

## Reduction potentials of heteropolyacid catalysts probed by scanning tunneling microscopy and UV-visible spectroscopy

Min Hye Youn, Dong Ryul Park, Ji Chul Jung, Heesoo Kim, Mark A. Barteau\* and In Kyu Song<sup>†</sup>

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

\*Department of Chemical Engineering, Center for Catalytic Science and Technology,  
University of Delaware, Newark, DE 19716, U.S.A.

(Received 7 June 2006 • accepted 31 July 2007)

**Abstract**—Reduction potentials of heteropolyacid (HPA) catalysts were probed by scanning tunneling microscopy (STM) and UV-visible spectroscopy. Correlations between reduction potentials and NDR (negative differential resistance) peak voltages, and between reduction potentials and absorption edge energies of HPA catalysts were established. The reduction potentials of HPA catalysts have been shown to follow similar trends to the NDR peak voltages of self-assembled HPA monolayers and the absorption edge energies of bulk HPAs. In the UV-visible spectra of HPA catalysts, lower absorption edge energies corresponded to higher reduction potentials of the HPAs.

Key words: Heteropolyacid, Scanning Tunneling Microscopy, UV-visible Spectroscopy, Reduction Potential, Oxidation Catalysis

### INTRODUCTION

Heteropolyacids (HPAs) have attracted much attention as oxidation catalysts [Pope, 1983; Kozhevnikov, 1995; Hill and Prosser-McCarthy, 1995; Okuhara et al., 1996; Lee et al., 1997]. Fundamental understanding of the reduction potential (oxidizing power) of HPA catalysts is of great importance in designing HPA catalysts for selective oxidation reactions [Song et al., 1991, 2003; Barteau et al., 2003]. Reduction potentials of HPA catalysts have been investigated by quantum chemical molecular orbital studies [Weber, 1994] or measured by electrochemical methods in solutions [Pope and Varga Jr., 1966; Altenau et al., 1975; Song and Barteau, 2004].

Another promising approach to probe the reduction potentials of HPA catalysts is to measure the NDR (negative differential resistance) peak voltages of self-assembled HPA monolayers by scanning tunneling microscopy (STM) [Kaba et al., 1996; Song and Barteau, 2002, 2004]. UV-visible spectroscopy has also proven to be a powerful instrumental technique to track the reduction potentials of HPA catalysts [Youn et al., 2005, 2006; Barteau et al., 2006]. It was revealed that absorption edge energies of HPA catalysts determined from UV-visible spectra in solution at room temperature [Barteau et al., 2006] or in the solid state at a given temperature [Youn et al., 2005, 2006] were closely related to the reduction potentials of the HPA catalysts. It was also demonstrated that the absorption edge energy of an HPA catalyst in the solid state is greatly affected by the number of crystalline water molecules and that any comparison of reduction potentials of solid HPA catalysts by UV-visible absorption edge energies should be made under consistent treatment conditions [Youn et al., 2005, 2006].

In this work, absorption edge energies of solid HPA catalysts thermally treated at 330 °C were measured by UV-visible spectroscopy.

The absorption edge energies were then correlated with the reduction potentials of HPA catalysts measured by electrochemical methods in solution, and with the NDR peak voltages of self-assembled HPA monolayers measured by STM. Comprehensive correlations between NDR peak voltages, absorption edge energies, and reduction potentials of HPA catalysts were successfully established. This work demonstrates how one can probe the reduction potentials of HPA catalysts by simple spectroscopic measurements.

### EXPERIMENTAL

Commercially available  $\text{H}_3\text{PMo}_{12-x}\text{W}_x\text{O}_{40}$  ( $x=0, 3, 6, 9, 11, 12$ ),  $\text{H}_{3+x}\text{PMo}_{12-x}\text{V}_x\text{O}_{40}$  ( $x=1, 2$ ),  $\text{H}_{3+x}\text{PW}_{12-x}\text{V}_x\text{O}_{40}$  ( $x=1, 2$ ),  $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ , and  $\text{H}_3\text{AsMo}_{12}\text{O}_{40}$  were purchased from Sigma-Aldrich Chem. Co. and Nippon Inorganic Colors and Chem. Prior to the UV-visible spectroscopy measurements, all HPA samples were thermally treated at 330 °C for 1 h in an air stream in order to remove the water of crystallization (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) at room temperature. 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 [Kubelka and Munk, 1931], and to obtain absorption edge energies of HPA samples directly from the  $[F(R_\infty) \cdot h\nu]^{1/2}$  curves.

### RESULTS AND DISCUSSION

Fig. 1 shows the UV-visible spectra of selected HPA catalysts treated at 330 °C. Different absorption edges can be distinguished between the HPA catalysts. It was previously reported that UV-visible spectra of solid HPA samples were strongly affected by the number of crystalline water molecules, i.e., by the thermal treatment conditions [Youn et al., 2005, 2006]. This means that any compari-

<sup>†</sup>To whom correspondence should be addressed.

E-mail: inksong@snu.ac.kr

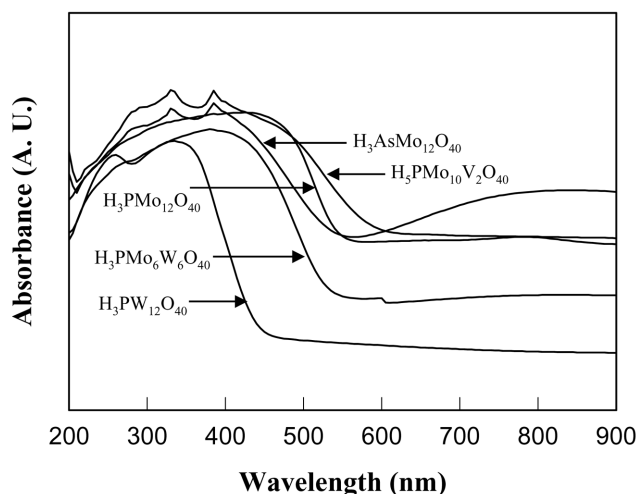


Fig. 1. UV-visible spectra of selected HPA catalysts treated at 330 °C.

son of UV-visible spectra of solid HPA catalysts should be made under the consistent thermal treatment conditions. In this work, therefore, all the HPA catalyst samples were thermally treated at 330 °C before UV-visible spectroscopy measurements were taken, in order to minimize the effect of crystalline water molecules and to obtain the UV-visible spectra under consistent conditions.

Fig. 2 shows the  $[F(R_{\infty}) \cdot h\nu]^{1/2}$  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. Different absorption edge energies were observed depending on the identity of the HPA. In the solid state, it was demonstrated that more reducible HPAs that are stronger oxidizing agents exhibited lower absorption edge energies [Youn et al., 2005]. This suggests that the absorption edge energies measured for solids can be utilized as a correlating parameter for the reduction potential of HPA catalysts.

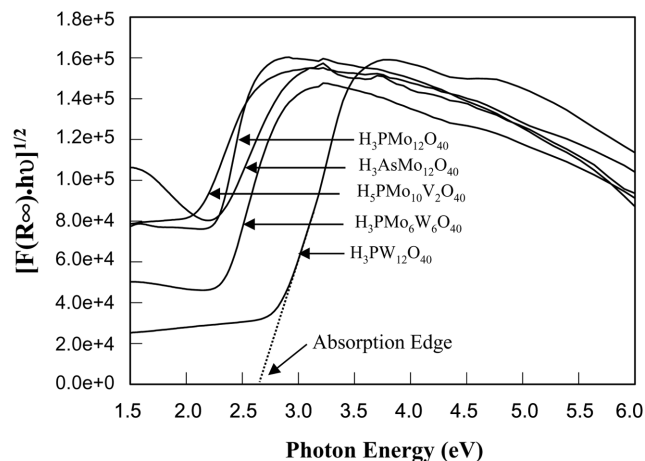


Fig. 2.  $[F(R_{\infty}) \cdot h\nu]^{1/2}$  curves of selected HPA catalysts treated at 330 °C.

Table 1 is a compilation of all the absorption edge energies of HPA catalysts measured in this work along with their reduction potentials and NDR peak voltages. Reduction potentials of HPA catalysts measured by electrochemical methods in solution were taken from the literature [Song and Barteau, 2004], as were NDR peak voltages of self-assembled HPA monolayers measured by STM. Fig. 3 shows the comprehensive correlations between NDR peak voltages, absorption edge energies, and reduction potentials of HPA catalysts, which were established from the data in Table 1. This figure shows that the NDR peak voltages and the absorption edge energies followed similar trends against the electrochemical reduction potentials. As the reduction potentials of HPAs increased, the NDR peak voltages became less negative and the absorption edge energies decreased. In other words, less negative NDR peak voltages and lower UV-visible absorption edge energies correspond to higher

Table 1. Reduction potentials, NDR peak voltages, and absorption edge energies of HPA catalysts

HPA catalyst	Reduction potential in solution (Ag/AgCl, volts) <sup>a</sup>	NDR peak voltage in solid (volts) <sup>b</sup>	Absorption edge energy in solid (eV) <sup>c</sup>	Absorption edge energy in solution (eV) <sup>d</sup>
H <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub>	−0.082	−0.95	1.98	2.65
H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	−0.491	−1.14	2.68	3.34
H <sub>4</sub> SiW <sub>12</sub> O <sub>40</sub>	−0.495	−1.19	2.68	3.36
H <sub>3</sub> AsMo <sub>12</sub> O <sub>40</sub>	0.183	−0.88	1.68	2.90
H <sub>3</sub> PMo <sub>9</sub> W <sub>3</sub> O <sub>40</sub>	−0.153	−1.01	2.00	2.73
H <sub>3</sub> PMo <sub>6</sub> W <sub>6</sub> O <sub>40</sub>	−0.197	−1.08	2.10	2.93
H <sub>3</sub> PMo <sub>3</sub> W <sub>9</sub> O <sub>40</sub>	−0.251	−1.15	2.14	N/A
H <sub>3</sub> PMo <sub>1</sub> W <sub>11</sub> O <sub>40</sub>	−0.490	−1.12	2.39	3.10
H <sub>4</sub> PW <sub>11</sub> V <sub>1</sub> O <sub>40</sub>	0.224	−0.81	1.95	2.56
H <sub>3</sub> PW <sub>10</sub> V <sub>2</sub> O <sub>40</sub>	0.050	−0.73	1.73	2.37
H <sub>4</sub> PMo <sub>11</sub> V <sub>1</sub> O <sub>40</sub>	0.261	−0.55	1.86	2.36
H <sub>3</sub> PMo <sub>10</sub> V <sub>2</sub> O <sub>40</sub>	0.233	−0.48	1.45	2.33

<sup>a</sup>Reduction potentials of HPA catalysts measured by electrochemical methods in solution were taken from the literature [Song and Barteau, 2004].

<sup>b</sup>NDR peak voltages of self-assembled HPA monolayers measured by STM were taken from the literature [Song and Barteau, 2004].

<sup>c</sup>HPA catalysts were thermally treated at 330 °C before UV-visible spectroscopy measurements were taken at room temperature.

<sup>d</sup>Absorption edge energies measured for 0.01 M aqueous HPA solution samples were taken from the literature [Barteau et al., 2006].

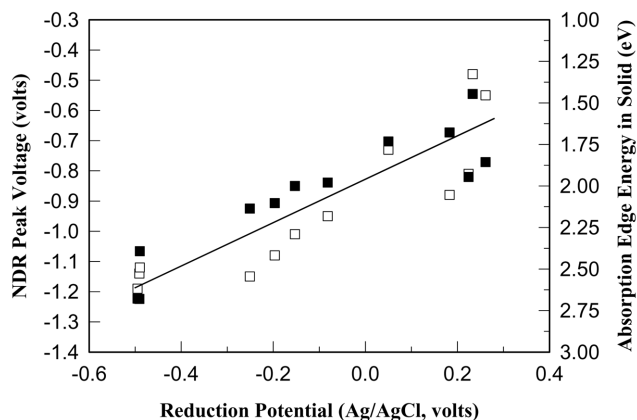


Fig. 3. NDR peak voltages and absorption edge energies plotted with respect to reduction potentials of HPA catalysts (open symbol=NDR peak voltage, closed symbol=absorption edge energy in solid).

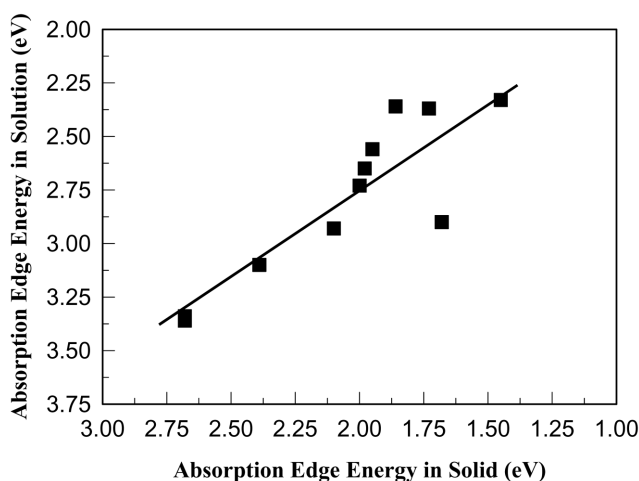


Fig. 4. Correlation between absorption edge energies of solid and solution state HPA catalysts, established from the data in Table 1.

reduction potentials of the HPA catalysts. The correlations of all three measurements, reduction potential, NDR peak voltage, and absorption edge energy, suggest that NDR peak voltage and absorption edge energy can serve as a correlating parameter or as an alternative parameter for the reduction potential of solid HPA catalyst. The above result demonstrates that HPAs as oxidation catalysts can be rationally designed by simple STM and UV-visible spectroscopy measurements.

Fig. 4 shows the correlation between absorption edge energies of solid and solution state HPA catalysts, established from the data in Table 1. Absorption edge energies measured for 0.01 M aqueous HPA solution samples were taken from the literature [Barteaue et al., 2006]. The two measures of absorption edge energies correlate well with each other, although the absorption edge energy in the solution state is consistently higher than that in the solid state. The difference in absorption edge energies between two measures reflects the effect of water molecules, as previously demonstrated [Youn et al., 2005; Barteaue et al., 2006]. What is important is that

absorption edge energies obtained from either solid HPAs or their solutions can be used as indicators of the reduction potential.

## CONCLUSIONS

Reduction potentials of HPA catalysts were probed by STM and UV-visible spectroscopy. It was observed that more reducible HPA catalysts showed NDR behavior at less negative applied voltages in the tunneling spectra, and at the same time, exhibited lower absorption edge energies in the UV-visible spectra. The NDR peak voltages (measured in solid) and the absorption edge energies (measured in either solid or solution) could be utilized as a correlating parameter for the reduction potentials of HPA catalysts. It is concluded that HPAs as oxidation catalysts can be rationally designed by simple STM and UV-visible spectroscopy measurements.

## ACKNOWLEDGMENT

This work was supported by the Korea Research Foundation Grant funded by the Korean Government (MOEHRD) (KRF-2005-041-D00204).

## REFERENCES

- Altenau, J. J., Pope, M. T., Prados, R. A. and So, H., "Model for heteropoly blues. Degree of valence trapping in vanadium(IV)- and molybdenum(V)-substituted Keggin anions," *Inorg. Chem.*, **14**, 417 (1975).
- Barteaue, M. A., Lyons, J. E. and Song, I. K., "Surface chemistry and catalysis on well-defined surfaces: Nanoscale design bases for single-site heterogeneous catalysts," *J. Catal.*, **216**, 236 (2003).
- Barteaue, K. P., Lyons, J. E., Song, I. K. and Barteaue, M. A., "UV-visible spectroscopy as a probe of heteropolyacid redox properties: Application to liquid phase oxidation," *Topics Catal.* (2006): in press.
- Hill, C. L. and Prosser-McCarthy, C. M., "Homogeneous catalysis by transition metal oxygen anion clusters," *Coord. Chem. Rev.*, **143**, 407 (1995).
- Kaba, M. S., Song, I. K. and Barteaue, M. A., "Ordered array formation and negative differential resistance behavior of cation-exchanged heteropoly acids probed by scanning tunneling microscopy," *J. Phys. Chem.*, **100**, 19577 (1996).
- Kozhevnikov, I. V., "Heteropoly acids and related compounds as catalysts for fine chemical synthesis," *Catal. Rev. -Sci. Eng.*, **37**, 311 (1995).
- Kubelka, P. and Munk, F., "Ein beitrag zur optik der farbanstriche," *Z. Tech. Phys.*, **12**, 593 (1931).
- Lee, W. Y., Song, I. K., Lee, J. K., Park, G. I. and Lim, S. S., "Design of heteropoly compound-imbedded polymer film catalysts and their application," *Korean J. Chem. Eng.*, **14**, 432 (1997).
- Okuhara, T., Mizuno, N. and Misono, M., "Catalytic chemistry of heteropoly compounds," *Adv. Catal.*, **41**, 113 (1996).
- Pope, M. T. and Varga Jr, G M., "Heteropoly blues. I. Reduction stoichiometries and reduction potentials of some 12-tungstates," *Inorg. Chem.*, **5**, 1249 (1966).
- Pope, M. T., *Heteropoly and isopoly oxometalates*, Springer-Verlag, New York (1983).
- Song, I. K., Moon, S. H. and Lee, W. Y., "Catalytic properties of ther-

- mally decomposed 12-molybdophosphoric and 10-molybdo-2-vanadophosphoric acids," *Korean J. Chem. Eng.*, **8**, 33 (1991).
- Song, I. K. and Barteau, M. A., "Bulk redox properties of heteropolyacids determined from surface properties of nanostructured heteropolyacid monolayers," *J. Mol. Catal. A*, **182-183**, 185 (2002).
- Song, I. K. and Barteau, M. A., "Scanning tunneling microscopy and tunneling spectroscopy of heteropolyacid self-assembled monolayers: Connecting nano properties to bulk properties," *Korean J. Chem. Eng.*, **19**, 567 (2002).
- Song, I. K., Kim, H. S. and Chun, M.-S., "On the reduction potential of cation-exchanged heteropolyacids (HPAs)," *Korean J. Chem. Eng.*, **20**, 844 (2003).
- Song, I. K. and Barteau, M. A., "Redox properties of Keggin-type heteropolyacid (HPA) catalysts: Effect of counter-cation, heteroatom, and polyatom substitution," *J. Mol. Catal. A*, **212**, 229 (2004).
- Song, I. K. and Barteau, M. A., "Correlation of negative differential resistance (NDR) peak voltages of nanostructured heteropolyacid (HPA) monolayers with one electron reduction potentials of HPA catalysts," *Langmuir*, **20**, 1850 (2004).
- Weber, R. S., "Molecular orbital study of C-H bond breaking during the oxidative dehydrogenation of methanol catalyzed by metal oxide surfaces," *J. Phys. Chem.*, **98**, 2999 (1994).
- Youn, M. H., Kim, H., Jung, J. C., Song, I. K., Barteau, K. P. and Barteau, M. A., "UV-visible spectroscopy studies of  $H_3PMo_{12-x}W_xO_{40}$  heteropolyacid (HPA) catalysts in solid state: Effects of water content and polyatom substitution," *J. Mol. Catal. A*, **241**, 227 (2005).
- Youn, M. H., Kim, H., Song, I. K., Barteau, K. P. and Barteau, M. A., "UV-visible spectroscopy study of solid state 12-molybdophosphoric acid catalyst," *React. Kinet. Catal. Lett.*, **87**, 85 (2006).