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Selective Oxidation of Methacrolein to Methacrylic Acid on Carbon Catalysts

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Abstract:

Different carbon structures (activated carbon, carbon nanotubes, graphene and graphite) were investigated for the replacement of heteropoly catalysts for the oxidation of methacrolein to methacrylic acid. Activated carbon showed the best catalytic performance with higher catalytic activity than molybdovanaphosphoric acid at lower temperatures. The catalytic performance of activated carbon was further improved by the addition of heteroatoms, such as P, B, N and S. The latter occupy the electrophilic oxygen functional groups thus preventing further oxidation of methacrylic acid and improving reaction selectivity. The best catalytic performance results were obtained on activated carbon with 10wt% P, where methacrolein conversion, methacrylic acid selectivity and yield at 270 °C were 40.1, 70.8 and 30.3%, respectively. The results of the present work show a novel way to design non-metal catalysts for the selective oxidation of methacrolein to methacrylic acid.

Keywords: activated carbon, oxidation, heteropoly catalysts, methacrolein, methacrylic acid

1. Introduction

Methacrylic acid (MAA) is an important chemical intermediate, which is used for the production of methyl methacrylate, functional plastics, synthetic rubber and paints [1]. It is traditionally produced by the Acetone Cyanhydrin process that needs toxic HCN, corrosive H₂SO₄, and in which vast scale of NH₄SO₄ is produced as solid waste [2]. Oxidation of methacrolein (MAL) to MAA over heteropoly compounds, such as molybdophosphoric and molydbovanadylphosphoric is considered as a green production process of MAA [2-9]. However, heteropoly compounds used as catalysts have poor thermal stability, low catalytic activity and high cost. Metal-free compounds are emerging as catalysts for selective oxidation, oxidative dehydrogenation and oxygen reduction reactions in recent years [10-14]. Carbon-based catalysts show a promising future perspective for oxidative dehydrogenation reactions [13-15]. For oxidation reactions, some carbon materials, such as carbon nanotubes, graphene and nanodiamond have been used for the oxidation of acrolein to acrylic acid and ethylbenzene to aldehyde and carboxylic acid [16-22]. However, very little has been reported on ways to improve the catalytic performance of carbon-based catalysts for selective oxidation reactions. If oxidation of MAL to MAA could be efficiently catalyzed by carbon-based catalysts, such as activated carbon (AC), the cost of catalysts will be sharply reduced and thermal stability problems of catalysts will also be avoided.

In this work, various structures of carbon, namely: activated carbon, graphite, graphene oxide, carbon nanotubes, and oxidized graphite were investigated for the

oxidation of methacrolein to methacrylic acid. The carbon catalysts were also modified by doping some *nonmetal* elements. Their catalytic performance was also compared with $H_4PMo_{11}VO_{40}$ (HPAV), which is a heteropoly catalyst commonly used for the reaction of interest.

2. Experimental

2.1 Catalysts preparation

Activated carbon 1 and 2 (Sinopharm Chemical Reagent Co.) were washed by deionized water before usage. Graphite was purchased from Sinopharm Chemical Reagent Co., Ltd. Graphene oxide and multi-wall carbon nanotubes were purchased from Nanjing XFNANO Materials Tech Co. Ltd.

Glucose synthesized activated carbon was prepared by the following process. 50 g glucose (Sinopharm Chemical Reagent Co., Ltd, AC) was loaded in a corundum crucible, and the crucible was covered by tinfoil. It was calcined at 200 °C for 3 h, and the temperature was then increased to 450 °C and kept at this temperature for 4 h.

 $H_4PMo_{11}VO_{40}$ (HPMV) was prepared as reported [17]. 10 g MoO₃ (Sinopharm Chemical Reagent Co., Ltd.) and 0.574 g V₂O₅ (Tianjin Guangfu Fine Chemical Research Institute) were added to 200 mL deionized water, and the mixture was subsequently refluxed. Then, 0.728 g of 85% phosphoric acid (Sinopharm Chemical Reagent Co., Ltd.) was added to the suspension. The mixture was refluxed and vigorous stirred for 5 h. A deep-orange solution was formed. The insoluble solid was filtered. The solution was evaporated at 80 °C, and a bright dark red solid (HPAV) was

obtained.

Cs_{2.6}H_{1.4}PMo₁₁VO₄₀ was prepared as previously reported [23]. 5 g HPAV was dissolved into 10 mL deionized water and 1.42 g CsNO₃ was dissolved into 10 mL deionized water. The two resulting solutions were mixed and stirred for 2 h at 25 °C. This suspension was evaporated under stirring to dryness. The obtained orange solid was dried at 80 °C overnight. HPAV and Cs_{2.6}H_{1.4}PMo₁₁VO₄₀ were calcined under air flow at 360 °C before catalytic performance tests. These two catalysts were characterized by FT-IR and powder XRD (see Figs S1, S2, ESI).

2.2 Activated carbon modification

N-doped activated carbon was prepared by the method described below. Firstly, 0.5 g melamine (Sinopharm Chemical Reagent Co., Ltd) was added into 20 mL of deionized water and dissolved at 80 °C. 5 g activated carbon 1 was then added, and the mixture was stirred for 2 h. Then the water solvent in the mixture was evaporated at 80 °C. The solid obtained was dried in oven for 12 h and calcined at 450 °C in a close crucible for 4 h. N-doped activated carbon was prepared.

B-, P- and S-doped activated carbon were prepared by a similar process using HBO₃, H₃PO₄ and H₂SO₄, respectively (Sinopharm Chemical Reagent Co., Ltd). Acid was dissolved in some deionized water, and some activated carbon was added, while the mixture was stirred for 2 h and the water solvent was evaporated to dry at 80 °C. The solid was then dried in oven for 12 h and calcined at 350 °C in a close crucible for 4 h. The doped activated carbon was prepared and named B/AC, S/AC and xP/AC

(x=wt%P).

2.3 Characterization of catalysts

AC was analyzed by conducting thermogravimetry and differential thermal analysis (TG/DTA, DTG-60H, Shimadzu, Japan) on a simultaneous DTA-TG apparatus allowing both TGA and DTA curves to be recorded simultaneously. The heated program was from room temperature to 800 °C at the heating rate of 5 °C/min. FT-IR spectra of catalysts were collected on a FT-IR spectrometer (Nicolet iS5, Thermal Scientific). Powder X-ray diffraction (XRD) was performed on an X-ray diffractometer with a step of 0.2° (Rigaku SmartLab X-ray powder diffractometer, Cu K α radiation, 60 kV, 300 mA). The surface area and pore structure of catalysts were measured by a Surface Area and Pore Analyzer (Mocromeritics ASAP 2460, US). The elements concentration in solid catalysts was determined by X-ray Fluorescence (AXIOS-MAX). The X-ray photoelectron spectroscopy (XPS) spectra were recorded using a Kratos Axis Ultra DLD spectrometer with monochromatic Al Ka radiation. ³¹P NMR was performed on a Bruker Avance III (400M). Raman spectroscopy was conducted using a laser Raman spectrometer (HR800 UV, Horiba Scientific Co. Ltd) with a 100 mV laser, equipped with a wavelength of 514 nm and CCD detector.

2.4 Catalytic performance

Catalytic oxidation of MAL to MAA was performed under atmosphere pressure. 0.8 mL catalyst was loaded in a fix-bed micro-reactor, and the contact time was about

2 s. Temperature was increased to reaction temperature at first, then reactants mixtures of MAL (4.4vol.%), O₂ (11.1vol.%), H₂O (17.8vol.%) and N₂ (balance) were fed into the reactor to start the reaction. After the various reactions reached steady-state rates, the products were collected and analyzed by GC (7890B, Agilent Technologies Co. Ltd) which was equipped by a flame ionization detector, thermal conductivity detector and a capillary column (DB-FFAP) and packed column (TDX-01) for MAL, acetic acid and CO₂, and CO detection, respectively. MAL conversion, MAA selectivity and yield were calculated by the following Eqs. 1, 2 and 3, respectively. The carbon mass balance and byproducts selectivity were calculated via the Eqs. S1-S4 (see ESI).The carbon mass balance was better than 98%, and the selectivity of byproducts obtained is shown in Tables S3 and S4 (see ESI).

MAL conversion= (mole of MAL in feed gas—mole of MAL in tail gas)/ mole of MAL in feed gas $\times 100\%$ (1)

MAA selectivity=mole of MAA/mole of converted MAL \times 100% (2)

 $MAA yield=MAA selectivity \times MAL conversion$ (3)

3. Results and discussion

3.1 Characterization of catalysts

3.1.1 Thermal stability of catalysts

Firstly, AC was tested for its tolerance of hash reaction conditions, so the thermal stability of AC was tested by TG-DTA in air at 1 atm. As can be seen in Fig. S1 (ESI), AC was stable when temperature was lower than 600 °C. Hence, the thermal stability

of AC was good enough for this reaction, because the reaction temperature for the oxidation of MAL to MAA is much lower than $400 \,^{\circ}$ C.

3.1.2 XRD patterns, Raman and FT-IR spectra of carbon catalysts

The XRD patterns of AC1, B/AC, S/AC and xP/AC show similar patterns, where two peaks emerge at 24.5 ° and 43.5 °, respectively (Fig. S4, ESI), which suggest that all these carbon catalysts belong to amorphous carbon. The XRD patterns of graphite, graphene oxide and CNTs show the characteristic diffraction peaks at 26.5°, 11.5° and 25.6° (Fig. S5, ESI). The Raman spectra of AC1 and P/AC show that the modification of AC by H₃PO₄ would slightly increase the disorder degree (I_D/I_G increased from 0.91 to 0.93) [24]. However, AC prepared from glucose has the lowest disorder degree $(I_D/I_G = 0.73)$. To investigate the functional groups on carbon catalysts, FT-IR was performed. The main functional groups emerged in the spectrum of AC 1 are v_s (O-H) (3672.5 cm^{-1}) , $v_s(C=O)$ (2975.6, 2898 cm⁻¹), $v_s(-COOH)$ (1392 cm⁻¹), $v_s(C-O-C)$ (1052 cm^{-1}) and $v_s(\text{epoxy group})$ (870, 1229 cm⁻¹) (Fig. S6, ESI) [25, 26]. After the loading of H₃PO₄, two new IR vibration bands emerged at 1260 and 1073 cm⁻¹ which can be assigned to v_s (P=O) and v_s (P-O-P), respectively [27, 28]. It suggests that P was successfully loaded on AC. The vibrational IR band of v_s (epoxy group) shifted to 885.7 cm⁻¹ and v_s (C-O-C) was almost disappeared. Graphene oxide and graphite show similar vibrational IR bands with AC in FT-IR spectra (Fig. S6, ESI). The vibrational IR bands for the C-C in aromatic nucleus (1580 cm⁻¹) and unsaturated hydrocarbon (1626.7 cm^{-1}) , $v_s(-CH_3)$ (1460, 1404 cm⁻¹) appear in the spectra of CNTs [26]. It

suggests that some raw materials used for the fabrication of CNTs were not totally carbonized. The vibrational IR bands of v_s (C-O-C) and v_s (epoxy group) were negligible in the spectrum of CNTs.

3.1.3 XPS and ³¹P NMR analysis of carbon catalysts

Table 1. C 1s binding energy and mole ratios of different kinds of carbon in various types of carbon structures

Catalysts	π - π^*	COOR/	<i>C-0</i> /	<i>C=C</i> /	<i>C-C/</i>	Mole ratio of carbon
	eV	eV	eV	eV	eV	atom, %
AC 1	291.3	288.7	286.3	285.0	284.6	14:18:19:30:30
AC 2	291.2	288.3	286.3	(284.8	21:13:15:0:52
P/AC	291.3	287.9		285.6	284.8	21:13:0:23:44
B/AC	291.0	287.9		285.7	284.8	18:11:0:23:48
Used AC 1	292.1	288.8	286.3	285.0	284.5	15:16:19:37:13
Used AC 2	292.3	288.3	286.1	-	284.8	13:19:10:0:57
Used P/AC	292.1	288.4		285.7	284.8	18:16:0:24:42
Used B/AC	291.6	288.4		285.6	284.8	19:13:0:28:40
Glucose prepared AC	291.2	288.6	286.2	285.1	284.7	16:11:23:0.2:50
Graphite	290.6		286.1	285.4	284.8	17:0:17:9:55
Carbon nanotubes	291.5	287.7		285.5	284.8	16:8:0:21:38
Graphene oxide	291.7	288.2	286.0	284.8	284.6	17:14:27:25:17

In order to find out the functional groups and compositions on the different carbon structures catalysts surfaces, XPS analysis were performed. Five different kinds of carbon atoms were found on the surface of these types of carbon structures studied (Table 1, Fig. S7). The kind of carbon with the highest binding energy corresponds to carbon atoms with π - π ^{*}. The kind of carbon with binding energy of 288.3~290.7 eV can be assigned to carbon atoms with two or three oxygen atoms (COOR) in lactone, carboxylic acid, carboxylic anhydride, quinine and ketone [10]. The kind of carbon emerged ~286 eV is carbon atoms with one oxygen atoms in ether, phenol and lactone [10]. The other kinds of carbon species with two carbon atoms

refer to C=C (~285.2 eV) and C-C (~284.6 eV) in basal plane of sp^2 carbon exposing the hexagonal arrangement of carbon atoms [10]. The mole ratio of these five kinds of carbon atoms in AC 1 was found to be 1:1.3:1.4:2.2:2.2.

With the addition of P or B, the mole ratio of COOR kind of carbon increased, and that of C-O disappears, result similar to that seen by FT-IR. It suggests that P or B combined with C-O as reported previously [13]. The mole ratio of the kinds of carbon atoms with oxygen atoms increased obviously in AC 1, while these carbon atoms mole ratios decreased significantly in P/AC and B/AC catalysts. It suggests that AC was oxidized during assessment, while P and B could suppress the electrophilic groups and prevent the further oxidation of carbon catalysts during evaluation [13]. No C=C was found in AC 2 (Fig. S9, ESI). The mole ratio of C-O was much higher than that in AC 1. For AC prepared by glucose, more carbon atoms with oxygen atoms were detected than AC1. Only C-O was found on graphite, which suggests that only phenol groups existed on the surface of graphite. Two kinds of carbon atoms with oxygen atom on carbon nanotubes have similar mole ratio with these on AC. More oxygen contenting functional groups were found in graphene. The mole ratio of O-C=O on graphene was higher than that on AC 1 and carbon nanotubes, lower than that on P/AC, and similar with B/AC (Fig. S10-13, ESI). After the evaluation, the binding energy of different carbon species and their ratios changed slightly, which indicates that carbon catalysts retain their structure under reaction conditions.

The binding energy of P in P/AC and used P/AC is about 134.4 and 134.0 eV, respectively, which is lower than the binding energy of P in P_2O_5 and H_3PO_4 ,

respectively (Fig. S11, ESI). It suggests that these P atoms interacted with oxygen-containing functional groups on the surface of AC and some H₃PO₄ was not degraded during calcination. The binding energy of B in B/AC and used B/AC can be assigned to B₂O₃ [14]. The binding energy of Mo in AC 1 was about 233.6 eV, which can be related to Mo in MoO₃ (Fig. S7, S8, ESI). To further investigate P species in P doped AC, ³¹P NMR was performed. As seen in Fig. S14 (ESI), three chemical shift peaks emerged at -9.4, -23.34 and -37.39 ppm which correspond to P in pyrophosphoric acid, metaphosphoric acid and P₂O₅, respectively [29, 30]. All these phosphorus species were generated from the dehydration of H₃PO₄ during calcination.

3.2. Catalytic performance of different carbons and other materials

Catalysts	BET surface acrea/m ² ·g ⁻¹	Conversion%	Selectivity%	Yield%
AC 1	1018.1	40.9	33.3	13.6
AC 2	972.0	13.2	21.0	2.8
Glucose prepared AC	2.6	23.0	24.8	5.7
Graphite	10.2	9.5	3.6*	0.3
Graphene oxide	296.7	0.7	97.3*	0.7
Multi-wall carbon nanotubes	218.1	0	0	0
$H_4PMo_{11}VO_{40}$	3.3	6.7	39.8	2.7
$Cs_{2.6}H_{1.4}PMo_{11}VO_{40}$	167.6	84.8	44.2	37.5
Blank		0	0	0

Table 2. Catalytic performance results of different carbons materials at 290 °C

*No MAL conversion on graphite and graphene at 290 $^{\circ}$ C. The conversion of MAL and selectivity to MAA on these two catalysts correspond to 310 $^{\circ}$ C.

As shown in Table 2, three different kinds of AC, namely: AC 1, AC 2 and glucose synthesized AC, show good catalytic performance for the oxidation of MAL

to MAA. It should be noted that some metal elements exist in activated carbon. The XPS results showed that there are about 0.69 atom% Mo, 2.2 atom% Co and 0.18 atom% Bi in AC 1, and 0.03 atom% Mo, 0.14 atom% Co and 0.01 atom% Bi in AC 2. According to the XPS results, Mo was in the form of MoO_x and Mo atoms in carbon framework, and Bi and Co were mainly in the form of their metal oxides [31-33]. AC 2 contains less metal atoms than AC 1, and exhibits lower MAL conversion (13.2%) and much lower MAA yield (2.8%) than AC 1. It was speculated whether these metal elements are active sites for this reaction. To probe for this, activated carbon was prepared by glucose to make sure that no metal elements were contained. This glucose prepared AC resulted in a higher MAL conversion (24.8%) and MAA yield (5.7%) than AC 2 (Table 2). These results illustrate that these specific metal atoms in activated carbon should not be considered as active sites for this reaction. Graphite shows low MAL conversion and MAA yield on activated carbon, which might be due rather to its inert surface than its low surface area. Graphene shows also low MAL conversion (0.7%), but the highest MAA selectivity (Table 2). No MAL conversion was detected on carbon nanotubes. The reason might be the absence of epoxy groups on CNTs which was suggested to be the active site for the oxidation of acrolein to acrylic acid.

It was reported [17, 19] that oxygen-containing functional groups are active sites for oxidation reactions. HPMV shows much lower MAL conversion (6.7%) and slightly higher MAA yield (2.7%) than the activated carbon, whereas the catalytic performance of activated carbon is much lower than that of $Cs_{2.6}H_{1.4}PMo_{11}VO_{40}$ at

290 °C.

3.3 The effect of temperature on the catalytic performance of activated carbon, HPMV





Figure 1. MAL conversion (%), MAA selectivity (%) and MAA yield (%) on AC 1, HPAV and $Cs_{2.6}PMo_{11}VO_{40}$ solids at different reaction temperature (230-370 °C)

To effect of reaction temperature on the catalytic performance of HPAV, $Cs_{2.6}H_{1.4}PMo_{11}VO_{40}$ and AC was evaluated in the 270-370 °C range as depicted Fig. 1. The results show that AC starts to catalyze this reaction at 230 °C, while HPAV and $Cs_{2.6}H_{1.4}PMo_{11}VO_{40}$ show no activity and much lower activity, respectively, at 250 °C. More precisely, MAA yield is 1.3% on HPAV and 3.0% on $Cs_{2.6}H_{1.4}PMo_{11}VO_{40}$ compared to 8.8% on AC. With the increase of reaction temperature, MAL conversion

over these 3 catalysts increases. MAL conversion over AC and HPAV increases from 3.4 to 52.4% and 0 to 50.2%, respectively, with increasing reaction temperature from 230 to 370 °C. In the case of $Cs_{2.6}H_{1.4}PMo_{11}VO_{40}$, MAL conversion increases from 0 to 100% with increasing reaction temperature from 230 to 330 °C. Meanwhile, MAA selectivity on HPAV increases from 0% (230 °C) to 83.8% (330 °C). The highest MAA selectivity was obtained over AC and $Cs_{2.6}H_{1.4}PMo_{11}VO_{40}$, ca. 33.3 and 44.2%, respectively, which correspond to 290 °C. With further increasing reaction temperature, the MAA selectivity over AC and $Cs_{2.6}H_{1.4}PMo_{11}VO_{40}$ was found to decrease. Regarding MAA yield, AC shows higher values than HPAV and $Cs_{2.6}H_{1.4}PMo_{11}VO_{40}$ when the reaction temperature is lower than 320 and 270 °C, respectively. The results shown in Fig. 1 clearly indicate that AC shows better catalytic activity towards MAA than heteropoly acid catalysts at T \leq 270 °C.

3.4 Modification of activated carbon by different heteroatomsTable 3. Catalytic performance at 290 °C over activated carbon doped by different elements

Catalysts doped by different elements	BET surface area/ $m^2 \cdot g^{-1}$	Conversion%	Selectivity%	Yield%
Un-doped AC	1018.1	40.9	33.3	13.6
N-AC	936.5	36.7	21.0	7.7
B-AC	68.8	19.5	49.6	9.7
P-AC	929.4	34.1	64.6	22.0
S-AC	1008.1	50.2	40.8	20.5

To enhance the catalytic performance of AC, some non-metal elements were used to modify AC. Oxygen containing functional groups mainly include two kinds, namely, nucleophilic (ketone, quinine and carboxylic anhydride) and electrophilic

groups (such as phenol, ether, lactone, carboxylic acid and aldehyde) [11]. The electrophilic groups have stronger oxidizing ability than nucleophilic groups. The electrophilic groups tend to further oxidize the reactants [14]. Hence, we tried to suppress these electrophilic groups by the addition of some heteroatoms, such as N, B, P and S, to increase MAA selectivity. According to the results shown in Table 3, with the addition of N, both MAL conversion and MAA selectivity decrease. The addition of N in carbon catalysts can increase their charge and spin density, which would reduce the oxidizability and promote the formation of reactive oxygen species, which may lead to the further oxidation of MAA [17]. The MAL conversion and MAA yield decrease to 19.5% and 9.7% with the addition of B, respectively (Table 3). In the case of B addition, this can react with the electrophilic groups and suppress their reaction with MAL or MAA, so MAA selectivity would increase and MAL conversion decrease [13]. The addition of P has also the same ability [13]. Surprisingly, MAL conversion decreases by \sim 6%, and MAA yield increases to 22% with the addition of P in AC (Table 3). XPS results showed that the amount of electrophilic groups in Band P- doped AC decreased.

Sulfur (S) was also doped into AC and results are presented in Table 3. MAL conversion (50.2%), MAA selectivity (40.8%) and MAA yield (20.5%) on S/AC were all improved. The results demonstrate that the addition of P and S enhance the catalytic performance, and obviously P improves MAA selectivity. Based on this behavior, P was selected for further studies, aiming to optimize its loading for optimum catalytic performance.

3.5 Optimization of P amount in AC

P-doped AC showed the best catalytic performance. With the increase of P to 2 wt%, MAL conversion increases from 38.4 to 48.4%, and it decreases to 16.1% with P content further increasing to 20 wt% at 270 °C (Fig. 2). MAA selectivity increases from 30.3 to 80.8% with the increase of P content from 0 to 20% at 270 °C, whereas MAA yield increases from 11.6% (AC 1) to 30.3% (10% P/AC) and then decreases to 13% (20%P/AC) at 270 °C. MAL conversion and MAA yield on these catalysts show similar trends at 290 and 310 °C. The only difference is that the highest MAL conversion and MAA yield are obtained on 5 wt%P/AC at 290 and 310 °C, respectively. According to Frank et al. [13, 19], oxidation of acrolein to acrylic acid includes three steps. Acrolein is first adsorbed by ketone like groups, then interacts with electrophilic groups and is get oxidized to acrylic acid, and finally acrylic acid is desorbed from the catalyst's surface and the electrophilic groups are get re-oxidized by O_2 . Therefore, the decrease of MAL conversion with increasing P content after a given level is suggested to be due to the following reasons. P firstly reacts with electrophilic groups and reduces MAL conversion due to the activity of these groups. By the increase of P content, the electrophilic groups interact with P, and the excess of it interacts with the nucleophilic groups leading to the further decrease of MAL conversion due to these groups [13].

XPS results showed that much more electrophilic groups than nucleophilic groups were present in AC, for instance, the molar ratio of electrophilic to

nucleophilic groups was 4.3:1 in AC 1. Therefore, P firstly is combined with electrophilic groups to suppress the reaction between them and MAL, and the further oxidation of MAL to byproducts is avoided, which leads to the increase of MAA selectivity. With the increase of P content, more and more electrophilic groups are combined with P. After most of these groups interact with P compounds, the latter start to interact with nucleophilic groups, which lead to the decrease of effective adsorption sites of MAL. The latter then reacts with excess electrophilic groups, and the MAA selectivity decreases. With the increase of P content, MAL conversion increased, which also suggests that dopant P might provide new active sites for this reaction [28]. More research work is needed to better understand the mechanism of how P compounds improve the catalytic performance of carbon catalysts for the oxidation of an unsaturated aldehyde to the unsaturated carboxylic acid.



Figure 2. MAL conversion (%), MAA selectivity (%) and yield (%) on AC with different P content at 270, 290 and 310 °C

4. Conclusions

Methacrolein was oxidized to methacrylic acid by activated carbon and graphite. P-doped activated carbon showed much higher catalytic activity than $H_4PMo_{11}VO_{40}$ and much higher MAA selectivity than $Cs_{2.6}H_{1.4}PMo_{11}VO_{40}$. The methacrylic acid selectivity can be significantly improved by doping activated carbon with P, B and S. The best catalytic performance was obtained on activated carbon doped by 10 wt% P, on which methacrolein conversion methacrylic acid selectivity and yield were 42.8%, 70.8% and 30.3%, respectively. The mechanism of this reaction catalyzed by carbon

catalysts and the improvement of catalytic performance by the addition of P, B and S still needs further investigations for better understanding.

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Highlight

- Oxidation of methacrolein to methacrylic acid can be catalyzed by carbon
- Catalytic performance of activated carbon can be improved by the addition of P
- Activated carbon showed the best catalytic activity than other carbon materials

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