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Mixed salts of silver and ammonium derivatives of molybdovanadophosphoric acid to improve the catalytic performance in the oxidation of starch

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ABSTRACT

Mixed salts of silver and ammonium derivatives $Ag_x(NH_4)_{5-x}PMo_{10}V_2O_{40}$ (x = 0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0) were designed and synthesized through ion exchange along with precipitation. Different molar ratio of Ag^+ to NH_4^+ resulted in different surface areas, which could give different oxidative catalytic activity in oxidation of starch. Among all molybdovanadophosphoric salts, $Ag_{3.5}(NH_4)_{1.5}PMo_{10}V_2O_{40}$ was found to be the most active catalyst in starch oxidation with the highest degree of substitution (DS = 0.62 mol/100 g). And $Ag_{3.5}(NH_4)_{1.5}PMo_{10}V_2O_{40}$ could be reused several times without significant loss of its catalytic activity.

1. Introduction

The development of novel routes for the transformation of renewable biomass into useful chemicals is of great importance and interesting for establishing sustainable chemical processes [1]. As one of the most abundant sources of biomass, starch might be the most promising sustainable feedstocks for production of chemicals [2]. Oxidized starch, as one of the most important modified starch, is widely used in industries such as paper, textile, laundry finishing, building material, and food to provide surface sizing and coating property [3]. The most common used oxidized starch was mainly produced by reacting starch with oxidizing reagents under controlled conditions. Many inorganic oxidizing reagents have been employed for oxidation of starch including alkaline hydrogen peroxide, [4] sodium hypochlorite, [5] nitrogen oxides, [6] peracetic acid, [7] or sodium periodate [8]. The above processes showed

efficient, but over oxidation always happened resulting in low yields, and environmental problems occurred that large amount of waste discharged. Thus, more attractive processes are urged to be developed using H_2O_2 [9] or O_2 [10] as environmentally acceptable oxidants. Hydrogen peroxide is a kind of attractive, green, and clean oxidant for liquid phase oxidation, for water is the only by-product in oxidation reactions, which make it much cheaper and safer than most other organic and inorganic oxidants. By now, metal cations or metal complexes, mostly focusing on Fe^{2+} and Cu^{2+}, have been extensively used in starch oxidation by H_2O_2 [11] (Table S1). The highest DS (DS represents the degree of substitution) of 0.73 mol CO_2H per 100 g has been obtained catalyzed by Fe complexes [12]. However, the solubility of such catalysts in products would lead to the separation problem, and the impurities of products could interfere the stability. Therefore, a key element of the have-described catalytic oxidation of starch is the use of environmentally benign oxidants, H_2O_2 or O_2, in combination with the ideal catalysts.

Polyoxometalates (POMs) are a unique class of fascinating metal oxygen cluster species leading to potential applications in catalysis, medicine, material science, and magnetism [13]. Among POMs, the Keggin-type molybdovanadophosphoric acids, $H_5PV_2Mo_{10}O_{40}$, have been found a wide use for selective oxidation of different organic compounds with H_2O_2 [14–17]. The above achievement promoted many research groups to devote their efforts to use POMs as catalysts for catalytic refining of biomass [18]. However, the well

solubility of polyoxometalate in the water or other polar solvent and its relatively lower specific surface area limited the application. To deal with this problem, two adaptive methods are proposed. One method is to immobilize POMs on certain inorganic supporters as SiO_2 [19], SBA-15 [20], activated carbon or carbon nanotubes [21]. Yet, they suffered from leaching of the active POMs into liquid-phase during selective oxidation processes. Another method is to exchange the protons with large cations (Cs^+, Ag^+, K^+, and NH_4^+) to form insoluble salts and construct the micro or mesoporous structures, which would further improve the catalytic performances [22,23]. There are some reports on catalytic oxidative reactions by $M_nH_{5-x}PMo_{10}V_2O_{40}$ ($M = Cs^+$, Ag^+ or NH_4^+) [24–26]. Hill and co-workers have first reported the synthesis of $Ag_5PMo_{10}V_2O_{40}$ and demonstrated its better stability and catalytic activity than $Na_5PMo_{10}V_2O_{40}$ (soluble salt) [27]. The preferable catalytic activity was supposed to derive from the synergistic effect of Ag^+ and V^{5+}, but the influence of silver content on the catalytic activity has not been systematically studied. From the above literatures, it can be seen that only one type of cation to substitute the protons of POMs have been extensively reported. Mixed salts of POMs with different cations, however, have not been significantly explored. During our research, $Ag_3PW_{12}O_{40}$ was found to be one kind of insoluble salt in water with undesirably small surface areas [28]. Therefore, the synthesis of phosphovanadomolybdate salts containing the mixture salts of silver and ammonium becomes meaningful and important. Through this designation, the insoluble POMs with high surface areas might be obtained, which is more advisable for oxidative catalysis.

Here, combination salts of silver and ammonium cations incorporated in molybdovanadophosphorates, $Ag_x(NH_4)_{5-x}PMo_{10}V_2O_{40}$ ($x = 0$, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0), have been reported and characterized in detail. Also, they were tested as oxidative catalysts for starch oxidation by H_2O_2, which demonstrated that this kind of POM catalysts can uniquely catalyze the oxidation of starch with highly efficient utilization of hydrogen peroxide and can be reused for some times.

2. Experimental

2.1. Materials

All reagents were of AR grade and used without further purification. $H_5PMo_{10}V_2O_{40}$ and $H_3PMo_{12}O_{40}$ were synthesized according to the literature [29].

2.2. Preparation of catalysts

To an aqueous $H_5PMo_{10}V_2O_{40}$ solution (0.1 M), aqueous $AgNO_3$ solution (0.1 M) was added to substitute protons with stirring vigorously. Then a freshly prepared solution of NH_4NO_3 (0.1 M) with different usages was added dropwise to the above mixture. After 1 h, the slurry was aged 20 h under room temperature to form yellow crystalline precipitates. The powder was washed with deionized water to remove unreacted $H_5PMo_{10}V_2O_{40}$, $AgNO_3$, and NH_4NO_3 until no more $AgNO_3$ being detected and then dried at 200 °C for 2 h.

Similarly, $Ag_{3.5}(NH_4)_{1.5}PMo_{12}O_{40}$ was synthesized in the same way except that the $H_5PMo_{10}V_2O_{40}$ was replaced by $H_3PMo_{12}O_{40}$.

2.3. Starch oxidation

In a typical reaction protocol, 1 g of starch and 4 mg of catalyst was mixed with 2 mL of distilled water in a three-necked flask, and the slurry was heated to 80 °C with vigorously stirring for a specified time. Then hydrogen peroxide was added to trigger the reaction. In order to confirm the best utility of H_2O_2, the total

amount of hydrogen peroxide was added intermittently other than the whole amount at one time. In addition, the addition interval of H_2O_2 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 were required. After reaction, the mixture was filtrated immediately to separate insoluble catalyst for reuse. And the filtrate was cooled down to room temperature to separate unreacted starch by centrifuge. Finally, the soluble product was obtained by evaporation of water at 40 °C and the water-soluble product (i.e., oxidized starch) of starch was almost 0.85 g.

2.4. Determination of carboxyl content [30]

Three hundred milligrams of resulting material (white paste) was dissolved in distilled water (20 mL), and a few drops of phenolphthalein solution in EtOH were added as an indicator. The solution was titrated with 0.1 M of NaOH solution until the color of the solution changed to pink. The degree of oxidation with respect to the percentage of carboxyl groups (mol/100 g) presented in the polymer was calculated according to the following equation:

$$\text{Carboxyl content (mol/100g)} = \frac{c \times (V - V_0) \times 100}{0.3 \times 1000}$$

where c = molar concentration of sodium hydroxide, $V - V_0$ = consumption volume of sodium hydroxide.

2.5. Physical measurements

Elemental analysis (Leeman Plasma Spec (I) ICP-ES), a P-E 2400 CHN elemental analyzer, IR spectroscopy (KBr discs on a NicoletMagna), X-ray diffraction (XRD) (Rigaku Dmax 2000 X-ray diffractometer with Cu Ka radiation), and Nitrogen adsorption (ASAP 2010 M surface analyzer) were used to study the components, structure, and morphology of catalysts. The ^{31}P MAS NMR measurements were obtained using a Bruker AM500 spectrometer at 202.5 MHz. Energy dispersive X-ray analysis (EDX) was also performed to take into account of the C, N, Ag, P, V, and Mo elements.

3. Results and discussion

3.1. Catalyst characterization

From the elemental analysis results of the series of catalysts (Table 1), the molecular formula of different compounds were confirmed to be $Ag_x(NH_4)_{5-x}PMo_{10}V_2O_{40}$ ($x = 0\sim5.0$).

Table 1 The IR spectrum (Fig. 1a) of $Ag_{3.5}(NH_4)_{1.5}PMo_{10}V_2O_{40}$ gave bands at 1059, 966, 865, and 792 cm^{-1}, which are characteristics of υ_{as}(P–O$_a$), υ_{as}(Mo–O$_d$), υ_{as} (Mo–O$_b$–Mo), and υ_{as} (Mo–O$_c$–Mo). The peak at 603 cm^{-1} is assigned to V–O asymmetric stretching vibration. The above results suggested that $Ag_{3.5}(NH_4)_{1.5}PMo_{10}V_2O_{40}$ retains its parent Keggin structure [31]. Besides, the peak at 1406 cm^{-1} is assigned to N–H vibration of NH_4^+.

The XRD patterns of $Ag_{3.5}(NH_4)_{1.5}PMo_{10}V_2O_{40}$ (Fig. 2b) were basically corresponding with its parent $H_5PMo_{10}V_2O_{40}$ (a) (JCPDS no. 84-0234), and other diffraction peaks were probably accounted for the incorporation of Ag^+ and NH_4^+. These results further demonstrated that the $Ag_{3.5}(NH_4)_{1.5}PMo_{10}V_2O_{40}$ retained the Keggin structure after exchanging protons by silver and ammonium cations.

In order to determine the structure of POM anion, the ^{31}P MAS NMR of $Ag_{3.5}(NH_4)_{1.5}PMo_{10}V_2O_{40}$ has been tested (Fig. 3). Compared to its parent $H_5PMo_{10}V_2O_{40}$ ($\delta = 4.14$ ppm), one peak splitted into two signal peaks respectively at 2.99 and 3.96 ppm due to the interaction between $PMo_{10}V_2O_{40}^{5-}$ anion and cations.

It is known that the substitute of protons by metal cations could dramatically increase the surface areas of POM derivatives