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Hydrogen peroxide as an oxidant in starch oxidation using molybdovanadophosphate for producing high carboxylic content

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Abstract

$(NH_4)_5H_6PV_8Mo_4O_{40}$ is an improved bi-functional catalyst that has been used on oxidizing starch by hydrogen peroxide. The effects of oxidation with hydrogen peroxide on the carboxyl content were studied systematically to produce high polyhydroxycarboxylic acids even when using very low amounts of catalyst. $(NH_4)_5H_6PV_8Mo_4O_{40}$ exhibited the best catalytic performance with a carboxylic content of 0.648 mol per 100 g, which could be attributed to the synergy of its Brønsted acidity and strong efficient oxidant center. This catalyst can perform controllable starch oxidation and can be recycled for reuse.

Keywords: Polyoxometalates; starch oxidation; hydrogen peroxide.

1. Introduction

The interest in the production of chemicals and materials from biomass is increasing due to the rapid rate at which fossil fuels are being depleted; escalating energy consumption is being coupled with rising environmental awareness among nations, which has led to increased focus on alternate, viable, ecofriendly, and renewable energy sources.[1] Starch, as one of the most abundant resources, represents an important bio-renewable and bio-degradable raw material for food industry. Although in natural state it has limited industrial applications due to its low shear stress resistance and thermal decomposition; when coupled with high retro-gradation and syneresis, such shortcomings may be overcome by starch modification.[2] Native starches are modified by use of various physical, chemical and enzymatic methods; one of the most often used chemical methods is oxidation. During that process, the hydroxyl groups of the glucose units are oxidized into carboxyl groups[3]; while the granular structure of the starch must remain intact during oxidation.

Therefore, the carboxyl contents of oxidized starch as well as the degree of degradation are generally used to indicate the level of oxidation; which primarily depend on the hydroxyl groups at C-2, C-3 and C-6 positions.

The main reason as to why starch is chemically treated before commercial use, is to split the long glucose chains of the polymer molecules to reduce the high viscosity of unmodified starch solutions; thus increasing and obtaining the maximum possible amounts of starch in technical applications. Some different oxidizing agents can be used to oxidize starches, such as: sodium hypochlorite and hydrogen peroxide[4-8], nitrogen oxidizes[9], ozone[10], and sodium periodate[11,12]. These oxidizing agents are efficient but lead to large amounts of waste and some toxic byproducts[13]. The starch oxidation process should involve a green oxidant like H_2O_2 or O_2 in combination with an accessible and inexpensive catalyst. Several catalytic approaches have been proposed to improve the oxidation of starch, emphasizing mainly on synthetic interest in this transformation. Many catalytic systems have been used to activate H_2O_2 in starch oxidization, such as: Na_2WO_4[14], FePcS[15], $MTO/H_2O_2/LiBr$[16], $CH_3ReO_3/H_2O_2/HBr$[16], $Ch_5PV_2Mo_{10}O_{40}$[17]. $FeSO_4$[18], $CuSO_4$[19]. The comparison of these catalysts are shown in Fig. S1 The serious drawback is that over oxidation results in the depolymerization of the glycosidic bond with low yields of insoluble product, hence this narrows its range of application. Therefore, the quest for an efficient and clean method of starch oxidation remains as an important challenge.

Polyoxometalates (POMs) is a field of increasing importance, they have several advantages as catalysts which make them economically and environmentally attractive. Strong Brφnsted acidic and efficient oxidants exhibit fast reversible multi-electron redox transformations under rather mild conditions; which clearly indicates that they could be acidic and redox-bifunctional catalysts in homogeneous and heterogeneous systems[20-23]. Their acid-base and redox properties can vary a wide range, simply by changing their chemical composition. It has been long known that tungsten and molybdenum compounds are efficient catalysts for oxidation by hydrogen peroxide[24].

Our group had paid more attention to the investigation of the Keggin structure $PV_nMo_{12-n}O_{40}^{(3+n)-}$ in terms of oxidative catalysis[25-27]. The proposed reaction based on vanadium substituted POMs includes hydroxyl and hydroperoxy radicals generated by the homolytic cleavage of H_2O_2 and its vanadium center; whose mechanism is similar to that of Fenton type reactions. The most important aspect is to obtain the high selectivity through the right catalysts. From previous work, we had mainly focused on vanadium catalyzing polysaccharides. Since vanadium has good catalytic activity, we increased the content of vanadium in the polyoxometalate to allow controllable starch oxidation with high carboxyl content.

The aim of this work is to seek an easily prepared catalyst. In this paper, we report on starch oxidation catalyzed by molybdovanadophosphates; where only a small amount of catalyst is sufficient enough to achieve oxidation and efficient of utilization of H_2O_2 to form carboxyl groups at 80%. $(NH_4)_5H_6PV_8Mo_4O_{40}$ (NPVMo) has strong Brφnsted acidity and many vanadium active sites. Here we present the catalytic oxidation of starch by using $(NH_4)_5H_6PV_8Mo_4O_{40}$ (NPVMo) as a catalyst with H_2O_2 as oxidant under atmospheric pressure; to produce its corresponding oxidative product with high efficiency and high selectivity under mild reaction conditions.

2. Experimental

2.1 Materials

All the chemicals and reagents used in this work were analytical grade or better without further purification. The native Starch (with over 90% amylose) was purchased from Sigma-Aldrich. 0.1M of NaOH was used to determine the content of carboxyl by titration.

2.2 Physical measurements

Elemental analysis using a Leeman Plasma Spec (I) ICP-ES and a P-E 2400 CHN elemental analyzer. IR spectra (4000–400 cm^{-1}) were recorded in KBr discs on a Agilent Cary 630 spectrometer. The ^{31}PNMR (85% H_3PO_4 external standard) measurements were obtained using a Bruker AM500 spectrometer at 202.5 MHz. XPS were recorded on an Escalab-MK II photoelectronic spectrometer with Al K (1200 eV). Cyclic voltammetry was measured in range of +1.4 ev to -0.8 ev in dilute sulphuric acid at glassy-carbon electrode working electrode and Ag/AgC1 reference electrode, using Pt as supporting electrolyte. UV-vis spectra (200-800 nm) were recorded on a Cary 500 UV-vis-NIR spectrophotometer.

2.3 Catalyst preparation

The compound $(NH_4)_5H_6PV_8Mo_4O_{40}$ (NPVMo) was synthesized according to Ref.,[28] $NaVO_3$ (7.32 g, 60 mmol) was dissolved in water (38 mL) and mixed with $Na_2MoO_4·2H_2O$ (8.22 g, 34 mmol) in water (12 mL). Then added dropwise 85% H_3PO_4 (4.5 mL) in water (10 mL) to the solution, and continuously stirred at 95 □ for an hour. After cooling, the solution was transferred into a saturated ammonium chloride solution (150 mL) to form clean brown precipitate (ca. 9 g). Then recrystallized the resulting precipitate from 0.25 M H_2SO_4 (20 mL) to afford molybdovanadophosphate (NPVMo).

2.3 Preparation of oxidized starch

The oxidation procedure was performed in a glass reactor. Typically, 1 g of native starch was mixed with 0.1 mL (0.0001wt%) NPVMo solution, then it was heated up to the desired temperature and vigorously stirred for a period time. To ensure the high utility of H_2O_2 (30 wt%), we added the hydrogen peroxide at intervals instead of the whole amount at one time. The addition of H_2O_2 depended on the length of experiment, usually at a rate of 500 μL every 2 h where the reaction time was 10 h and 22.2 mmol hydrogen peroxide was required.

After the reaction, we added a certain amount of alcohol to the mixture to precipitate the oxidized starch; then we separated the catalyst by centrifuge at 10000 rtp for 30 min. The ethanol was evaporated and the supernatant containing the catalyst was left in the liquid for reusing. Under vacuum condition, the final product was dried under 40 ℃ for 48 h to give about 900 mg of a white paste.

2.4 Determination of carboxyl content[29]

300 mg of product was dissolved in 20 mL H_2O and then a few drops of a phenolphthalein indicator was added. The solution was titrated with 0.1 M of NaOH to determine the content of carboxyl groups (mol_{CO_2H} per 100 g).

3. Results and discussion

3.1. Catalyst characterization

From the element analysis, the N, H, P, Mo, V contents (N, 4.80 ; H, 2.15 ; P, 2.12 ; V, 23.2 ; Mo, 24.6%) of the catalyst are consistent with the theoretical value (N 4.50, H 1.67, P 1.99, V 26.2, M_O 24.6%;). This result confirmed the chemical formula of the catalyst is $(NH_4)_5H_6PV_8Mo_4O_{40}$.

Fig. 1 is the ^{31}PNMR of NPVMo and gave a number of signals, Grate et al.,[30] have discovered ^{31}PNMR of $[PV_2Mo_{10}O_{40}]^{5-}$ has five positional isomers, so it is probable that many positional isomers are present for the NPVMo.

Fig. 1

Using FT-IR spectroscopy to identify the keggin unit structural and changes during oxidizing starch is a good method, Fig. 2 gives the six characteristic IR spectrum peaks of NPVMo ranging from 700 - 1600 cm^{-1},which shows four main peaks for different oxygen bonds of the keggin structure, that is P-O (internal oxygen connecting P) at 1059 cm^{-1}, Mo-O (terminal oxygen bonding to Mo) at 943 cm^{-1}, V-O-V at 854cm^{-1} and 749 cm^{-1}.

Fig. 2

It is important to figure out the valence of each element in the catalyst. Fig. 3 gives the XPS of NPVMo. There is a peak at 517.5 eV which can be attributed to V^{4+} and V^{5+}. The peak at 402 eV showed NH_4^+ existing in the structure, and at 232.6 eV is Mo^{6+}.

Fig. 3

3.2. The activity of NPVMo

To compare with the previous work[25,26], we increased the content of vanadium to realize the controllable selective oxidation. The oxidized starch catalyzed by NPVMo was carried out under the protocol conditions such as, 1 g starch, 0.1 mL (0.001 wt%) of catalyst, 0.5 mL of distilled water, 2.5 mL of hydrogen peroxide at 70 □ for 10 h. The catalyst showed good activity on oxidizing starch, the carboxyl content can reach 0.648 mol$_{CO_2H}$ per 100 g. Therefore, it can be concluded that increasing the content of vanadium can improve the activity of molybdovanadophosphates. Accordingly, we made a comparison around different relevant catalysts including: no catalyst < Na_2MoO_4 < Na_3VO_4 < NH_4Cl < $H_5PMo_{11}VO_{40}$ < $H_5PMo_{10}V_2O_{40}$ < Fenton reagent < NPVMo. The active comparison of different catalysts is shown in Fig. 4. These results elucidated that vanadium plays a major role in the oxidation of starch. The oxidized starch and native starch have been characterized by FT-IR spectroscopy Fig. S2. The presence of an intense υ_{CO} band at 1728 cm^{-1} can be attributed to carboxylic groups which indicated that NPVMo exhibited a catalytic behavior on oxidizing starch by H_2O_2.

Fig. 4

The reason that the NPVMo exhibits a high activity and selectivity on the oxidation of starch than others is that Starch in an aqueous solution can be gelled with a certain adsorption properties and can adsorb polyoxoanions. When the starch was mixed with the catalyst, water and then a certain amount of hydrogen peroxide to activate the reaction, it can be seen the state of starch changed after a period of reaction time, until 10 h, the solution became clear. Thus the catalyst by adsorption of starch activation of hydrogen peroxide, enables the starch surface oxidation to occur.

It is very important to control conditions to prepare oxidized starch. The main influencing factors were: reaction time, temperature, water usage, H_2O_2 concentration and catalyst dosage; they were studied systematically as seen on Fig 5.

The oxidation of starch by H_2O_2 supposedly depends on water usage, which determines the dispersion of the catalyst and starch molecules .Fig 5a shows the carboxyl content as a function of water usage from 0.5 mL to 2.5 mL. As the usage of water increasing, it was discovered that the carboxyl content had a maximum at 1.0 mL. While further increasing the water content, it can be observed that there is a decrease trend; this is because increasing water can dilute the concentration of H_2O_2 and decrease the catalyst activity.

It is known that the temperature can directly affect the oxidized starch system; whilst the adequate temperature can activate the H_2O_2 and catalyst. On the contrary, a very high temperature will lead to starch carbonization; which will inactivate the catalyst and accelerate the decomposition of H_2O_2. As shown in Fig. 5b, from 40 ℃-80 ℃ the carboxyl content had increased and then a decreased as the temperature increased. The most appropriate temperature was 70 ℃, where we got the best result.

As a predominant factor, the reaction time significantly effects starch oxidation, Fig. 5c gives the carboxyl content increased gradually with increasing time from 2 h to 12 h, further raising the temperature did not result in higher carboxyl contents.

Fig. 5d shows the effect of the usage of catalyst. It can be observed that a little amount of catalyst has a good performance with $H_5PMo_{10}V_2O_{40}$ (the best result is 0.5 mol_{CO_2H} per 100 g). When decreasing the amount of catalyst the weight of product increased, so we controlled the catalyst dosage at 0.1 mL (0.0001 wt%) in starch oxidation and got the best result of 0.648 mol_{CO_2H} per 100 g.

The influence of H_2O_2 concentration is shown in Fig. 5e; where the reaction was carried out at 70 ℃ for 10 h with 0.1 mL (0.0001 wt%) catalyst. Obviously, the carboxyl content had increased by increasing the 30% H_2O_2 from 0.5 to 2.5 mL. Although further increasing the H_2O_2 concentration gave higher carboxyl content, the total weight of product had apparently decreased. Which could be explained as the catalyst always kept its activity. As a result, the optimum H_2O_2 concentration was found to be 2.5 mL.

The re-usage of catalyst is shown in Fig. 5f. Since the catalyst has the best activity on oxidizing starch and the cyclic voltammetry for NPVMo shows it has better reversibility Fig. 6. So in the same system we separated the product and reused the remaining liquid as catalyst and solvent; we found that the activity of the catalyst had decreased less, even when we re-used it five times.

Fig 5. Fig 6

3.3 The possible mechanism

Fig. 7 give the possible mechanism of NPVMo catalytic oxidation of starch by H_2O_2. Firstly, the proton in the POM interacted with the starch and attacked the hydroxyl group of C-2, C-3, and C-6 position in starch molecules. Then the vanadium in the POM oxidized the protonation of starch molecules to form oxidized starch; whilst the POM was reduced to reduction state. At last, the POM transformed back to its original vanadium heteropolyacid form by adding hydrogen peroxide. During the reaction we saw that the color changed but the structure of POM did not change. We have characterized the change of the POM using UV-vis, Fig. 7a indicated the fresh POM which has the characteristic peak of a keggin structure. Fig. 7b shows the reduction state of the POM, we can observe that the peak has a little shift which depicts the reduction of POM. Then we added H_2O_2 to the reduction POM, we found that the Uv-vis of this system had overlapped with the initial peak (Fig. 7 right c). This confirmed that the NPVMo catalyzed oxidized starch has not change its structure; which furthermore indicates that the catalytic cycle was completed.

Fig .7

4. Conclusion

The bi-functional catalyst $(NH_4)_5H_6PV_8Mo_4O_{40}$ with strong Brφnsted acidity and efficient oxidant has been synthesized and characterized by a series of characterization methods: FT-IR spectra, ^{31}PNMR, XPS etc. The catalyst exhibited the most excellent degree of oxidation in catalytic oxidation of starch by H_2O_2 under the mild conditions. At the central point of the experimental design, with 2.5 mL 30% hydrogen peroxide and 0.1 mL (0.0001 wt%) catalyst, we observed the highest values of the sum of carboxyl contents (0.648 mol_{CO_2H} per 100 g). When compared with the traditional catalyst such as $FeSO_4$, its competitive advantages are (1) usage of less amount of catalyst (2) the high utilization rate of H_2O_2 (3) easy synthesis of $(NH_4)_5H_6PV_8Mo_4O_{40}$ (4) highly efficient (0.648 mol_{CO_2H} per 100 g) in producing polyhydroxycarboxylic acids.

5. Acknowledgments

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Figure Caption

Fig. 1 The ^{31}PNMR of NPVMo which was dissolved in D_2O and standard H_3PO_4 (85%).

Fig. 2 The IR spectra of NPVMo.

Fig. 3 The XPS of NPVMo.

Fig. 4 The active comparison of different catalysts. Reaction conditions: starch (1 g), H_2O_2 (2.5 mL, 30 %), H_2O(0.5 mL), 0.1 mL 0.0001 wt% of catalyst, 70 ºC for 10h. (1) No catalyst; (2) Na_2MoO_4; (3) Na_3VO_4; (4) NH_4Cl; (5) $H_5PMo_{11}VO_{40}$; (6) $H_5PMo_{10}V_2O_{40}$; and (7) Fenton reagent; and (8) NPVMo.

Fig. 5 Parameters affecting the oxidation reaction including temperature (a), H_2O_2 concentration (b), temperature (c), reaction time (d), catalyst usage (e), H_2O_2 concentration and (f), The catalyst activity in five reaction cycles. Reaction conditions: starch (1 g), H_2O_2 (2.5 mL, 30 %), H_2O (0.5 mL), 0.1 mL 0.0001 wt% of catalyst, 70 ºC for 10h.

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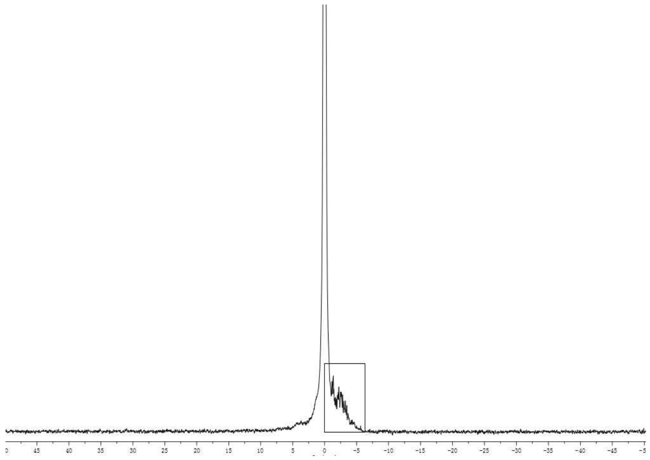

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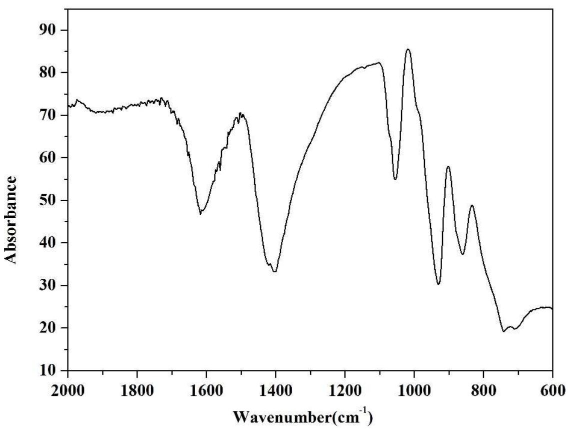

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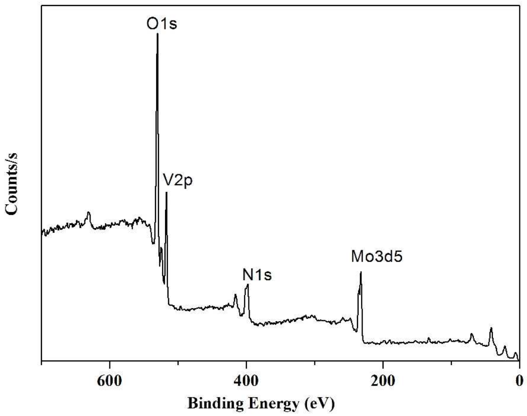

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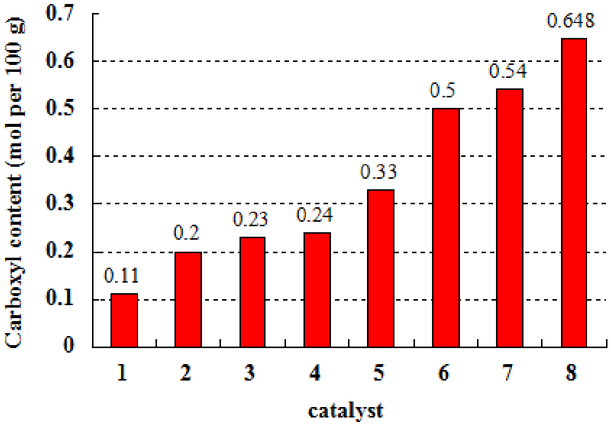

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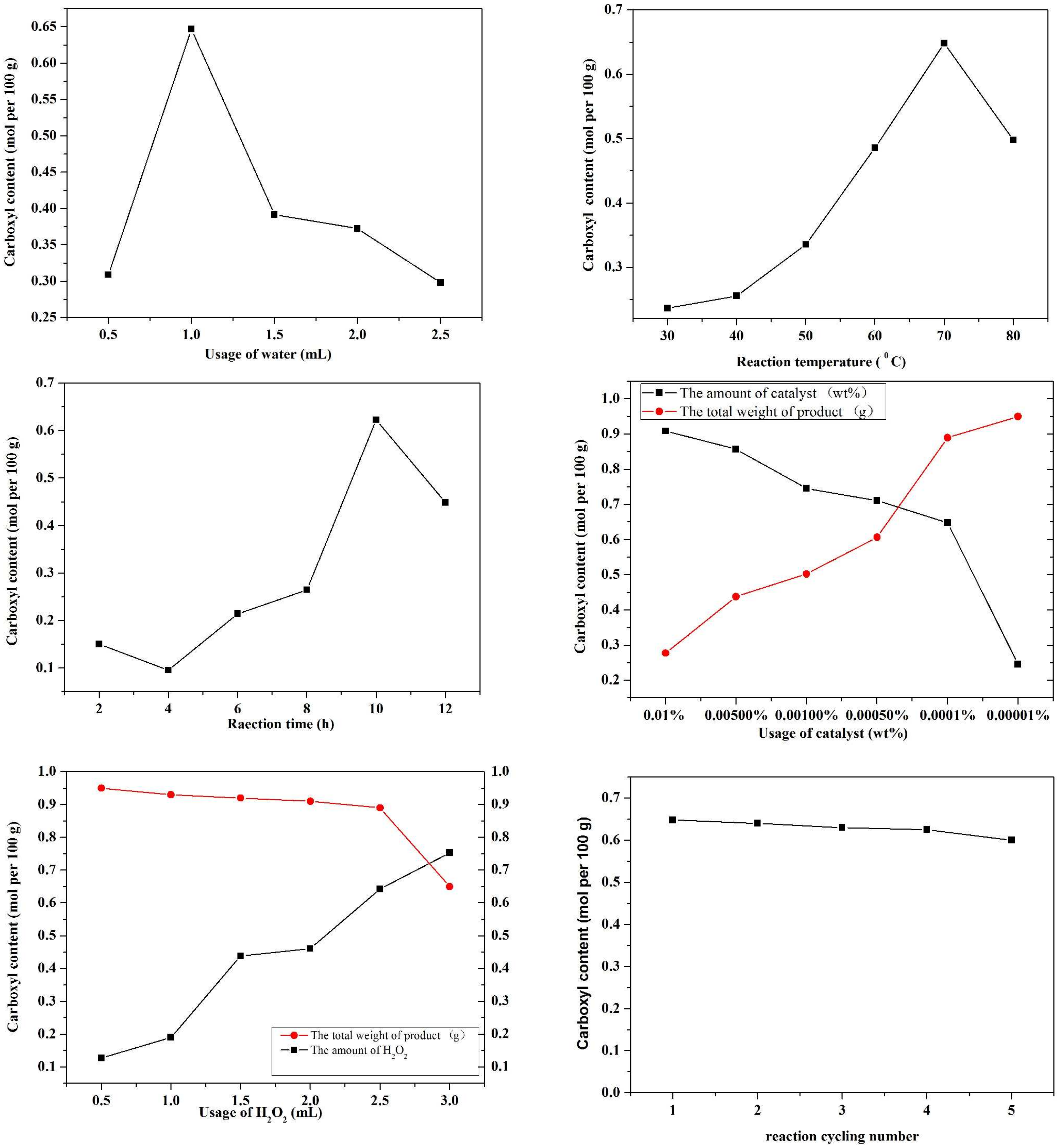

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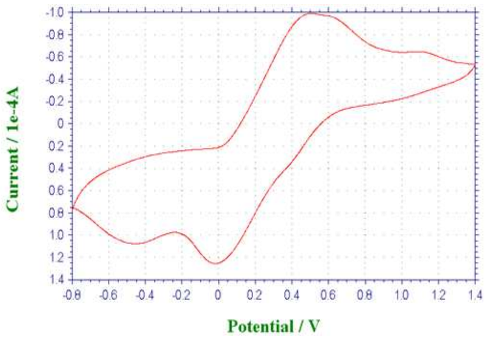

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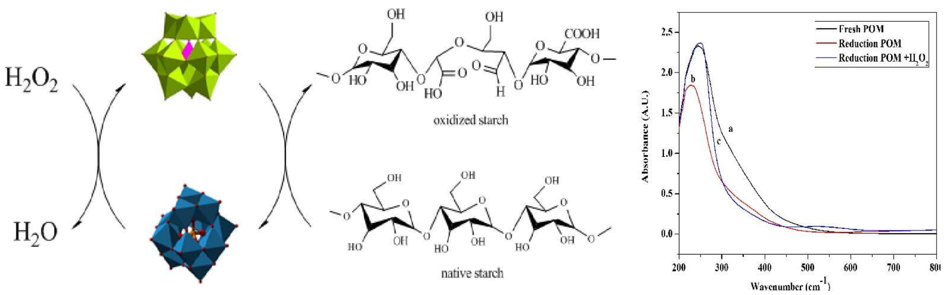

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