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Short communication

Effect of metal-substitution on the redox behaviors of mono-transition metal-substituted Wells–Dawson tungstoarsenates

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ABSTRACT

Mono-transition metal (Mo, V, and Nb)-substituted Wells–Dawson tungstoarsenates were investigated to elucidate the effect of metal-substitution on their redox behaviors. In the electrochemical analysis, an additional redox transition was observed for molybdenum- and vanadium-substituted tungstoarsenates, while a negatively shifted redox transition was observed for niobium-substituted tungstoarsenate. First electron reduction potential of the catalysts showed the consistent trend with UV–visible absorption edge energy of the catalysts. Oxidative dehydrogenation of benzylamine to dibenzylimine was carried out as a model reaction to probe oxidation catalysis. Yield for dibenzylimine increased with increasing first electron reduction potential and with decreasing UV–visible absorption edge energy.

1. Introduction

Heteropolyacids (HPAs) are polymeric metal–oxygen clusters that exhibit various physicochemical properties. HPAs are structurally well-defined than any other metal oxides and their physicochemical properties can be easily tuned by changing the constituent elements. This means that the design of HPAs is possible at molecular level to meet the need for specific catalytic applications.

HPAs are strong oxidizing agents or excellent redox catalysts because the addenda atoms in heteropolyanion frameworks are in their highest oxidation states. Thus, several structural classes of HPAs have been investigated as catalysts in the oxidation reactions and photocatalytic redox reactions [1–3]. Previous researches [4,5] on the oxidative dehydrogenation of alcohols over HPAs have suggested that the redox transition of HPAs occurs during the catalysis and the rate-determining step involves the reduction of HPAs by hydrogen and electron from the substrate. It is obvious that systematic researches on the redox nature of HPAs should be preferentially conducted before the catalytic applications. However, much progress has not been made on the redox nature of Wells–Dawson HPAs due to the structural diversity of mixed-addenda HPAs [6].

In this work, mono-transition metal (Mo, V, and Nb)-substituted Wells–Dawson tungstoarsenates were prepared to elucidate the effect of transition metal-substitution on their redox behaviors. Redox behaviors of the catalysts were examined by electrochemical analysis. UV–visible spectroscopy measurement was also conducted as a simple diagnostic for electronic structure. Gas-phase oxidative dehydrogenation of benzylamine was carried out to track the oxidation catalysis of mono-transition metal-substituted Wells–Dawson tungstoarsenates.

2. Experimental

2.1. Preparation of catalyst

α-$K_6As_2W_{18}O_{62}$, α_2-$K_6As_2W_{17}Mo_1O_{62}$, and α_2-$K_7As_2W_{17}V_1O_{62}$ were prepared as described in the previous literature [7]. α_2-$K_7As_2W_{17}Nb_1O_{62}$ was prepared by direct incorporation of niobium into mono-lacunary tungstoarsenate (α_2-$K_{10}As_2W_{17}O_{61}$). For this, 0.4 g of oxalic acid (Sigma-Aldrich) was dissolved in 30 ml of deionized water. After complete dissolution, 0.110 g of niobium chloride (Sigma-Aldrich) was added to the solution. 1.70 g of mono-lacunary tungstoarsenate, which was prepared as described in the previous work [7], was separately dissolved in 20 ml of deionized water. These two solutions were then mixed. The mixed solution was treated with hydrochloric acid (Samchun Chem.) until the pH of the solution becomes ca. 1.0 and it was refluxed for 4 h. The resulting transparent solution was cooled to room temperature. The solution was added to 300 ml of methanol (Sigma-Aldrich) and the resultant was placed at 4 °C overnight. After a few days, white precipitate was collected and dried under room temperature to obtain α_2-$K_7As_2W_{17}Nb_1O_{62}$.

Formation of Wells–Dawson heteropolyanion framework was confirmed by diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy using a Nicolet 6700 (Nicolet) spectrometer. Chemical

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compositions of the catalysts were analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis using an ICPS-1000IV (Shimadzu) instrumentation. In this work, mono-transition metal-substituted tungstoarsenates were denoted as denoted as $As_2W_{17}M_1$ (M = W, Mo, V, and Nb).

2.2. Characterization

Electrochemical analysis was conducted to examine the electrochemical redox behaviors of mono-transition metal-substituted tungstoarsenates. Cyclic voltammograms were acquired using a conventional three-electrode system (Autolab 302N, Eco Chemie). Glassy carbon with a diameter of 3.0 mm, platinum rod, and saturated calomel electrode (KCl saturated) were used as a working electrode, a counter electrode, and a reference electrode, respectively. Each tungstoarsenate was dissolved in 0.5 M sodium sulfate electrolyte to prepare the sample solution (1 mM). The sample solution was pretreated with He flow prior to electrochemical measurements. Cyclic voltammograms were obtained at a scan rate of 25, 50, 100, 150, and 200 mV/s.

UV–visible spectroscopy measurement was performed as a simple diagnostic for electronic structure of mono-transition metal-substituted tungstoarsenates. UV–visible spectra were acquired using a Lambda-35 (Perkin-Elmer) spectrometer. The sample solution (1 mM) was prepared by dissolving each tungstoarsenate in deionized water to minimize the peripheral effect of coordinated water. Kubelka–Munk function ($F(R_\infty)$) was employed to convert reflectance spectrum into equivalent absorption spectrum using $BaSO_4$ as a white standard [8]. Absorption edge energy was directly obtained from Tauc plot.

2.3. Catalytic test

Gas-phase oxidative dehydrogenation of benzylamine was carried out over mono-transition metal-substituted tungstoarsenates. 0.4 g of each catalyst was charged into the tubular quartz reactor and it was pretreated with a mixed stream of nitrogen (30 ml/min) and oxygen (10 ml/min) at 300 °C for 1 h. Benzylamine (7.2 mmol/h) was sufficiently vaporized by passing through the preheating zone and it was continuously fed into the reactor together with a mixed stream of nitrogen and oxygen. Catalytic reaction was carried out at 300 °C for 5 h. Reaction products were periodically sampled and were analyzed 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 products separation. Conversion of benzylamine and yield for each product were calculated on the basis of carbon balance.

3. Results and discussion

3.1. Formation of heteropolyanion framework

Fig. 1 shows the DRIFT spectra of mono-transition metal-substituted tungstoarsenates. Several characteristic bands attributed to asymmetric vibrations of M (metal) = O_t (terminal oxygen), As–O, and M–O–M bonds were observed in the range of 1000–700 cm^{-1}, in good agreement with the results of previous literature [7]. For all catalysts, As–O bands appeared as a weak shoulder due to the intense and broad M–O–M bands. All the mono-transition metal-substituted tungstoarsenates exhibited slightly shifted bands compared to non-substituted one ($As_2W_{17}W_1$). Chemical compositions of arsenic, tungsten, and substituted-transition metal in the catalysts determined by ICP-AES analyses were in good agreement with the designed values (not shown here), supporting the successful formation of mono-transition metal-substituted tungstoarsenates. In this work, mono-transition metal-substituted tungstoarsenates were prepared by direct incorporation of transition metal into mono-lacunary tungstoarsenate (α_2-$K_{10}As_2W_{17}O_{61}^{10-}$), which was derived from α-$K_6As_2W_{18}O_{62}$ via selective removal of WO_6 unit of cap site. Thus, transition metal could be selectively incorporated in the cap site of Wells–Dawson tungstoarsenate framework, providing the uniform structure to examine the effect of transition metal-substitution (in the cap site) on the redox behavior.

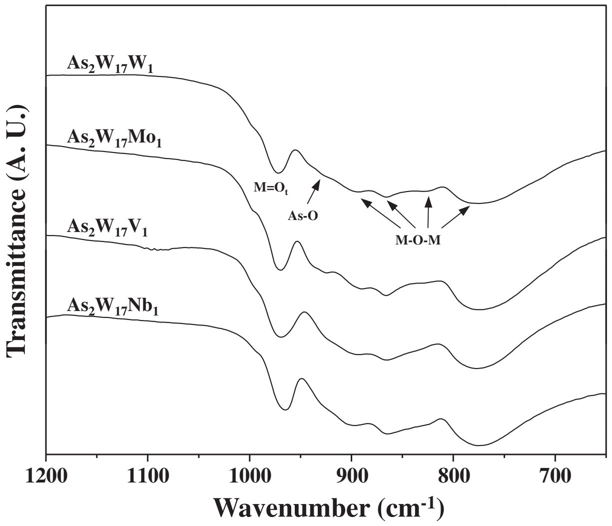

Fig. 1. DRIFT spectra of mono-transition metal-substituted tungstoarsenates.

3.2. Cyclic voltammetry

Electrochemical analysis was conducted to examine the electrochemical redox behaviors of mono-transition metal-substituted tungstoarsenates. Fig. 2 shows the cyclic voltammograms of mono-transition metal-substituted tungstoarsenates obtained at a scan rate of 50 mV/s. All the catalysts exhibited reversible and stepwise redox transitions. Overall shapes of cyclic voltammograms were nearly unchanged even after several cycles of measurements, indicating that the catalysts were hydrolytically stable during the electrochemical measurements. Each peak current monotonically increased against the square root of scan rate, indicating that redox transitions shown in Fig. 2 were the diffusion-controlled reversible process that could be expressed by Randles–Sevcik equation [9].

$As_2W_{17}W_1$ exhibited four stepwise tungsten-centered redox couples. However, significantly different redox transitions were observed for mono-transition metal-substituted tungstoarsenates. For molybdenum- and vanadium-substituted tungstoarsenates, they exhibited an additional molybdenum- or vanadium-centered redox couple at higher potential region [10,11]. This indicates that molybdenum and vanadium centers in the tungstoarsenate frameworks are electrochemically more accessible and easier to be reduced than tungsten center. However, niobium-substituted tungstoarsenate did not exhibit any additional redox couple but showed a negatively-shifted redox couple compared to non-substituted one ($As_2W_{17}W_1$). In this work, first electron reduction potential was taken as a representative parameter for reducibility [12]. First electron reduction potential increased in the order of $As_2W_{17}Nb_1$ (−0.162 V) < $As_2W_{17}W_1$ (+0.049 V) < $As_2W_{17}Mo_1$ (+0.243 V) < $As_2W_{17}V_1$ (+0.378 V), indicating that vanadium center was more effective to enhance the reducibility of tungstoarsenate framework than the other metal centers.

3.3. UV–visible spectroscopy

Previous research [13] has suggested that energy state and composition of the lowest unoccupied orbital (LUMO) play important roles in determining the redox behaviors of heteropolyanions. It is obvious