-hydroxymethylfurfural yield and selectivity as a function of the phosphorous content: (■) the fructose conversion; (▼) the 5-HMF selectivity; (▲) the 5-hydroxymethylfurfural yield; (□) the phosphorous content. The phosphorous contents of the samples were determined by XPS method

Brønsted acidic catalyst can catalyze dehydration of fructose to form 5-hydroxymethylfurfural. In addition, the strength of Brønsted acid sites has a remarkable effect on the fructose conversion and the 5-hydroxymethylfurfural selectivity. This result also shows that the P content is not linear with the 5-hydroxymethylfurfural selectivity, but has good relation with the fructose conversion.

Conclusion

In summary, a novel surface modified activated carbon, phosphorylated activated carbon, was used to catalyze dehydration of fructose to produce 5-hydroxymethylfurfural. The samples exhibit a good activity for the dehydration of fructose to 5-hydroxymethylfurfural in DMSO solvents, making them potential substitutes for the mineral acid, with the advantages of low-cost and easy separations. The fructose conversion is mainly correlated with the phosphate group of the catalyst.

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