

Short communication

# UV–visible absorption edge energy of heteropolyacids (HPAs) as a probe of catalytic performance of HPAs in the oxidative dehydrogenation of isobutyric acid

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## Abstract

UV–visible spectroscopy studies of heteropolyacid (HPA) catalysts in solid were carried out with an aim of utilizing absorption edge energies as a probe of catalytic oxidation performance of the HPA catalysts. The absorption edge energies were correlated with the catalytic performance of HPA catalysts in the oxidative dehydrogenation of isobutyric acid. The correlation between catalytic oxidation performance and absorption edge energies of HPA catalysts demonstrated that the absorption edge energies could be utilized as a correlation parameter for the reduction potentials (oxidizing powers) of the HPA catalysts, and furthermore, as a probe of catalytic oxidation performance of the HPA catalysts.  
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**Keywords:** Heteropolyacid; UV–visible spectroscopy; Absorption edge energy; Isobutyric acid; Oxidation

## 1. Introduction

Heteropolyacids (HPAs) have been widely investigated as homogeneous and heterogeneous oxidation catalysts [1–5]. Therefore, fundamental understanding of the reduction potential (oxidizing power) of HPA catalysts is very important for the rational design of HPA catalysts for selective oxidation reactions. To determine the reduction potential (oxidizing power) of HPA catalysts, several theoretical and experimental techniques have been employed. Typical examples include quantum chemical molecular orbital calculations [6,7] and electrochemical measurements in solution [8–10]. Scanning tunneling microscopy (STM) is also proven to be a useful instrumental technique to track the reduction potential of the HPA catalysts [11–14].

Another promising method to probe the reduction potential of HPA catalysts is to determine the absorption edge energy by UV–visible spectroscopy measurements in solution [15] or in solid [16,17]. It was revealed that absorption edge energies

of HPA catalysts determined from UV–visible spectra in solution or in solid were closely related to the reduction potentials (oxidizing powers) of the HPA catalysts; the smaller absorption edge energies of HPA catalysts corresponded to the higher reduction potentials of the HPA catalysts [15–17]. It was also demonstrated that absorption edge energy of an HPA catalyst in solid was greatly affected by the number of crystalline water molecules and that any comparison of reduction potential of solid HPA catalysts by UV–visible absorption edge energy should be made under consistent treatment conditions [17].

Absorption edge energy in the UV–visible spectrum of an HPA catalyst measures the energy required for electron transfer from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) [18]. The band gap energy between the HOMO and the LUMO of an HPA catalyst reflects the reduction potential of the HPA catalyst; the smaller band gap energy corresponds to the higher reduction potential of the HPA catalyst [7,19]. Therefore, it is expected that absorption edge energy of HPA catalyst measured by UV–visible spectroscopy reflects the reduction potential (oxidizing power) of HPA catalyst, and in turn, may track the catalytic oxidation performance of the HPA catalyst.

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In this work, absorption edge energies of selected HPA catalysts, which were thermally treated at 330 °C, were measured by UV–visible spectroscopy. The absorption edge energies were then correlated with the catalytic performance of HPA catalysts in the oxidative dehydrogenation of isobutyric acid performed at 330 °C, with an aim of utilizing absorption edge energies as a correlating parameter for the reduction potentials of the HPA catalysts. It is known that the oxidative dehydrogenation of isobutyric acid into methacrylic acid is a typical bulk-type reaction; the reaction mainly occurs in the bulk phase of HPA catalysts [1,4].

## 2. Experimental

Commercially available  $\text{H}_3\text{PMo}_{12-x}\text{W}_x\text{O}_{40}$  ( $x = 0, 3, 6, 9, 11, 12$ ) and  $\text{H}_{3+x}\text{PMo}_{12-x}\text{V}_x\text{O}_{40}$  ( $x = 0, 1, 2$ ) were purchased from Sigma–Aldrich Chem. Co. and Nippon Inorganic Colors and Chem. Cation-exchanged HPA samples,  $\text{Zn}_{3/2}\text{PMo}_{12}\text{O}_{40}$  and  $\text{Bi}_1\text{PMo}_{12}\text{O}_{40}$ , were prepared according to the published method [20]. Prior to the UV–visible spectroscopy measurements, all HPA samples were thermally treated at 330 °C for 1 h in order to minimize the effect of crystalline water molecules. UV–visible spectra of solid HPA catalysts were obtained with a Lambda-35 spectrometer (Perkin-Elmer). The Kubelka–Munk function ( $F(R_\infty)$ ) was used to convert reflectance measurements into equivalent absorption spectra using the reflectance of  $\text{BaSO}_4$  as a reference [21], and to obtain absorption edge energies of HPA samples directly from the  $[F(R_\infty)h\nu]^{1/2}$  curves.

Vapor-phase oxidative dehydrogenation of isobutyric acid into methacrylic acid was carried out in a continuous flow fixed-bed reactor at an atmospheric pressure. Each catalyst (0.5 g) was charged into a tubular quartz reactor, and the catalyst was pretreated with a mixed stream of nitrogen (10 ml/min) and oxygen (10 ml/min) at 350 °C for 1 h. The reaction temperature was maintained at 330 °C. Isobutyric acid ( $1.6 \times 10^{-3}$  mol/h) was sufficiently vaporized by passing a pre-heating zone and fed into the reactor continuously together with oxygen, water vapor and nitrogen carrier. Feed composition (mole ratio) was isobutyric acid (0.14):oxygen (1.0):water vapor (1.48):nitrogen (1.0). The catalytic reaction was carried out for 5 h. The products were periodically sampled, and analyzed with GC (HP 5890 II, FID).

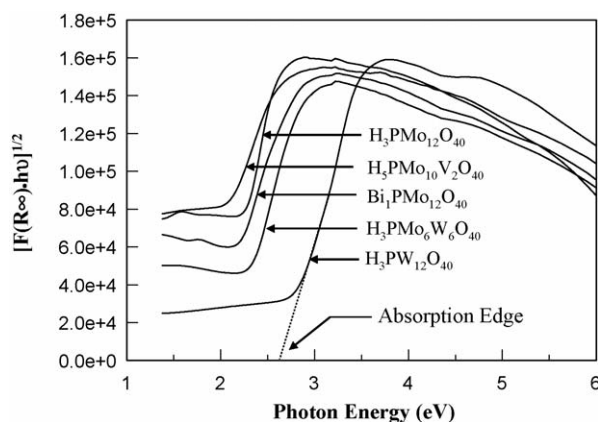


Fig. 1.  $[F(R_\infty)h\nu]^{1/2}$  curves of selected HPA catalysts treated at 330 °C, showing different absorption edge energies.

Conversion of isobutyric acid, selectivity for methacrylic acid and yield for methacrylic acid were calculated on the basis of carbon balance.

## 3. Results and discussion

Fig. 1 shows the  $[F(R_\infty)h\nu]^{1/2}$  curves of selected HPA catalysts treated at 330 °C. Absorption edge energies were determined by the intercept of a linear fit to the absorption edge. Fig. 1 clearly demonstrates that different absorption edge energies can be distinguished between the HPA catalysts. Absorption edge energies of solid HPA catalysts treated at 330 °C are listed in Table 1.

It was previously demonstrated that the absorption edge energy of an HPA catalyst measured in solid was consistently smaller than that measured in solution [15,17]. In aqueous solutions, the secondary structures of HPAs are dissociated and the heteropolyanions are solvated by water molecules. Therefore, UV–visible spectra of HPAs in solution give directly comparable result [15]. On the other hand, UV–visible spectra of solid HPA samples are greatly affected by the number crystalline water molecule, i.e., by the thermal treatment condition [17]. Therefore, any comparison of UV–visible spectra of solid HPA catalysts should be made under the consistent treatment

Table 1  
Absorption edge energy and catalytic performance of HPA catalyst

HPA	Absorption edge energy in solid (eV) <sup>a</sup>	Conversion of isobutyric acid (%) <sup>b</sup>	Selectivity for methacrylic acid (%) <sup>b</sup>	Yield for methacrylic acid (%) <sup>b</sup>
$\text{H}_3\text{PMo}_{12}\text{O}_{40}$	1.980	65.4	46.0	30.0
$\text{H}_3\text{PW}_{12}\text{O}_{40}$	2.680	17.2	40.6	7.0
$\text{H}_3\text{PMo}_9\text{W}_3\text{O}_{40}$	2.000	60.7	45.3	27.5
$\text{H}_3\text{PMo}_6\text{W}_6\text{O}_{40}$	2.103	46.5	45.0	20.9
$\text{H}_3\text{PMo}_3\text{W}_9\text{O}_{40}$	2.136	32.1	44.3	14.2
$\text{H}_3\text{PMo}_1\text{W}_{11}\text{O}_{40}$	2.393	21.1	42.5	9.0
$\text{H}_4\text{PMo}_{11}\text{V}_1\text{O}_{40}$	1.857	85.8	50.6	43.3
$\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$	1.446	88.0	45.7	40.2
$\text{Zn}_{3/2}\text{PMo}_{12}\text{O}_{40}$	1.930	68.2	45.7	31.2
$\text{Bi}_1\text{PMo}_{12}\text{O}_{40}$	1.780	86.4	48.1	41.6

<sup>a</sup> HPA catalysts were thermally treated at 330 °C for UV–visible spectroscopy measurements.

<sup>b</sup> Vapor-phase oxidative dehydrogenation of isobutyric acid was carried out at 330 °C.

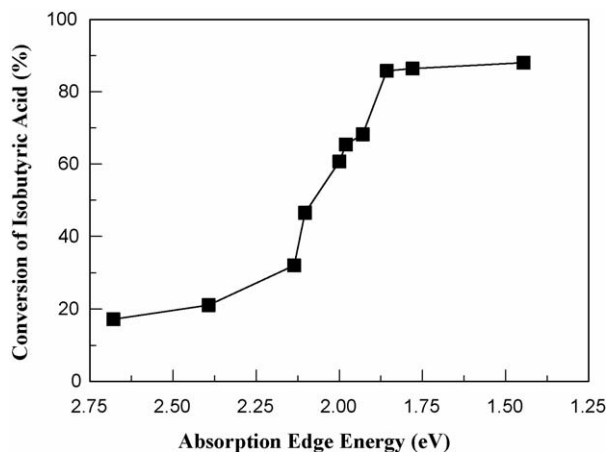


Fig. 2. Correlation between isobutyric acid conversions and absorption edge energies.

conditions. In the solid state HPAs, it was previously observed that more reducible HPAs that are stronger oxidizing agents exhibited smaller absorption edge energies [17]. This suggests that the absorption edge energies measured in solid can be utilized as a correlation parameter for the reduction potential of HPA catalysts.

In order to verify that the absorption edge energies of HPA catalysts can serve as a probe of catalytic oxidation performance of HPAs, vapor-phase oxidative dehydrogenation of isobutyric acid into methacrylic acid was carried out at 330 °C, the same temperature employed for HPA treatment for UV–visible spectroscopy measurements. The catalytic performance data obtained after 5 h-reaction are listed in Table 1. Fig. 2 shows the correlation between isobutyric acid conversions and absorption edge energies. The correlation clearly demonstrates that isobutyric acid conversions were increased with decreasing absorption edge energies (with increasing reduction potentials) of the HPA catalysts. This implies that absorption edge energies measured by UV–visible spectroscopy can serve as a correlation parameter or as an alternative parameter for the reduction potentials (oxidizing powers) of the HPA catalysts.

More comprehensive correlations between catalytic oxidation performance and absorption edge energies are shown in Fig. 3. Fig. 3 shows the correlations between methacrylic acid yields and absorption edge energies, and between methacrylic acid selectivities and absorption edge energies. In this reaction, acetone, propylene, CO and CO<sub>2</sub> were mainly produced as by-products. What is noticeable is that yields and selectivities for methacrylic acid showed volcano curves with respect to the absorption edge energies. The maximum yield and selectivity for methacrylic acid were observed at the absorption edge energy of 1.86–1.85 eV. This indicates that an HPA catalyst should have moderate oxidizing power (reduction potential) for the maximum yield of methacrylic acid under these reaction conditions. This example clearly demonstrates that absorption edge energies measured by UV–visible spectroscopy can be utilized as a probe of reduction potential (oxidizing power), and furthermore, as a probe of catalytic oxidation performance of the HPA catalysts. It also implies that HPA catalysts can be rationally designed to

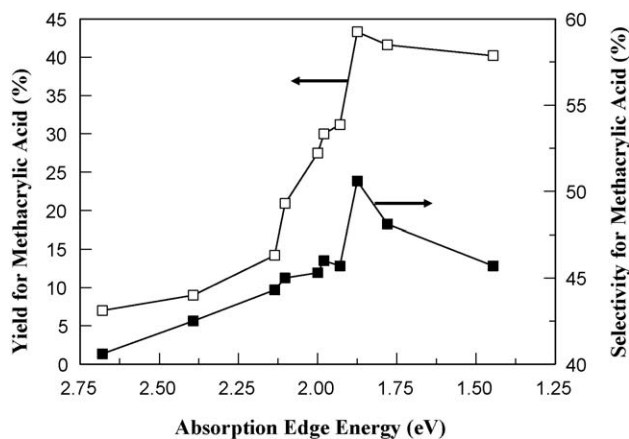


Fig. 3. Correlations between methacrylic acid yields and absorption edge energies (open symbols), and between methacrylic acid selectivities and absorption edge energies (closed symbols).

have a certain level of oxidizing power to meet the need for a desired selective oxidation reaction, on the basis of absorption edge energies measured by UV–visible spectroscopy.

#### 4. Conclusions

The correlations between catalytic oxidation performance (oxidative dehydrogenation of isobutyric acid) and absorption edge energies of HPA catalysts in solid demonstrated that conversions of isobutyric acid were increased with decreasing absorption edge energies (with increasing reduction potentials) of the HPA catalysts, while yields and selectivities for methacrylic acid showed volcano curves with respect to the absorption edge energies. The absorption edge energies of HPA catalysts in solid could be utilized as a correlation parameter for the reduction potentials (oxidizing powers) of the HPA catalysts, and furthermore, as a probe of catalytic oxidation performance of the HPA catalysts. It is concluded that HPA catalysts can be rationally designed for a desired selective oxidation reaction on the basis of absorption edge energies measured by UV–visible spectroscopy.

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