Redox properties and oxidation catalysis of potassium salts of transition metal-substituted α_2-$K_8P_2W_{17}O_{61}$($M\cdot OH_2$) ($M = Mn^{II}$, Zn^{II}, Fe^{II}, Co^{II}, Cu^{II}, and Ni^{II}) Wells-Dawson heteropolyacids

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ABSTRACT

Potassium salts of transition metal-substituted α_2-$K_8P_2W_{17}O_{61}$($M\cdot OH_2$) ($M = Mn^{II}$, Zn^{II}, Fe^{II}, Co^{II}, Cu^{II}, and Ni^{II}) Wells-Dawson heteropolyacids were prepared to investigate their redox properties and oxidation catalysis. Successful formation of α_2-$K_8P_2W_{17}O_{61}$($M\cdot OH_2$) catalysts was confirmed by FT-IR, ^{31}P NMR, and ICP-AES measurements. Reduction potential and absorption edge energy of α_2-$K_8P_2W_{17}O_{61}$($M\cdot OH_2$) catalysts were determined by an electrochemical method and UV–vis spectroscopy in solution, respectively. Absorption edge energy of α_2-$K_8P_2W_{17}O_{61}$($M\cdot OH_2$) catalysts decreased with increasing reduction potential of the catalysts. It was also found that reduction potential of α_2-$K_8P_2W_{17}O_{61}$($M\cdot OH_2$) catalysts increased and absorption edge energy of the catalysts decreased with decreasing Tanaka electronegativity of substituted transition metal. Vapor-phase benzyl alcohol oxidation was also carried out as a model reaction in order to probe oxidation catalysis of α_2-$K_8P_2W_{17}O_{61}$($M\cdot OH_2$) catalysts. Yield for benzaldehyde increased with increasing reduction potential and with decreasing absorption edge energy of α_2-$K_8P_2W_{17}O_{61}$($M\cdot OH_2$) catalysts. Reduction potential and absorption edge energy of α_2-$K_8P_2W_{17}O_{61}$($M\cdot OH_2$) catalysts could be utilized as a probe of oxidation catalysis of the catalysts.

1. Introduction

Heteropolyacids (HPAs) are early transition metal-oxygen anion clusters that have been widely employed as catalysts for various homogeneous and heterogeneous reactions [1,2]. HPAs exhibit wide range of molecular sizes, compositions, and structures. One of the great advantages of HPAs is that their catalytic properties can be easily tuned by changing the constituent metal components such as counter-cation, central heteroatom, or framework polyatom [3]. For example, vanadium-substituted HPAs showed a better catalytic activity than non-substituted HPAs in several oxidation reactions [4,5]. Various elements including metals, semimetals, or even non-metals can be incorporated into the HPA framework. Therefore, a number of HPAs and their salts can be designed as a promising catalyst for selective oxidation reactions [3,6].

Due to the importance of comprehensive understanding about redox properties in designing HPA as an oxidation catalyst, systematic researches on the redox properties and oxidation catalysis of various HPA catalysts have been conducted [7,8]. There are several theoretical and experimental methods to determine the reduction potential of HPA catalysts, including quantum chemical

molecular orbital study [9], scanning tunneling microscopy investigation [10,11], and electrochemical measurement [12]. Among these measurements, the most conventional method to determine the reduction potential (oxidizing power) of HPA catalysts is an electrochemical measurement in solution. However, reduction potential of HPA catalysts determined by an electrochemical measurement in solution is highly sensitive to experimental conditions such as pH, concentration of electrolyte, and identity of electrodes. Therefore, reduction potentials measured in consistent experimental conditions only give comparable results. Another promising technique to probe reduction potential of HPA catalysts is to measure the absorption edge energies by UV–vis spectroscopy [13]. Absorption edge energy of HPA catalysts reflects the energy required for electron transfer from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) [14]. It has been reported that energy gap between the HOMO and the LUMO has a direct relationship with reduction potential (oxidizing power) of the HPA catalysts [9,15].

Among various structural classes of HPAs, Wells-Dawson HPAs has attracted recent attention as a promising catalyst due to their excellent catalytic activity in several oxidation reactions [2,16]. Nonetheless, previous researches on the redox properties and oxidation catalysis of HPA catalysts have been focused on Keggin HPAs [14,17–19], and much progress has not been made on Wells-Dawson HPAs. Therefore, systematic investigation on the redox

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properties and oxidation catalysis of Wells-Dawson HPAs would be of great interest.

In this work, potassium salts of transition metal-substituted α_2-$K_8P_2W_{17}O_{61}(M\cdot OH_2)$ ($M = Mn^{II}$, Zn^{II}, Fe^{II}, Co^{II}, Cu^{II}, and Ni^{II}) Wells-Dawson heteropolyacids were prepared in order to investigate their redox properties and oxidation catalysis. Reduction potentials and absorption edge energies of α_2-$K_8P_2W_{17}O_{61}(M\cdot OH_2)$ catalysts were determined by an electrochemical method and UV–vis spectroscopy in solution, respectively. Vapor-phase benzyl alcohol oxidation was carried out as a model reaction to probe oxidation catalysis of α_2-$K_8P_2W_{17}O_{61}(M\cdot OH_2)$ catalysts. Correlations between redox properties (reduction potential and absorption edge energy) and catalytic oxidation activity of α_2-$K_8P_2W_{17}O_{61}(M\cdot OH_2)$ catalysts were then established.

2. Experimental

2.1. Preparation and characterization of catalysts

α_2-$K_8P_2W_{17}O_{61}(M\cdot OH_2)$ ($M = Mn^{II}$, Zn^{II}, Fe^{II}, Co^{II}, Cu^{II}, and Ni^{II}) catalysts were prepared by a modified method described in the literatures [20,21]. For example, α_2-$K_8P_2W_{17}O_{61}(Mn^{II}\cdot OH_2)$ catalyst was prepared as follows via mono-lacunary heteropolyanion. α-$K_6P_2W_{18}O_{62}\cdot 14H_2O$ was prepared according to the method in the literature [22]. In order to prepare α_2-$K_{10}P_2W_{17}O_{61}$ mono-lacunary heteropolyanion, 70 g of α-$K_6P_2W_{18}O_{62}\cdot 14H_2O$ was dissolved in 250 ml of deionized water. 1 M aqueous solution of potassium hydrogen carbonate ($KHCO_3$) was added dropwise into α-$K_6P_2W_{18}O_{62}$ solution, and pH of the solution was maintained at 7.5. After stirring the solution for 30 min, white precipitate was obtained. The crude white crystal was then recrystallized from water. The recrystallized white crystal was successively washed with deionized water, ethanol, and diethyl ether. The resulting solid was dried at 50 °C overnight to obtain α_2-$K_{10}P_2W_{17}O_{61}\cdot 15H_2O$.

In order to incorporate Mn^{II} into mono-lacunary heteropolyanion framework, 10 g of α_2-$K_{10}P_2W_{17}O_{61}\cdot 15H_2O$ was dissolved in 60 ml of boiling water, and 0.434 g of manganese chloride tetrahydrate ($MnCl_2\cdot 4H_2O$) was separately dissolved in 20 ml of boiling water. These two solutions were then mixed with vigorous stirring. After stirring the solution for 1 h, 15 g of potassium chloride (KCl) was added into the mixed solution. Orange-colored precipitate was then formed. The crude crystal was recrystallized from water. The resulting crystal was washed with deionized water, and it was dried in atmosphere overnight to obtain final catalyst (α_2-$K_8P_2W_{17}O_{61}(Mn^{II}\cdot OH_2)$). All the α_2-$K_8P_2W_{17}O_{61}(M\cdot OH_2)$ ($M = Mn^{II}$, Zn^{II}, Fe^{II}, Co^{II}, Cu^{II}, and Ni^{II}) catalysts were thermally treated at 350 °C for 2 h in a stream of nitrogen prior to characterization and catalytic reaction. In this work, potassium salts of α_2-$K_8P_2W_{17}O_{61}(M\cdot OH_2)$ Wells-Dawson HPA catalysts with different transition metal ($M = Mn^{II}$, Zn^{II}, Fe^{II}, Co^{II}, Cu^{II}, and Ni^{II}) were denoted as WD-Mn^{II}, WD-Zn^{II}, WD-Fe^{II}, WD-Co^{II}, WD-Cu^{II}, and WD-Ni^{II}, respectively.

Successful formation of α_2-$K_8P_2W_{17}O_{61}(M\cdot OH_2)$ catalysts was confirmed by FT-IR (Nicolet, Nicolet 6700), ^{31}P NMR (Bruker, AVANCE 600), and ICP-AES (Shimadzu, ICPS-1000IV) analyses. ^{31}P NMR measurements were performed using D_2O as a solvent and 85% aqueous H_3PO_4 as an external reference.

2.2. Electrochemical and UV–vis spectroscopy measurements

Reduction potentials of α_2-$K_8P_2W_{17}O_{61}(M\cdot OH_2)$ ($M = Mn^{II}$, Zn^{II}, Fe^{II}, Co^{II}, Cu^{II}, and Ni^{II}) catalysts were measured by an electrochemical method in solution. 1 mM sample solution was prepared by dissolving each catalyst in 0.5 M Na_2SO_4 solution. The sample solution was then purged with nitrogen (50 ml/min) for 3 min, and it was then maintained for 1 min prior to the cyclovoltammetry measurement. Electrochemical measurement was performed using a Potentiostat/Galvanostat (Eco Chemie, Autolab 302N) instrument with a computer-controlled cyclovoltammetry system. The working electrode was Pt disk with an electrode diameter of 0.2 mm. A platinum rod and Ag/AgCl (NaCl saturated) were used as a counter electrode and a reference electrode, respectively. The cyclovoltagram was obtained at a scan rate of 10 mV/s.

UV–vis spectroscopy of α_2-$K_8P_2W_{17}O_{61}(M\cdot OH_2)$ ($M = Mn^{II}$, Zn^{II}, Fe^{II}, Co^{II}, Cu^{II}, and Ni^{II}) catalysts was performed at room temperature using a Lambda-35 spectrometer (Perkin-Elmer). 1 mM aqueous solution of each catalyst was used for UV–vis spectroscopy measurement. The Kubelka–Munk function ($F(R_\infty)$) [23] was used to convert reflectance measurement into equivalent absorption spectrum using the reflectance of $BaSO_4$ as a reference. Absorption edge energy was directly obtained from the $[F(R_\infty)h\nu]^{1/2}$ curve.

2.3. Oxidation of benzyl alcohol

Catalytic oxidation of benzyl alcohol over α_2-$K_8P_2W_{17}O_{61}(M\cdot OH_2)$ ($M = Mn^{II}$, Zn^{II}, Fe^{II}, Co^{II}, Cu^{II}, and Ni^{II}) catalysts was carried out in a continuous-flow quartz reactor under atmospheric pressure. Each catalyst (0.5 g) charged into a quartz reactor was pretreated with a mixed stream of nitrogen (10 ml/min) and oxygen (10 ml/min) at 350 °C for 1 h. Benzyl alcohol (1.45×10^{-3} mol/h) was sufficiently vaporized by passing through a pre-heating zone and was continuously fed into the reactor together with a mixed stream of oxygen (10 ml/min) and nitrogen (10 ml/min). The reaction was carried out at 330 °C for 6 h. During the reaction, reaction products were periodically sampled and analyzed with a gas chromatograph (HP 5890II, FID) equipped with a capillary column (Supelco VOCOL™ column, 60 m × 0.25 mm). Conversion, selectivity, and yield were calculated on the basis of mole balance.
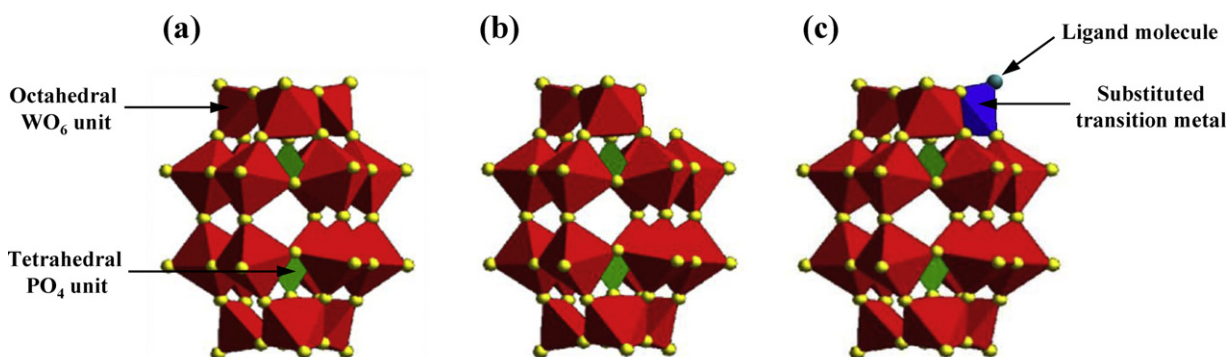

Fig. 1. Molecular structures of (a) α-$P_2W_{18}O_{62}{}^{6-}$, (b) α_2-$P_2W_{17}O_{61}{}^{10-}$, and (c) $P_2W_{17}O_{61}(M\cdot L)^{8-}$ (L = ligand molecule) heteropolyanions.