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Short Communication

Redox behavior and oxidation catalysis of $H_nXW_{12}O_{40}$ ($X = Co^{2+}$, B^{3+}, Si^{4+}, and P^{5+}) Keggin heteropolyacid catalysts

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ABSTRACT

Redox behavior and oxidation catalysis of $H_nXW_{12}O_{40}$ ($X = Co^{2+}$, B^{3+}, Si^{4+}, and P^{5+}) Keggin heteropolyacid catalysts were investigated. Successful formation of $H_nXW_{12}O_{40}$ catalysts was confirmed by diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy. Reduction potentials of $H_nXW_{12}O_{40}$ catalysts were determined by electrochemical measurements. First electron reduction potential of $H_nXW_{12}O_{40}$ catalysts decreased with increasing overall negative charge of heteropolyanion. $H_nXW_{12}O_{40}$ catalysts were then applied to the liquid-phase oxidation of benzaldehyde to benzoic acid. Yield for benzoic acid increased with increasing first electron reduction potential.

1. Introduction

Heteropolyacids (HPAs) are early transition metal–oxygen anion clusters that exhibit a wide range of molecular structures and compositions. Because of their structural and chemical versatility, HPAs have found successful applications in electrochemistry [1], medicine [2], material science [3], and catalysis [4]. Among various HPA structural classes, Keggin HPAs have been widely employed as catalysts because of their outstanding structural stability, acid–base property, and unique redox property.

Comprehensive understanding about redox behavior of HPAs is very important in designing HPAs as an oxidation catalyst [5,6]. One of the most conventional methods to investigate the redox behavior of HPA catalysts is to determine the reduction potential (oxidizing ability) of HPAs by electrochemical measurement in solution. However, electrochemical measurement is strongly influenced by a number of experimental conditions. Electrochemical measurement under consistent experimental conditions only gives comparable results, and therefore, direct comparison of results in literatures is not a simple task. It is obvious that there is a need for systematic investigations about redox properties of HPAs using electrochemical measurements to provide a basis for designing HPAs as an oxidation catalyst. Nevertheless, only a few electrochemical investigations have been made and limited information is currently available.

In this work, redox behavior and oxidation catalysis of $H_nXW_{12}O_{40}$ ($X = Co^{2+}$, B^{3+}, Si^{4+}, and P^{5+}) HPA catalysts were investigated. Successful formation of $H_nXW_{12}O_{40}$ HPA catalysts was confirmed by diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy. Reduction potentials of $H_nXW_{12}O_{40}$ catalysts were determined by electrochemical measurements. Reduction potential was determined under consistent environments to provide a systematic basis to estimate the redox behavior of heteroatom-substituted HPA catalysts. A correlation between first electron reduction potential and overall negative charge of heteropolyanion was established. $H_nXW_{12}O_{40}$ catalysts were then applied to the homogeneous liquid-phase oxidation of benzaldehyde to benzoic acid. The catalytic activity was also correlated with the redox behavior (first electron reduction potential) of $H_nXW_{12}O_{40}$ catalysts. Through this work, we have successfully demonstrated that first electron reduction potential determined by electrochemical measurements was well correlated with catalytic performance in the oxidation of benzaldehyde.

2. Experimental

2.1. Catalyst preparation

$H_nXW_{12}O_{40}$ ($X = Co^{2+}$, B^{3+}, Si^{4+}, and P^{5+}) HPA catalysts were prepared according to the methods in the literatures [7–10]. As-synthesized alkali-metal salts were converted into acid forms by etherate method using sulfuric acid and ethyl ether. Successful formation of $XW_{12}O_{40}^{n-}$ heteropolyanion frameworks was confirmed by diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy using a Nicolet 6700 (Nicolet) spectrometer. Each HPA catalyst was thermally treated at 200 °C for 3 h prior to characterization and catalytic reaction.

2.2. Electrochemical measurements

Cyclovoltammograms of $H_nXW_{12}O_{40}$ ($X = Co^{2+}$, B^{3+}, Si^{4+}, and P^{5+}) HPA catalysts were measured by a conventional three-electrode system.

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Electrochemical measurements were carried out using a Potentiostat/Galvanostat (Eco Chemie, Autolab 302N) instrument. Glassy carbon electrode with diameter of 3.0 mm and platinum rod were used as a working electrode and a counter electrode, respectively. Saturated calomel electrode (KCl saturated) was used as a reference. Each HPA catalyst (1 mM) was dissolved in 0.5 M Na_2SO_4 aqueous solution and purged for 20 min under nitrogen flow (20 ml/min) prior to electrochemical measurement. Cyclovoltammograms were acquired at scan rates of 25, 50, 75, 100, 125, and 150 mV/s under the atmospheric conditions.

2.3. Homogeneous liquid-phase oxidation of benzaldehyde

Homogeneous liquid-phase oxidation of benzaldehyde was carried out over $H_nXW_{12}O_{40}$ ($X = Co^{2+}$, B^{3+}, Si^{4+}, and P^{5+}) HPA catalysts in a glass reactor equipped with a reflux condenser. Benzaldehyde (10 ml, 0.098 mol) was charged into a reactor. Acetonitrile (100 ml) was successively charged into the reactor as a solvent. Reactor was heated to 80 °C and then each HPA catalyst (0.3 g) was added into the reactor. Liquid-phase oxidation of benzaldehyde was carried out for 1 h under oxygen bubbling (30 ml/min). Reaction products were sampled and analyzed after 1 h-reaction using a gas chromatograph (YL6100 GC, Younglin) equipped with a flame ionization detector. DB-5 (Agilent, 60 m × 0.32 mm) capillary column was used for product separation. Conversion of benzaldehyde and selectivity for benzoic acid (a main product) were calculated on the basis of carbon balance. Yield for benzoic acid was calculated by multiplying conversion of benzaldehyde and selectivity for benzoic acid.

3. Results and discussion

3.1. Catalyst characterization

Fig. 1 shows the DRIFT spectra of $H_nXW_{12}O_{40}$ ($X = Co^{2+}$, B^{3+}, Si^{4+}, and P^{5+}) HPA catalysts. The spectrum of $H_6CoW_{12}O_{40}$ catalyst exhibited the characteristic bands at 960, 889, and 761 cm^{-1}, which were assigned to $W=O_d$, $W–O_b–W$, and $W–O_c–W$ stretching vibrations, respectively. The characteristic band for $Co–O_a$ stretching vibration (445 cm^{-1}) was not observed in the scan range. The spectrum of $H_5BW_{12}O_{40}$ catalyst exhibited the characteristic bands at 955, 904, 814, and 753 cm^{-1}, which were assigned to $W=O_d$, $W–O_a$, $W–O_b–W$, and $W–O_c–W$ stretching vibrations, respectively. There were three characteristic bands for $B–O_a$ stretching vibrations at 1410, 1004, and 504 cm^{-1} [11]. The band at 1004 cm^{-1} corresponding to $B–O_a$ stretching vibration appeared in the scan range. The spectrum of $H_4SiW_{12}O_{40}$ catalyst exhibited the characteristic bands at 979, 885, and 787 cm^{-1}, which were assigned to $W=O_d$, $W–O_b–W$, and $W–O_c–W$ stretching vibrations, respectively. The bands for $Si–O_a$ were observed at 1020 and 924 cm^{-1} [12]. The spectrum of $H_3PW_{12}O_{40}$ catalyst exhibited the characteristic bands at 984, 888, and 810 cm^{-1}, which were assigned to $W=O_d$, $W–O_b–W$, and $W–O_c–W$ stretching vibrations, respectively. The band for $P–O_a$ was observed at 1080 cm^{-1}. Unlike other polyatom-substituted heteropolyanions or other structural classes of heteropolyanions, X–O bands of $H_nXW_{12}O_{40}$ HPA catalysts did not show any band splitting, indicating the existence of T_d local symmetry of a central XO_4 unit that is a characteristic feature of α-Keggin structure. All positions of characteristic IR bands of $H_nXW_{12}O_{40}$ HPA catalysts were in good agreement with the results of previous works [11–13], indicating successful formation of heteropolyanion frameworks.

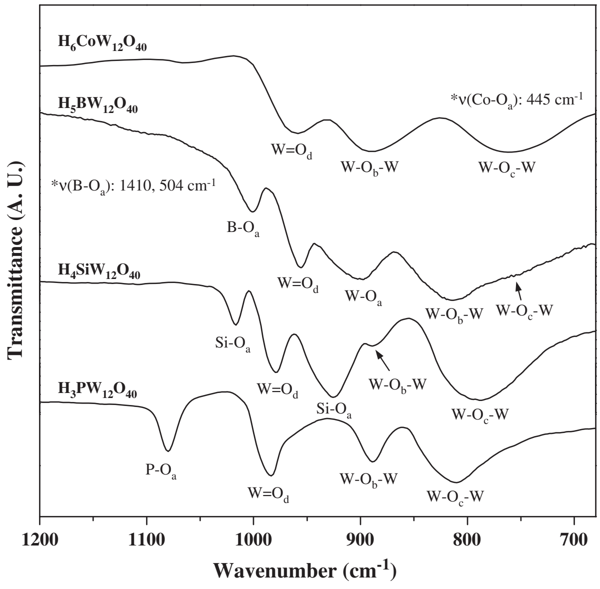

Fig. 1. DRIFT spectra of $H_nXW_{12}O_{40}$ ($X = Co^{2+}$, B^{3+}, Si^{4+}, and P^{5+}) HPA catalysts. O_a: oxygen connected to the central heteroatom, O_b: corner-shared oxygen, O_c: edge-shared oxygen and O_d: terminal oxygen.

3.2. Electrochemical measurement

Fig. 2 shows the cyclovoltammograms of $H_nXW_{12}O_{40}$ ($X = Co^{2+}$, B^{3+}, Si^{4+}, and P^{5+}) HPA catalysts at a scan rate of 100 mV/s. Electrochemical measurements were performed under consistent experimental conditions to provide comparable results. All $H_nXW_{12}O_{40}$ HPA catalysts exhibited well-defined reversible and stepwise one- or two-electron redox transitions during the electrochemical measurements. Five couples of one-electron redox waves were observed for $H_3PW_{12}O_{40}$ catalyst. Three couples of redox waves were observed for $H_4SiW_{12}O_{40}$ catalyst with electron ratio of 1:1:2. Two couples of redox waves with electron ratio of 2:1 were observed for $H_5BW_{12}O_{40}$ catalyst. Three couples of one-electron redox waves were observed for $H_6CoW_{12}O_{40}$ catalyst. Overall shapes of cyclovoltammograms were maintained at a scan rate up to 150 mV/s, and only peak current increased monotonically. Each inset figure in Fig. 2 shows the dependence of peak current on square root of scan rate (plotted for peak current of first electron reduction). Peak current was proportional to square root of scan rate, indicating that this process was a diffusion-controlled process which was expressed by the Randles–Sevcik equation [11]. It has been suggested that reducibility (oxidizing ability) of HPAs can be determined by the highest potential in the cyclovoltammograms [14]. Therefore, first highest reduction potential was taken as representative reduction potential to estimate reducibility of HPAs in this work. First electron reduction potential increased in the order of $H_6CoW_{12}O_{40}$ (−0.554 V) < $H_5BW_{12}O_{40}$ (−0.511 V) < $H_4SiW_{12}O_{40}$ (−0.227 V) < $H_3PW_{12}O_{40}$ (−0.020 V). Fig. 3 shows the correlation between first electron reduction potential and overall negative charge of heteropolyanion in a series of $H_nXW_{12}O_{40}$ ($X = Co^{2+}$, B^{3+}, Si^{4+}, and P^{5+}) HPA catalysts. The correlation shows that first electron reduction potential decreased with increasing overall negative charge of heteropolyanion. Among HPA catalysts tested, $H_3PW_{12}O_{40}$ catalyst with the smallest overall negative charge showed the highest reduction potential.

It is well known that added electrons to α-Keggin heteropolytungstates were delocalized over tungsten sites. This indicates that each redox transition during the electrochemical measurements corresponded to the electron transfer in tungsten sites, and nature of central atom would not directly but indirectly affect the reduction potential [15]. Variation of reduction potentials can be rationalized by taking into account of its enthalpy, entropy, and electronic properties. However, enthalpy and entropy terms show small variation because overall size of heteropolyanion is nearly identical regardless of the nature of central atom in a series of α-Keggin heteropolytungstates, indicating that variation in reduction potentials is mainly due to electronic properties [16]. Previous density functional theory (DFT) calculations [17,18] have reported the effect of heteroatom charge on electronic structure using a clathrate model, in which tetrahedral XO_4^{n-} units are encapsulated