



Redox properties and oxidation catalysis of potassium salts of transition metal-substituted α_2 -K₈P₂W₁₇O₆₁(M·OH₂) (M = Mn^{II}, Zn^{II}, Fe^{II}, Co^{II}, Cu^{II}, and Ni^{II}) Wells-Dawson heteropolyacids

Jung Ho Choi, Jeong Kwon Kim, Sunyoung Park, Ji Hwan Song, In Kyu Song*

School of Chemical and Biological Engineering, Institute of Chemical Processes, Seoul National University, Shinlim-dong, Kwanak-ku, Seoul 151-744, South Korea

ARTICLE INFO

Article history:

Received 28 December 2011

Received in revised form 8 March 2012

Accepted 26 March 2012

Available online 3 April 2012

Keywords:

Heteropolyacid

Transition metal

Reduction potential

Absorption edge energy

Oxidation catalysis

ABSTRACT

Potassium salts of transition metal-substituted α_2 -K₈P₂W₁₇O₆₁(M·OH₂) (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 -K₈P₂W₁₇O₆₁(M·OH₂) catalysts was confirmed by FT-IR, ³¹P NMR, and ICP-AES measurements. Reduction potential and absorption edge energy of α_2 -K₈P₂W₁₇O₆₁(M·OH₂) catalysts were determined by an electrochemical method and UV–vis spectroscopy in solution, respectively. Absorption edge energy of α_2 -K₈P₂W₁₇O₆₁(M·OH₂) catalysts decreased with increasing reduction potential of the catalysts. It was also found that reduction potential of α_2 -K₈P₂W₁₇O₆₁(M·OH₂) 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 -K₈P₂W₁₇O₆₁(M·OH₂) catalysts. Yield for benzaldehyde increased with increasing reduction potential and with decreasing absorption edge energy of α_2 -K₈P₂W₁₇O₆₁(M·OH₂) catalysts. Reduction potential and absorption edge energy of α_2 -K₈P₂W₁₇O₆₁(M·OH₂) catalysts could be utilized as a probe of oxidation catalysis of the catalysts.

© 2012 Elsevier B.V. All rights reserved.

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

* Corresponding author. Tel.: +82 2 880 9227; fax: +82 2 889 7415.

E-mail address: inksong@snu.ac.kr (I.K. Song).