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Polyoxometalate-based Ionic liquid as thermoregulated and environmentally friendly catalyst for starch oxidation

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ABSTRACT

A new kind of polyoxometalate (POM) ionic liquid ($[(CH_3)_3NCH_2CH_2OH]_5PV_2Mo_{10}O_{40}$) (abbreviated as $Ch_5PMo_{10}V_2O_{40}$) has been synthesized by a precipitation/ion exchange method with choline chloride and $H_5PMo_{10}V_2O_{40}$ as precursors. The produced salt turned out to be an original ionic liquid (IL) catalyst and exhibited a novel switchable property based on temperature variation. In this regard, it refers to a thermoregulated feature that elevated temperature leads to the miscibility of catalyst and substrate. As decreasing the temperature, the catalyst precipitates and becomes heterogeneous form to be separated automatically from the reaction mixture. The combination of POMs with choline chloride was also proved to be effective in catalyzing the oxidation of starch, which showed higher or nearly identical performance with traditional catalysts, such as $FeSO_4$. Results demonstrated the catalyst was easily separated from the products and the retrieved $Ch_5PMo_{10}V_2O_{40}$ could be repeatedly used without appreciable loss of its performance, which highlighted the practical application of this important biomass.

1. Introduction

Growing concerns about global warming and the limitation of fossil fuels are pushing scientists to spare their efforts on the production of chemicals and fuels from biomass in a more efficient and sustainable way [1]. Among the different options, starch is one kind of abundant feedstocks for the production of hydrophilic starch, which is generally obtained from the partial oxidation of native starch, and is widely used in paper and textile industries. The hydrophilic starch, as sugar acid, is primarily achieved by controlling oxidation of starch through biocatalysis or chemical catalysis [2]. Several oxidative processes can be accounted including the use of alkaline hydrogen peroxide [3], nitrogen oxidizes [4], sodium hypochlorite [5], peracetic acid [6], oxone [6] and sodium periodate [7]. The above processes showed efficient, but brought about environmental problems that large amount of waste was seriously discharged, and sometimes over oxidation resulting in low yields. Thus, more attractive processes are urged to be developed by using H_2O_2 or O_2 as environmentally acceptable oxidants. By now, easily acceptable and inexpensive transition-metal catalysts have been used [8–10] in H_2O_2 or O_2 system. Fe or Cu salts have been reported to catalyze starch oxidation in yields up to 90–99%, but lower carbonyl and carboxyl contents ($0.04\ \mathrm{mol_{CO}}$ per 100 g, $DS_{C=O} = 0.066$, $0.009\ \mathrm{mol_{CO_2H}}$ per 100 g, $DS_{CO_2H} = 0.014$. DS means the degree of substitution) [8] were obtained. Inorganic salt, Na_2WO_4, exhibited a relatively high catalytic activity in oxidizing of starch with H_2O_2, yielding exclusively oligmomeric polyhydroxycarboxylic acids with a high acid concentration ($0.11 - 0.25\ \mathrm{mol_{CO_2H}}$ per100 g) [10]. Iron phthalocyanie (FePcS) gave the oxidative compounds with carbonyl and carboxylic groups as $0.05\ \mathrm{mol_{CO}}$ per 100 g, $DS_{C=O} = 0.08$, $0.024\ \mathrm{mol_{CO_2H}}$ per 100 g, DS $\mathrm{mol_{CO_2H}} = 0.04$, respectively [11]. Fenton-type reagents $FeSO_4$ and $CuSO_4$ showed efficient to transform starch into polyhydroxycarboxylic acids with the highest yields, $0.61\ \mathrm{mol_{CO_2H}}$ per 100 g [12], which was the best result reported to date. However, the solubility of catalyst in products would give rise to the difficulty on separation, and the system stability may be further interfered by the impurities. Another relatively higher degree of oxidation was acquired by the three-component system $CH_3ReO_3/H_2O_2/HBr$ in water–acetic acid mixture for the selective oxidation of the C6 hydroxymethyl group yielding the corresponding carboxylic acid with $0.52\ \mathrm{mol_{CO}}$ per 100 g [13]. Even though, the above system required large amount of CH_3ReO_3 to ensure the activity due to the deactivation. Therefore, an essential element of the as-described catalytic oxidation of starch is the use of environmentally benign oxidants, H_2O_2 or O_2, in combination with ideal catalyst.

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Recently, polyoxometalates (POMs) have drawn much attention due to their diverse availability in electronic, magnetic, redox, medicine and photonic fields, etc. Among numerous applications of POMs, catalysis is by far the most attractive one for its high flexibility in modification of the redox properties, ease of handling, environmental compatibility, non-toxicity and experimental simplicity [14]. One of catalytically important subclass of Keggin compounds are the mixed vanadium (V)-substituted polyoxometalates. Mizuno and Kamata had reviewed the recent developments on the catalytic oxidation of hydrocarbons with hydrogen peroxide by vanadium-based polyoxometalates [15]. The proposed reaction based on vanadium substituted POMs includes hydroxyl and hydroperoxy radicals generated by homolytic cleavage of H_2O_2 and vanadium center, whose mechanism is similar to that of Fenton type reactions. Thus, vanadium substituted POMs with Keggin structure, $PV_2Mo_{10}O_{40}{}^{5-}$, was chosen in the present work to catalyze the oxidation of starch to produce carbonyl and carboxyl groups.

The application of ionic liquids as environmentally benign reaction solvents for synthesis and catalysis has received extensive attention [16] during these years. Moreover, POM-based ILs have also attracted substantial investigations in chemistry field in recent years [17–20]. Accordingly, we have interacted choline chloride (ChCl; $HOCH_2CH_2N(Me)_3{\cdot}Cl$), which is one of the most economically and readily available ionic liquids, with $H_5PMo_{10}V_2$ as alternative to realize the oxidation of starch. Owing to its less expensive than most other ionic liquids, low toxic to humans, environmentally friendly and non-flammable characters [21], choline chloride has been used in the conversion of carbohydrates into 5-hydroxymethylfurfural [21–23]. The combination of ChCl with Lewis acids, such as $ZnCl_2$, has also been investigated in o-acetylation of cellulose and monosaccharides [24].

To the best of our knowledge, there is no report on the combination of ChCl with POMs to act as oxidative catalysts in the conversion of starch into carboxylic acids. The aim of this work is to seek a simple approach to prepare POM catalysts which could be used as heterogeneous catalysts to catalyze starch oxidized to its corresponding oxidative product with high efficiency under mild reaction conditions.

2. Experimental

2.1. Materials

All chemicals were purchased from commercial sources and were used as received without further purification. 0.1 M of NaOH solution was used for determining the carboxyl content by titration. $H_5PV_2Mo_{10}O_{40}$ was synthesized according to Ref. [25], and identified by IR spectroscopy.

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 ^{31}P NMR (85% H_3PO_4 external standard) measurements were obtained using a Bruker AM500 spectrometer at 202.5 MHz. X-ray diffraction (XRD) patterns of the catalyst were collected on Rigaku Dmax 2000 X-ray diffractometer with Cu Kα radiation ($\lambda = 0.154178$ nm) (Rigaku Corporation). TEM image was determined by JEM-2100F instrument. Energy dispersive X-ray analysis (EDX) was performed to take into account of the C, N, P, V and Mo elements.

2.3. Catalyst preparation

$Ch_5PMo_{10}V_2O_{40}$ was synthesized by mixing aqueous solution of ChCl and $H_5PV_2M_{10}O_{40}$ with a molar ratio of 5:1. Once $H_5PV_2M_{10}O_{40}$ solution added dropwise into the solution of ChCl, an orange precipitate was observed immediately. Then removed the solid by filtration and washed with diluted water until no free of POMs and chloride ($AgNO_3$ test) found. Finally dried in air under ambient conditions. IR (1% KBr pellet, 4000–400 cm^{-1}): 1050, 943, 874, and 787 cm^{-1}. Anal. Calcd for $Ch_5PMo_{10}V_2O_{40}$: C, 13; N, 3.1; P, 1.3; V, 4.5 and Mo, 42.5%. Found: C, 11; N, 3.7; P, 2.3; V, 4.3 and Mo, 43.1%.

2.4. Starch oxidation

In a typical reaction protocol, 1 g of starch and 4 mg of catalyst was mixed with 1.5 mL distilled water in the reactor, and heated to required temperature with continually and vigorously stirred for a period. Then the oxidation reaction was activated by addition certain amount of hydrogen peroxide. In order to make the starch oxidized completely as much as possible, the hydrogen peroxide was added intermittently other than the whole amount at once. Furthermore, the H_2O_2 addition interval depends on the length of experiment, usually at a rate of 900 μL/2 h when 10 h reaction time and 4.5 mL hydrogen peroxide was required. After reaction, the soluble product was filtrated immediately and dried at room temperature to get white paste resulting material, which weight was almost up to 0.95 g.

The recycle reaction was carried out using 10 g of starch and 40 mg of catalyst. After reaction, the soluble product was filtrated and the remaining mixture contained water, unreacted H_2O_2 and catalysts. Than the catalyst was separated by centrifuge at 4000 rpm, washed with water for reused. The leaching amount of the catalyst was determined by ICP-ES.

2.5. Determination of carboxyl content [12]

300 mg of resulting material (white paste) was dissolved in distilled water (20 mL), and a few drops of phenolphthalein solution in EtOH were added as indicator. The solution was titrated with 0.1 M of NaOH solution until the color of the solution changed to pink.

3. Results and discussion

3.1. Characterization of $[(CH_3)_3NCH_2CH_2OH]_5PV_2Mo_{10}O_{40}$

From the results of the elemental analyses, the C, H, N, Mo, P and V contents in catalyst are C, 2.76; H, 0.71; N, 0.70; P, 1.45; Mo, 40.92; V, 4.22%, respectively. Compared with the calculated values C, 2.66; H, 0.62; N, 0.62; P, 1.37; Mo, 42.60; V, 4.52%, the results are satisfactory.

The FT-IR spectra are quite useful to identify structural and bonding changes in the Keggin unit present in POM-based IL hybrid materials. Fig. 1a gave the four characteristic peaks of IR spectrum of $Ch_5PMo_{10}V_2O_{40}$ at 1055, 951, 867, 791 cm^{-1}, respectively. Compared to its parent $[PV_2Mo_{10}O_{40}]^{5-}$ with four characteristic peaks of P-O stretching (~1064 cm^{-1}), $M{-}O_{ter}$ stretching (~964 cm^{-1}), $Mo{-}O_c{-}Mo$ stretching of inter bridges between corner-sharing MoO_6 octahedra (~876 cm^{-1}), and $Mo{-}O_e{-}Mo$ stretching of intra bridges between edge-sharing MoO_6 octahedra (~814 cm^{-1}), four characteristic peaks of Keggin structure are intact. In addition, the peaks at 3394, 3028 and 1473 cm^{-1} were attributed to C—H, and C—N, respectively, showing that quaternary ammonium existed in $Ch_5PMo_{10}V_2O_{40}$.

As can be seen from ^{31}P MAS NMR spectra of $H_5PV_2Mo_{10}O_{40}$ and $Ch_5PMo_{10}V_2O_{40}$ (Fig. 2), the peak at 4.75 ppm for $Ch_5PMo_{10}V_2O_{40}$,