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Aerobic oxidation of starch catalyzed by isopolyoxovanadate $Na_4Co(H_2O)_6V_{10}O_{28}$

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ABSTRACT

The partial oxidation of starch was achieved in the presence of oxygen with $Na_4Co(H_2O)_6V_{10}O_{28}\cdot 18H_2O$ (abbreviated as CoV_{10}) as catalyst. The oxidation degree of starch was determined by FT-IR, XRD and SEM measurements, which indicated that the aerobic oxidation of starch was promoted by oxidative catalyst CoV_{10}. The application of CoV_{10} could give a high oxidation degree (DO) of 1.35 COOH/100 GU and 2.07 CO/100 GU with 86 wt.% yield of solid starch under mild reaction conditions (pH = 6; reaction time, 8 h; temperature, 50 °C; catalyst amount, 8 mg, when 1.5 g starch was used as substrate; atmospheric pressure). Among some vanadium compounds, CoV_{10} exhibited 4-fold activity higher than orthovanadate due to its coordination effect of cobalt and $V_{10}O_{28}$. Meanwhile, CoV_{10} could be recycled for six times with only a slight decrease in activity. Thus, CoV_{10}/O_2 is one of the most efficient systems for partial oxidation of starch reported so far.

1. Introduction

Starch, as a natural polysaccharide, has been a subject of academic and industrial interest for many decades because of its renewability, biodegradability, abundance and low cost. However, the hydrophilic OH groups of the unmodified starch molecule tend to form intermolecular and intramolecular hydrogen bonds limiting the application of the material for certain applications (Zhang, Zhang, Wang, & Wang, 2009). This limitation of native starch has attracted increasing attention on modifying and transforming starch into a wide range of products, such as bioplastics, ethanol fuel, and fine chemicals, as well as adhesives, surfactants and vitamins (i.e., vitamin B1, B11, and C by fermentation) (Tolvanen et al., 2011). Among all modification processes, oxidation of starch is the most important one to obtain oxidized starch for the utilization in paper, textile, laundry finishing and binding materials industries to provide surface sizing and coating properties (Sánchez-Rivera, García-Suaírez, Velázquez del Valle, GutierrezMeraz, & Bello-Pérez, 2005). In the oxidative process of starch, hydroxyl groups, primarily at C-2, C-3 and C-6 positions, are replaced by carboxyl and carbonyl groups (Kuakpetoon & Wang, 2006), while granular structure of the starch must remain intact during oxidation. Therefore, the carboxyl and carbonyl contents of oxidized starch as well as the degree of degradation are generally used to indicate the level of oxidation.

Many types of oxidative systems have been investigated for starch oxidation, such as, MTO/H_2O_2/LiBr (Herrmann, Rost, Tosh, Riepl, & Kuhn, 2008), H_2O_2–FePcS (Tolvanen, Mäki-Arvela, Sorokin, Salmi, & Murzin, 2009), H_2O_2–Na_2WO_4 (Lukasiewicz, Bednarz, & Ptaszek, 2011), H_2O_2–MSO_4 (M = Cu, Fe) (Aouf et al., 2010), H_2O_2–$[(CH_3)_3NCH_2CH_2OH]_5PV_2Mo_{10}O_{40}$ (Chen et al., 2013), and other non-hydrogen peroxide systems (e.g., nitrogen oxidants (Painter, Cesàro, Delben, & Paoletti, 1985; Kochkar, Morawietz, & Hölderich, 2001), sodium hypochlorite (Nieuwenhuizen, Kieboom, & Bekkum, 1985; Floor, Kieboom, & Bekkum, 1989; Forssell, Hamunen, Autio, Suortti, & Poutanen, 1995; Besemer & De Nooy, 1995; Teleman, Kruus, Ämmälahti, Buchert, & Nurmi, 1999), peracetic acid (Bragd, Besemer, & Bekkum, 2002) and sodium periodate (Veelaert, Wit, & Tournois, 1994; Veelaert, Wit, Gotlieb, & Verhé, 1997 a,b) etc.). In H_2O_2 system, one of the most common drawbacks is that over oxidation results in depolymerization of the glycosidic bond with low yields of insoluble product, and thereby narrows the range of application. Therefore, the partial oxidation is much more difficult to control compared to the completely oxidation of starch to carboxylic acid and other small molecules, since it involves not only to accelerate the oxidation occurred only at the C6 primary hydroxyl groups but also to restrict the cleavage of vicinal

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diols on C2 and C3. The non-hydrogen peroxide systems showed high efficiency, but brought about environmental problems that large amount of waste was seriously discharged. Taking account of the environmental, safety, economic and specific application concerns, the utilization of O_2 as oxidizing agent for starch oxidation is becoming even more desirable. In addition, oxygen is not only the most moderate one compared to other oxidants, but also could easily control the partial oxidation of starch to certain oxidation level. So far, there are only a few reports on oxidation of starch using air or oxygen as oxidant. However, either homogeneous copper (Achremowicz, Gumul, Bala-Piasek, Tomasik, & Haberko, 2000) or vanadium (Bala-Piasek & Tomasik, 1999; Sheng et al., 2011) was utilized as a catalyst which brought the problem in separation. Besides, the complexation of starch with inorganic salts had been observed in the first two literatures, which brought impurities into the product. In the last one, an economic, environmental and simple way has been achieved using oxygen as oxidant in 28 wt.% NaOH solution without any catalysts, which obtained a highly efficiency result with the content of carboxyl 3.60 g/100 g (Sandhu, Kaur, Singh, & Lim, 2008). However, a lot of water soluble oxidized starch which was not that desirable was obtained in above system. So, there were some contradictories between oxidation degree and high yield of insoluble products. Therefore, the oxidation of native starch using molecular oxygen as oxidant under mild conditions is still challenging. It is of critical importance to develop an alternative catalyst which can activate oxygen to oxidize starch for green chemistry advantages.

Polyoxometalates (POMs) are a class of metal oxide clusters of early transition metals (V, Mo, W, Nb, etc.) with strong Brønsted acidity, fast reversible multi-electron redox transformations under mild conditions, and adjustable acid–base and redox properties over a wide range, which allow them as acidic and redox-bifunctional catalysts in homogeneous and heterogeneous systems(Liu, Möhwald, Volkmer, & Kurth, 2006; Coronado, Giménez-Saiz, & Gómez-García, 2005; Bi, Zhou, Wang, & Dong, 2008; Long, Tsunashima, & Cronin, 2010; Miras, Wilson, & Cronin, 2009). Among many POMs, vanadium-based POMs are of great interest owing to their structural diversity based on various charming types of {VOx} polyhedra (x = 4, 5, 6) and potential applications in oxidative catalysis (Aureliano, 2009). Especially, a lot more attention was focused on the investigation of Keggin structure $PMo_{12-n}V_nO_{40}^{(3+n)^-}$ in terms of oxidative catalysis, hardly any was paid on the other kind of isopolyoxovanadates (Pope, McCleverty, & Meyer, 2004). During our previous research, $Na_4Co(H_2O)_6V_{10}O_{28}{\cdot}18H_2O$ was proved to exhibit high antitumor activity due to its high oxidative property (Zhai et al., 2009). Besides, the inhibition role of decavanadate for mitochondria (Soares, Gutiérrez-Merino, & Aureliano, 2007); the interaction of V_{10} with ion pumps Aureliano, Fraqueza, & Ohlin, (2013) and recent in vivo studies with $V_{10}O_{28}^{6-}$ (Aureliano & Ohlin, 2014) was discussed by Aureliano (Only recently), $[C_8H_{17}N(CH_3)_3]_3H_3V_{10}O_{28}$ was found to be active in aerobic oxidation of dibenzothiophene (Tang et al., 2012). To date, only a few vanadium POMs were reported to be able to carry out aerobic oxidation of biomass to corresponding small acids (Albert, Wölfel, Bösmann, & Wassershe, 2012), but it is necessary to add some additives to accelerate the reaction rate. Almost all these reports were involved with the deep oxidation of biomass by POMs and O_2, because partial oxidation catalyzed by POMs is difficult to control in some senses. As a result, there is plenty room for the development of more efficient and wide-ranging catalysts using air or oxygen as oxidant under mild conditions as a new oxidation system. Here presented the catalytic oxidation of starch by using $Na_4Co(H_2O)_6V_{10}O_{28}{\cdot}18H_2O$ (abbreviated as CoV_{10}) as catalyst with oxygen as oxidant under atmospheric pressure and low temperature. This system showed high efficiency for partial oxidation of starch with negligible breakage of C—O—C linkages under mild conditions, and the catalyst could be recycled at least six times without obvious loss of its activity.

2. Experimental

2.1. Materials

All chemicals (analytical grade) were purchased from commercial sources and were used as received without further purification. Starch (derived from potato with over 90% amylose) was purchased from Sigma-Aldrich. 0.01 M of NaOH was used for determining the carboxyl content by titration. 0.1 M of HCl was used for determining carbonyl content.

2.2. Physical measurements

Elemental analysis was carried out 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 NicoletMagna 560 IR spectrometer (the ratio of KBr to sample is 150:1). X-ray diffraction (XRD) patterns of the oxidized starch were collected on Rigaku Dmax 2000 X-ray diffractometer with Cu *K*a radiation (λ = 0.154178 nm) in the 3° < 20° < 50° range. ^{13}C NMR spectra were recorded at 70.5 ^1C on a Bruker AV600 spectrometer at 600 MHz. Water-insoluble sample of native starch was dissolved in d_6-Me_2SO containing D_2O and water-soluble samples of oxidized starch were dissolved in D_2O, respectively. DR-UV–vis spectra (200–600 nm) were recorded on a Cary 500 UV–vis–NIR spectrophotometer. Cyclic voltammetry was measured in range of +1.00 to −2.00 V in DMF at Pt working electrode and Ag/AgC1 reference electrode using NEt_4Cl or NEt_4Br as supporting electrolyte. The morphology of the starch was observed with scanning electron microscope (FE-SEM, JSM-7500F, JEOL).

2.3. Catalyst preparation

The compound $Na_3(12H_2O)H_3V_{10}O_{28}{\cdot}2H_2O$ (abbreviated as NaV_{10}) was prepared according to a previous paper (Lee & Joo, 2003) and CoV_{10} was synthesized according to Zhai et al. (2009) with little modification, and identified by IR spectroscopy. Solid $Co(AC)_2{\cdot}4H_2O$ (1 mmol, 0.249 g) was added to a solution of $Na_3VO_4{\cdot}12H_2O$ (1 mmol, 0.4 g) in 10 mL H_2O. Then the mixture was adjusted to pH ≈ 6.0 with 4 M HCl. After being stirred for 1 h, the solution was filtered and stood at room temperature for two days. Orange–yellow crystals suitable for X-ray analysis were obtained (40.5 wt.% yield).

2.4. General oxidation procedure

The experiments were performed in a glass reactor with oxygen bubbling device. Typically, 1.5 g of previously gelatinized starch was suspended in a total volume of 10 mL of deionized water at room temperature and added into the reactor. Then, it was heated up to the desired temperature and the pH was adjusted to the desired level by the addition of 0.1 M NaOH or o.1 M HCl solution. After the catalyst (8 mg, 0.006 mmol) was added into the reactor without changing the pH of the reaction mixture, molecular oxygen was then bubbled through the reaction solution. After specified reaction time, the reaction solution was centrifuged in 3000 rpm (637 × g) for 10 min to separate the insoluble oxidized products and the aqueous part which containing catalyst and low-molecular-weight compounds (e.g., sugar acids and formic acid). Then, the insoluble oxidized starch was evaporated to dryness under high vacuum at room temperature for 4 h to give white paste for measuring the yields and the degree of oxidation. In order to separate the low-molecular-weight compounds from the soluble catalyst,

the aqueous phase was acidified with sulfuric acid and the low-molecular-weight compounds were extracted twice with the aid of ethyl acetate. Then the dissolved catalyst stayed in the residue aqueous solution, which was distilled under reduced pressure (bp 65 °C, 10 mmHg) to form yellowish powder (49.983 mg when 50 mg of catalyst was used, which recovery effect was 99.9%).

2.5. Determination of carboxyl content

The carboxyl content was determined as described Zhai et al. (2009). The solid air-dried oxidized starch (0.5 g) was suspended in distilled water (2.5 mL), stirred for 30 min and centrifuged. The residue was washed with distilled water, resuspended in 30 mL of distilled water and heated in a boiling water bath with continuous stirring for 30 min to achieve complete gelatinization. The heated samples were then titrated to pH 8.3 with 0.01 mol/L NaOH solution. The carboxyl content was expressed as the quantity of carboxyl groups per 100 glucose units (COOH/100 GU), calculated as follow:

$$\text{COOH}/100\,\text{GU} = \frac{(V_s - V_b) \times M \times 0.045 \times 100}{W}$$

where V_s is the volume of NaOH required for the sample (mL), V_b is the volume of NaOH used to test the blank (mL), M is the molarity of NaOH, W is the sample weight, respectively.

2.6. Determination of carbonyl content

The carbonyl content was determined as described by Smith, Whistler, and Paschal (1967). The solid air-dried oxidized starch (0.5 g) was suspended in distilled water (12.5 mL) and heated in a boiling water bath for 30 min with continuous stirring until completely gelatinized and then stored at 40 °C. The pH was adjusted to 3.2 with 0.1 mol/L HCl; hydroxylamine chloride solution (2 mL) was then added to the solution (prepared by dissolving 25 g of reagent grade hydroxylamine chloride in water, adding 100 mL of 0.5 mol/L NaOH and bringing the final volume to 500 mL). The reaction mixture was stirred for 4 h. The unreacted hydroxylamine was determined by a rapid titration to pH 3.2 with standardized 0.1 M HCl. A blank experiment with native starch and hydroxylamine reagent was performed similarly. The carbonyl content was expressed as the quantity of carbonyl groups per 100 glucose units (CO/100 GU), calculated as follow:

$$\text{CO}/100\,\text{GU} = \frac{(V_s - V_b) \times M \times 0.028 \times 100}{W}$$

where V_b is the volume of HCl used for the blank (mL), V_s is the volume of HCl required for the sample (mL), M is the molarity of HCl, and W is the sample weight, respectively.

3. Results and discussion

3.1. Catalytic activity

The catalytic activities of different catalysts (NaV_{10}, $Co(AC)_2{\cdot}4H_2O$, $Na_3VO_4{\cdot}12H_2O$ and CoV_{10}) were compared in terms of starch oxidation with oxygen as oxidant under reaction conditions: pH = 6; reaction time, 8 h; temperature, 50 °C; catalyst amount, 8 mg (0.006 mmol), atmospheric pressure (Table 1). The catalytic activity was in the range of $Na_3VO_4{\cdot}12H_2O < Co(AC)_2{\cdot}4H_2O < NaV_{10} < CoV_{10}$. $Na_3VO_4{\cdot}12H_2O$ is a simple vanadate salt, which was not active in oxidation of starch by oxygen under such reaction conditions. $Co(AC)_2{\cdot}4H_2O$ presented a relatively high carboxyl and carbonyl content with 0.64 COOH/100 GU and 1.47 CO/100 GU, respectively. This result demonstrated that cobalt salt could catalyze the oxidation of starch by oxygen, which might be a better candidate for starch oxidation because of its wide variable oxidation states. However, the insoluble products obtained were lesser than that by CoV_{10}, which means that the deep oxidation of starch occurred. It also can be seen from Table 1 that NaV_{10} exhibit high catalytic activity (0.98 COOH/100 GU and 1.10 CO/100 GU, respectively) in oxidation of starch by O_2, which was attributed to its vanadium center. Similar with $Co(AC)_2{\cdot}4H_2O$, the yield of insoluble oxidized starch of NaV_{10} was lower as well. As a result, the oxidation of starch with CoV_{10} was enhanced by the cooperation of Co cation to obtain 1.35 COOH/100 GU and 2.07 CO/100 GU with 86% solid product. This could be attributed to the synergistic effect between $[V_{10}O_{28}]^{6-}$ anion and Co cation.

Table 1
Oxidation of starch by oxygen with different catalysts[a].

Catalyst	Carboxyl content (COOH/100 GU)	Carbonyl content (CO/100 GU)	Yield of solid starch (wt.%)
CoV_{10}	1.35	2.07	86
NaV_{10}	0.98	1.10	76
$Co(AC)_2{\cdot}4H_2O$	0.64	1.47	77
$NaVO_4{\cdot}12H_2O$	0.12	0.79	92
[15]NH_4VO_3	0.36	1.89	85
[16]$CuSO4{\cdot}5H_2O$	0.71	1.96	55
[17]NO	0.00	0. 19	98

[a] Reaction conditions: starch, 1.5 g; pH = 6; reaction time, 8 h; temperature, 50 °C; catalyst amount, 8 mg.

Murzin etc. Tolvanen et al. (2009)) has reported a waste free method for starch oxidation with iron tetrasulfophthalocyanine (FePcS) as a catalyst and hydrogen peroxide (H_2O_2) as oxidant, which gave the highest COOH value of 1.6/100 GU and CO value of 3.0/100 GU so far. However, FePcS process only gave 67% yield of solid oxidative starch due to depolymerization and decomposition by H_2O_2. Compared to H_2O_2, the utilization of oxygen as oxidant is more economic and could obtain much more solid oxidized starch. Under present process, CoV_{10} gave solid oxidized starch with 1.35 COOH/100 GU and 2.07 CO/100 GU, respectively. Meanwhile, the loss of insoluble products was relatively low to give 86% yield of solid starch. It can be concluded that being partially oxidized by oxygen, native starch was successfully modified at high efficiency and high yield by this homogeneous catalyst CoV_{10}.

The changes of morphologies of the starch could indicate the degree of starch oxidation by O_2 and CoV_{10} (Fig. 1). It can be seen that the particles of both native and oxidized starches in different oxidized degree are polyhedral in shape with the same distribution of particle size with 5–20 μm in diameter. The granule surfaces of native starch are smooth, practically with no defects (Fig. 1a). After oxidation, starch retained its granular shape but some defects on the surface (Fig. 1b and c). Meanwhile, the surface defects increased with the increase of the oxidation degree. This indicated that the oxidation of starch took place from the surface of the granules to the interior of the granule (Kachkarova-Sorokina, Gallezot, & Sorokin, 2004).

Oxidation led the hydroxyl groups changed into carbonyl and carboxyl groups in starch molecules. The introduction of carbonyl groups could be confirmed by FT-IR spectroscopy (Fig. 2). For native starch (Fig. 2a), a typical bands at 3435 cm^{-1} was attributed to the O—H stretching vibration of OH groups in the glucose units, while the peaks at 2926, 1450 and 1370 cm^{-1}, respectively, were contributed to the C—H stretching and bending modes of the methylene (Sugama & Mater, 1997). The peak at 1640 cm^{-1} originates from the bending vibration of H—O—H in the absorbed H_2O. For oxidized starch, it is obviously that the emergence of strong new bands can be attributed to the formation of carboxylate groups at 1604 and 1350 cm^{-1} due to the asymmetric and symmetric stretching of

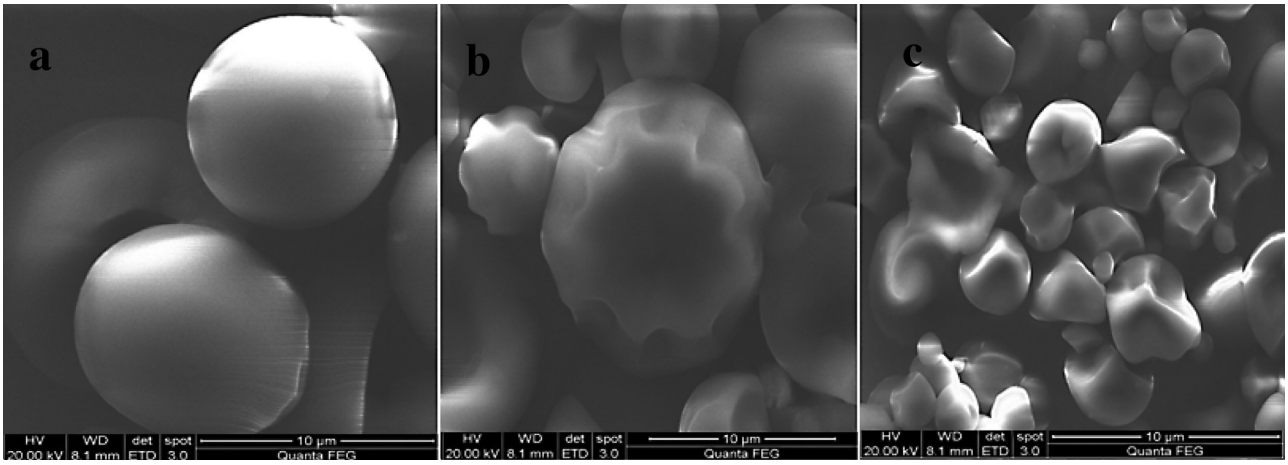

Fig. 1. SEM images of (a) native starch, (b) oxidized starch with carboxyl content 0.72 COOH/100 GU and carbonyl content 1.85 CO/100 GU, and (c) oxidized starch with carboxyl content = 1.35 COOH/100 GU and carbonyl content = 2.07 CO/100 GU.

COO^-, respectively. In addition, the oxidized starch gave the characteristic vibrational peak of carbonyl groups at 1741 cm^{-1} (Sugama & Mater, 1997). From above observations, we can reasonably presume that carboxyl and carbonyl groups have been introduced into molecular structure of starch through the oxidation reaction. Meanwhile, the intensity of the O—H stretching vibration became weaker, which indicated that native starch was successfully oxidized by oxygen, and hydroxyl groups were changed to carbonyl and/or carboxyl groups.

Native starch commonly exists about 15–45 wt.% crystallinity (Sugama & Mater, 1997) in a granular structure. It is proposed that the level of starch oxidation in terms of carboxyl group content was strongly related to their degrees of crystallinity. The XRD patterns of the native starch and two oxidized starches were given in Fig. 3. The native corn starch (Fig. 3a) has sharp peaks at 14.3, 17.2, 23.1, and 32.3°, respectively, which represents the typical pattern of native starch (Ma, Jian, Chang, & Yu, 2008). For oxidized starch with a carboxyl content 0.720 COOH/100 GU and carbonyl content 1.092 CO/100 GU (Fig. 3b), the peaks appeared at 2θ values of 17.1, 23.0 and 30.3°, respectively. However, the peak at 14.3° disappeared, indicating that the original crystal structure of the native starch was changed. That is to say that part of original crystalline structure was destroyed during the reaction and a new crystal structure formed. In Fig. 3c, there were no peaks to be found as the oxidative starch with the carboxyl content 1.35 COOH/100 GU and carbonyl content 2.07 CO/100 GU. This means that the crystal structure of native starch was completely destroyed and forming an amorphous phase of oxidized starch.

To further confirm the structural changes between the native and oxidized starches, the native and oxidized starch were analyzed by ^{13}C NMR spectroscopy in d_6-Me_2SO–D_2O (Fig. 4). The main units of native starch are obviously characterized by the signals at 59.90, 70.64, 82.00, 99.47and 104.27 ppm, which are attributed to C6, C2, C3, C5 and C4, respectively. The differences in the spectra of oxidized starch from that of native starch are seen distinctly. Strong signals assigned to carbonylic and carboxylic carbons are observed in downfield shifts from 175 to 185 ppm (Kato, Mastuo, & Isogai, 2004). As shown in Fig. 4, the signals of the C2, C3 and C6 hydroxyl groups decreased due to the carbonyl and carboxyl groups. The results reveal that the introduced carbonyl and carboxyl groups are caused by C6 and cleavage between the C2 and C3 and the oxidation did not cause C—O—C breakage.

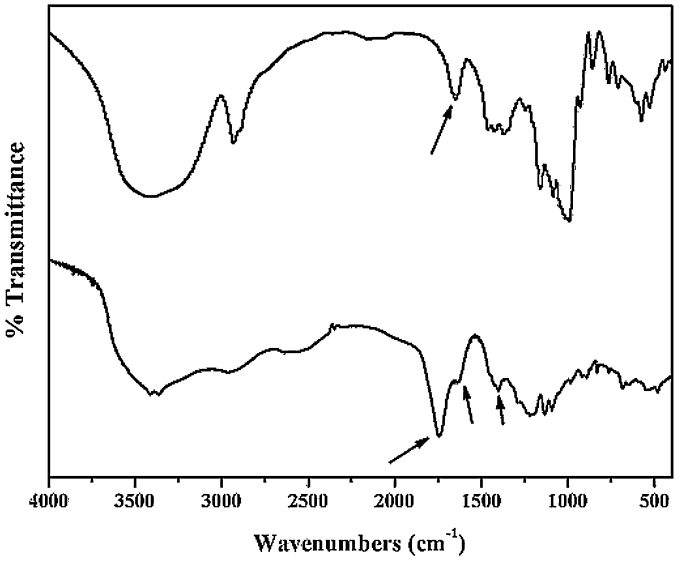

Fig. 2. FT-IR spectra of (a) native starch, (b) oxidized starch obtained under the optimal conditions.

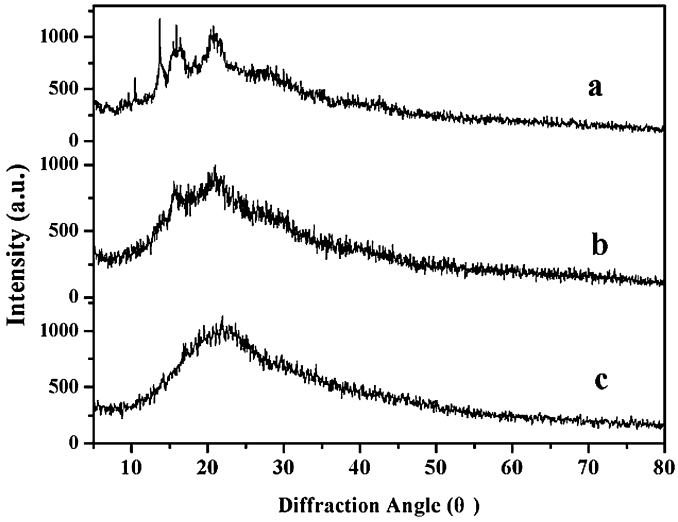

Fig. 3. The XRD patterns of (a) native starch, (b) oxidized starch with carboxyl content 0.72 COOH/100 GU and carbonyl content 1.85 CO/100 GU, and (c) oxidized starch with carboxyl content 1.35 COOH/100 GU and carbonyl content 2.07 CO/100 GU.

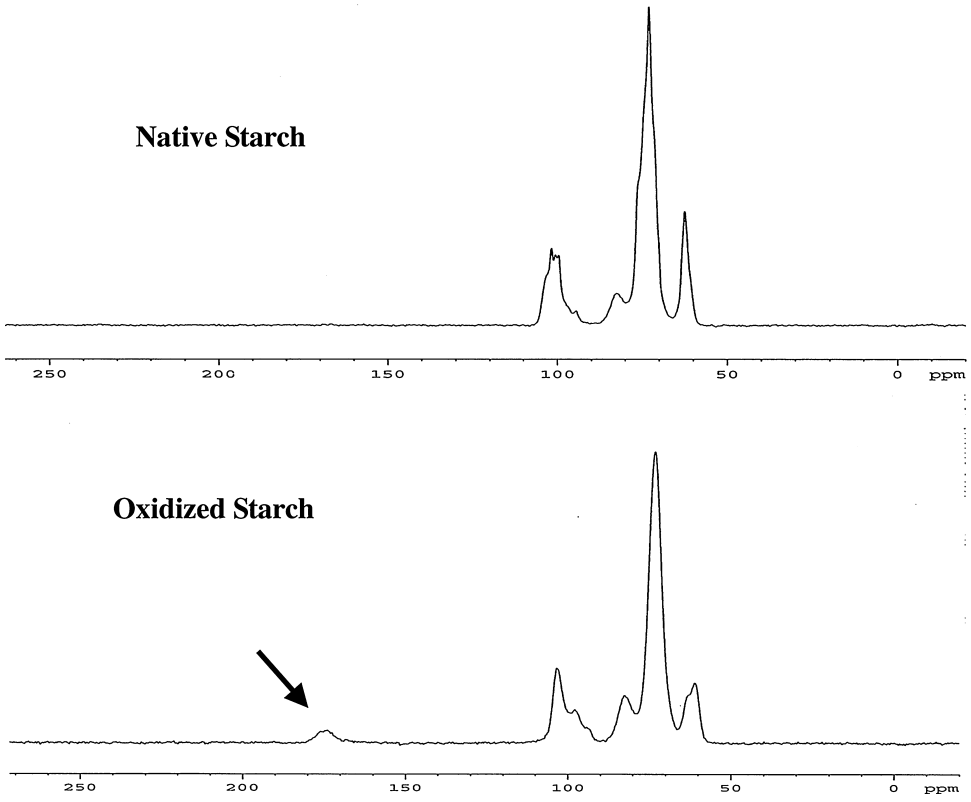

Fig. 4. ^{13}C NMR of native starch and oxidized starch.

3.2. Optimization of conditions for oxidation of starch

Main parameters affecting the oxidation reaction including temperature, reaction time, catalyst dosage, and pH value were investigated as following (Fig. 5).

The starch oxidation reaction was usually performed in a moderate alkaline solution in order to obtain high yield of carboxyl groups according to L. Yang (Crans, Smee, & Gaidamauskas, 2004), because the depolymerization of oxidized starch was easier under acidic conditions than under alkaline conditions. Furthermore, high pH values would generated low-molecular-weight products and then further resulted in lower yield of solid starch (Tolvanen et al., 2011). Therefore, in order to obtain both high oxidation degree and high yield of solid oxidized starch, the pH of the mixture would be controlled from 5 to 10. The pH values beyond 5 and 10 were not considered because of the hydrolysis of starch under acidic environment and the instability of isopolyoxovanadate catalyst under alkaline conditions. It can be seen from Fig. 5a, the pH value has a remarkable impact on oxidative degree and the yield of solid starch. An obvious increase can be observed when pH increased from 5 to 6 and the degree of oxidation reached to its maximum (COOH/100 GU = 1.35 and CO/100 GU = 2.07) at pH = 6, then dropped dramatically to 0.18 of COOH/100 GU and 0.998 of CO/100 GU at pH = 10, which could be ascribed to the instability of isopolyoxovanadate catalyst under alkaline conditions. The cyclic voltammetry of CoV_{10} under different pH values from 5 to 10 was measured to determine this point (Fig. S1). On the other hand, the yield of solid starch decreased gradually from 89 wt.% at pH = 5 to 32 wt.% at pH = 10 along with the increasing of pH values. So, the pH = 6 was more preferable as the yield still can reach as high as 86 wt.%.

The oxidation of starch by molecular oxygen was supposed to depend on temperature. Fig. 5b gave the results of the carboxyl and carbonyl content of oxidized starch as a function of temperature when the reaction was carried out using O_2 as oxidant in the presence of 8 mg CoV_{10} as catalyst for 8 h with pH = 6. It can be seen that both carboxyl and carbonyl content increased to its maximum with increasing the temperature up to 50 °C. Further raising the temperature only resulted in a slightly increase of the degree of oxidation. Compared with the increased degree of oxidation, however, the yield of solid starch saw an obvious decrease trend from 90 wt.% to 40 wt.% due to the higher degradation rate of starch molecule at higher temperature. The degradation of starch at higher temperature was attributed to the deep oxidation of starch to gluconic acid dissolved in water, which was determined by HPLC/MS. Take the yield of solid starch into consideration, 50 °C (where COOH/100 GU = 1.35 and CO/100 GU = 2.07) with a yield of 86 wt.% was chosen as the most appropriate temperature.

As a predominant factor, reaction time significantly affected the oxidation of starch (Fig. 5c). It demonstrated that the carboxyl and carbonyl content increased apparently with the reaction time up to 8 h, keep increasing the reaction time to 12 h, no further increase in the carboxyl or carbonyl content was obtained. Similarly, the yield of solid starch also declined gradually, which can be explained as the further oxidation of oxidized starch happened which reacted into small molecular products when lengthen the reaction time. Even though a rather high yield (93 wt.%) of solid starch was obtained when the reaction time was 2 h, the extremely low degree of oxidation will narrow the pragmatic application of oxidized starch. Consequently, 8 h was recommended as the most suitable reaction time. The catalyst amount was also a main factor affecting the reaction of starch oxidation (Fig. 5d). As shown in Fig. 4d, the carboxyl and carbonyl content increased markedly and reached to maximum values of COOH/100 GU = 1.35 and CO/100 GU = 2.07 when 8 mg of catalyst was used. Further increasing the catalyst amount, the degree of oxidation increased slightly with formation of light yellow oxidized starch, which supposed to be the generation of by-product. On the contrary, the yields of solid starch

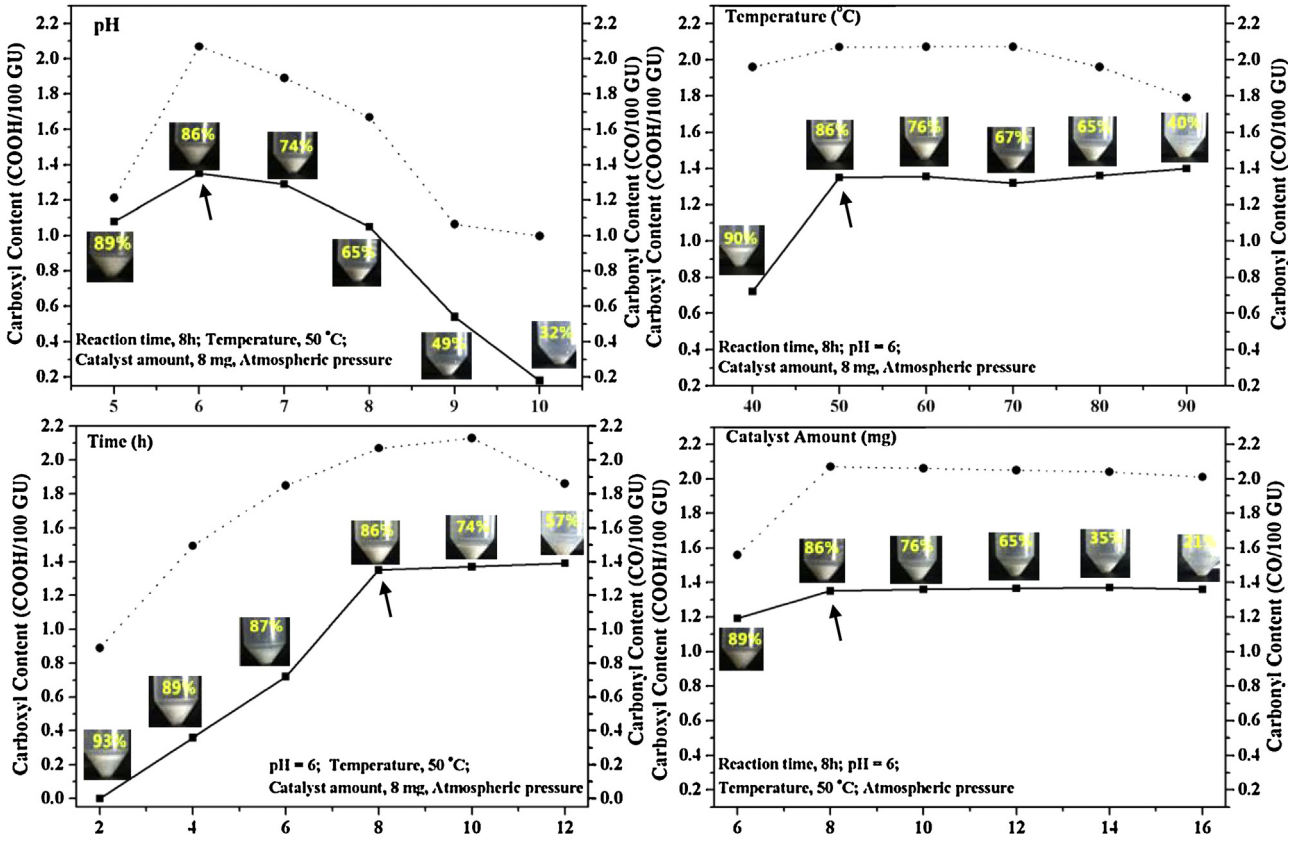

Fig. 5. Parameters affect the oxidation reaction including temperature, pH values, reaction time, and the amount of catalyst. Solid: carboxyl content, dot: carbonyl content. Squared image: the yield of solid oxidized starch.

showed the opposite trend as increasing the amount of catalyst, decreasing from 86 wt.% to 21 wt.%. The more catalyst was added, the more low-molecular-weight compounds was produced which lead to the reduced weight of solid oxidized starch. In terms of the yield and oxidative degree, the amount of catalyst was selected as 8 mg.

As a result, pH = 6; temperature, 50 °C; reaction time, 8 h; and catalyst amount, 8 mg would be the most favorable reaction conditions to achieve modified starch with both high degree of oxidation and high yield of solid starch to fulfill its practical application.

3.3. The regeneration of the catalyst

The regeneration of CoV_{10} is of practical and economic importance. The recycle reaction was carried out using 10 g of starch and 50 mg of catalyst. After the reaction, it can be easily achieved by distillation of the aqueous solvent under reduced pressure (bp 65 °C, 10 mmHg) to afford a yellowish powder (49.98 mg when 50 mg of catalyst was used). The IR spectra of CoV_{10} obtained before and after reaction (Fig. 6) indicated its stability during the oxidative reaction (Crans et al., 2004; Zhang, Wang, Zhao, & Wang, 2012; Frost, Erickson, Weier, & Carmody, 2005). Fresh CoV_{10} gave the strong

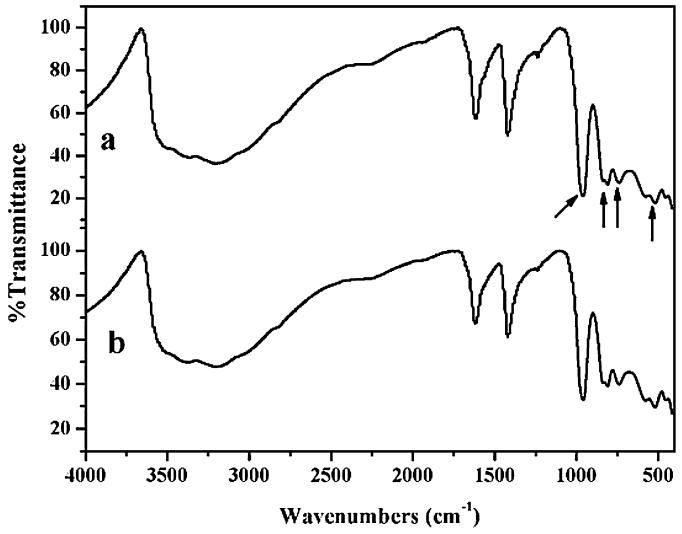

Fig. 6. FT-IR spectra of pure (a) CoV_{10} and (b) CoV_{10} after the oxidation of starch.

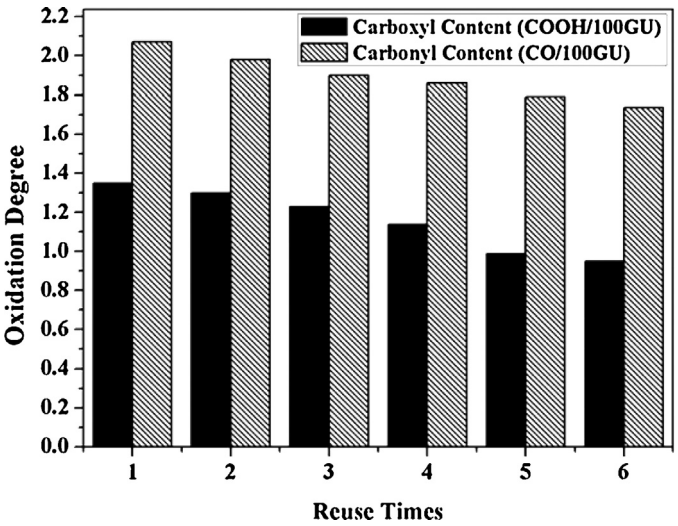

Fig. 7. The reusability of CoV_{10}.

band at 951 cm^{-1} assigned to the stretching vibrations the V=O terminal bonds. The bands at 835 and 739 cm^{-1} were corresponding to the asymmetric vibrations of the bridging V—O—V segments. While as, the bands at 592 and 525 cm^{-1} was attributed to the V—O—V the asymmetric vibrations. The IR spectrum of regenerated CoV_{10} gave the same characteristic peaks, showing its stability during the reaction and regeneration processes. Furthermore, the UV–vis spectra of spent and prepared CoV_{10} was provided to prove its stability (Fig. S2). The leaching amount of the catalyst was determined by ICP-ES, and the total amount of CoV_{10} leaching through six runs of the reaction was only 4.9% that of the initial amount. The catalytic activity of recovered catalyst was maintained efficiently after six repeated experiments (Fig. 7).

4. Conclusion

We have succeeded in preparing a crystal isopolyoxovanadate catalyst, Na4Co(H_2O)6V10O28·18H_2O, and demonstrated its superior catalytic activity over other methods on starch oxidation for its advantage of activating oxygen, which make it a possible to aerobic oxidation of starch. Therefore, this work considerably important and have a far-reaching impact on modifying refractory biomass, since there is hardly any successful examples at present.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2014.10.066.

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