

Spectroscopic and electrochemical characterization of heteropoly acids for their optimized application in selective biomass oxidation to formic acid

Supplementary Information

NMR Spectroscopy

The ^{31}P - and ^{51}V -NMR spectra were recorded on a JEOL ECX-400 MHz spectrometer. The following spectra show the ^{51}V -NMR (top) and ^{31}P -NMR spectra (bottom) of the 1 mmol HPA-n solutions at pH=1.3 and 25 °C without resolution enhancement in D_2O -solution.

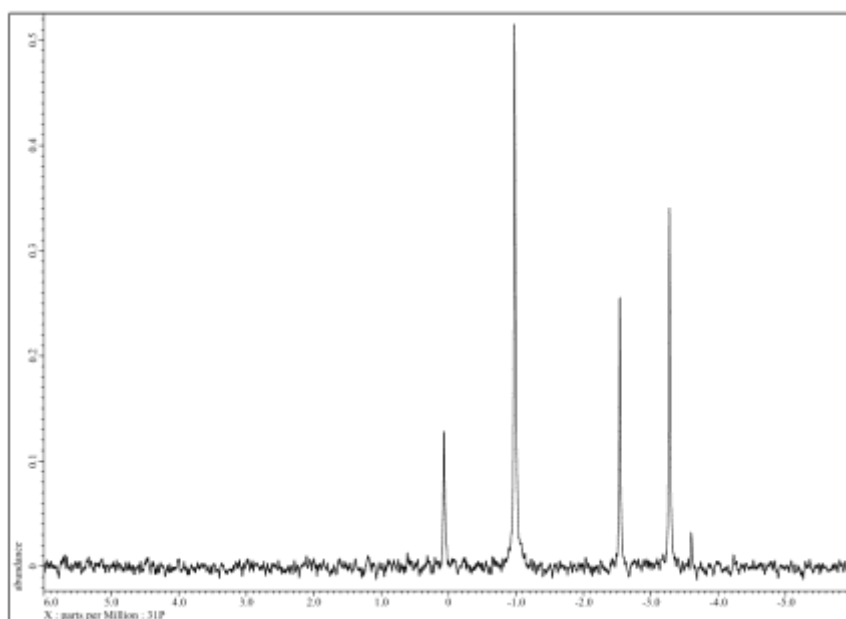


Figure 1: ^{31}P -NMR spectra of the 1 mmol HPA-0 solution at pH=1.3 and 25 °C without resolution enhancement.

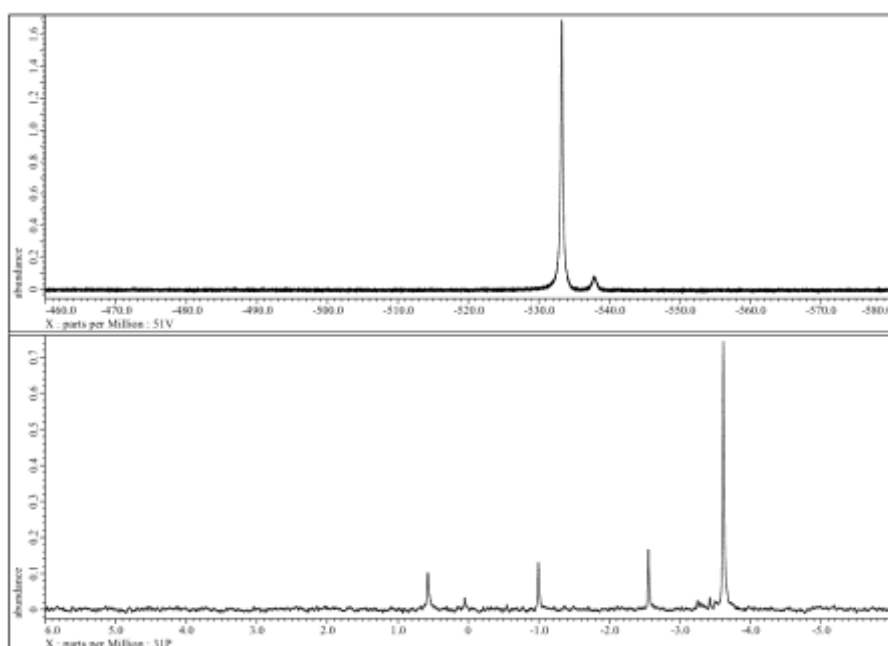


Figure 2: ^{51}V -NMR (top) and ^{31}P -NMR (bottom) spectra of the 1 mmol HPA-1 solution at pH=1.3 and 25 °C without resolution enhancement.

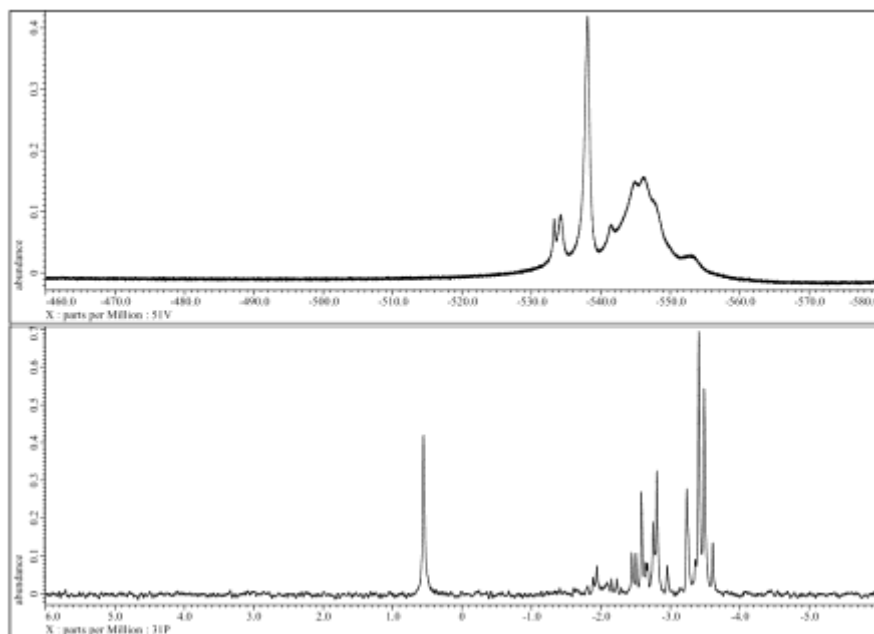


Figure 3: ^{51}V -NMR (top) and ^{31}P -NMR (bottom) spectra of the 1 mmol HPA-3 solution at pH=1.3 and 25 °C without resolution enhancement.

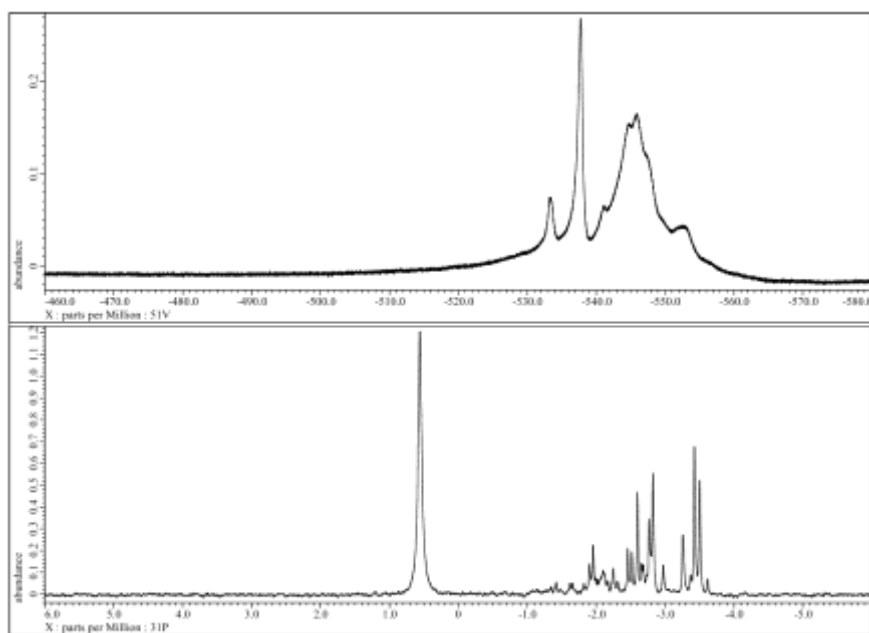


Figure 4: ^{51}V -NMR (top) and ^{31}P -NMR (bottom) spectra of the 1 mmol HPA-4 solution at pH=1.3 and 25 °C without resolution enhancement.

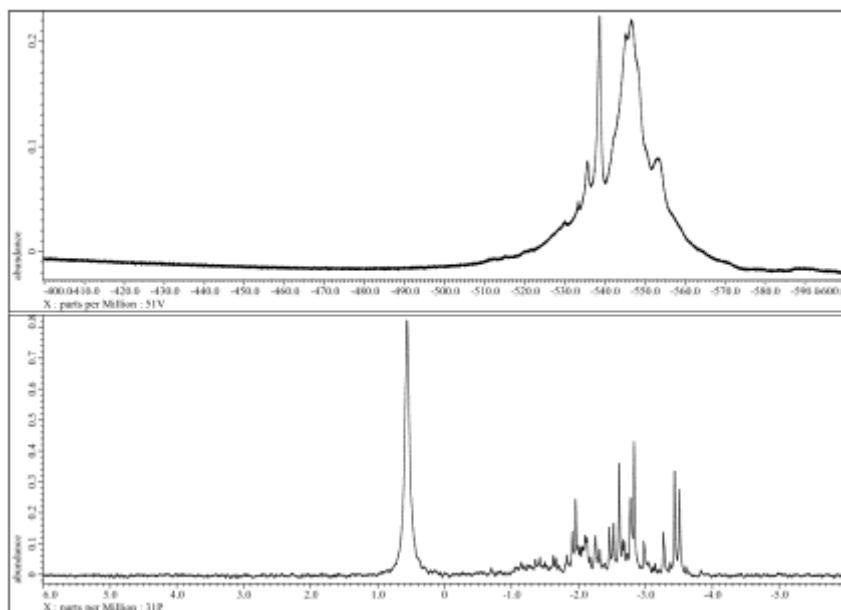


Figure 5: ^{51}V -NMR (top) and ^{31}P -NMR (bottom) spectra of the 1 mmol HPA-5 solution at pH=1.3 and 25 °C without resolution enhancement.

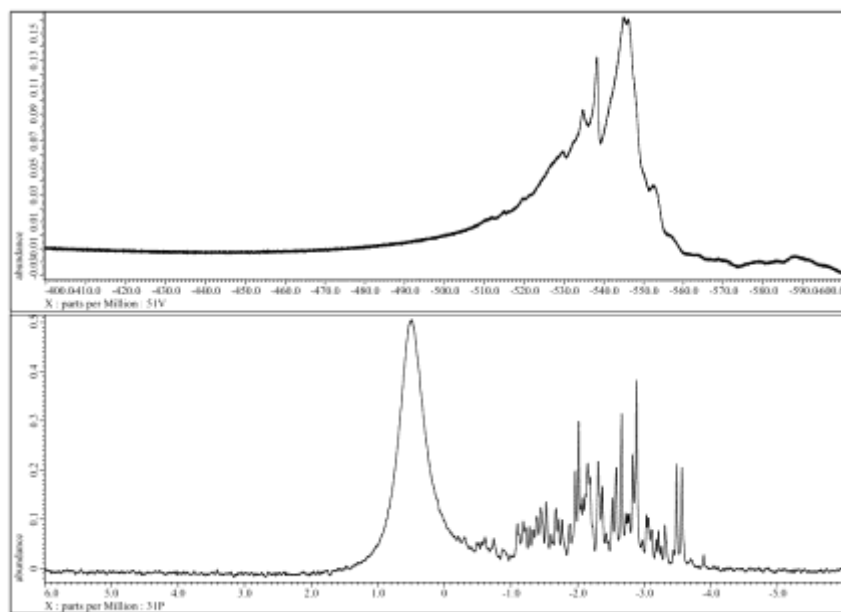


Figure 6: ^{51}V -NMR (top) and ^{31}P -NMR (bottom) spectra of the 1 mmol HPA-6 solution at pH=1.3 and 25 °C without resolution enhancement.

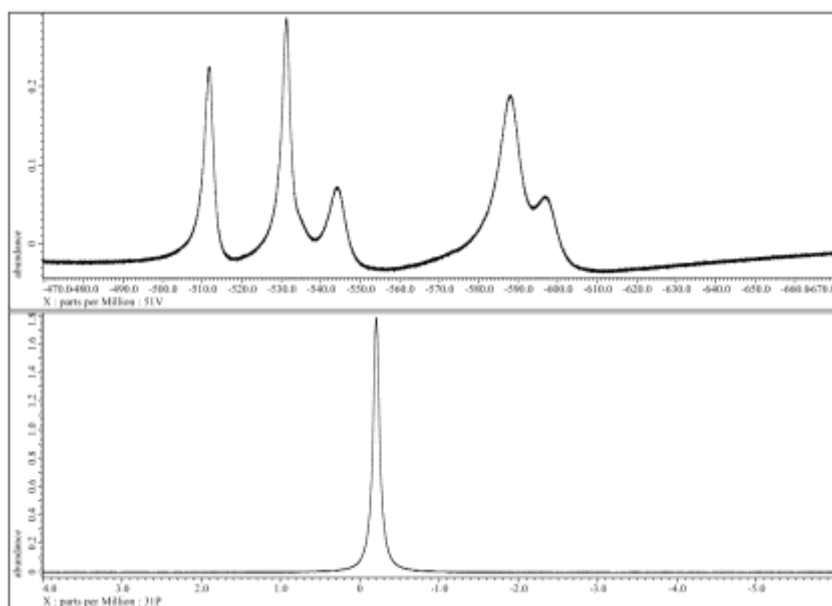


Figure 7: ^{51}V -NMR (top) and ^{31}P -NMR (bottom) spectra of the 1 mmol $\text{H}_5\text{PV}_{14}\text{O}_{42}$ solution at $\text{pH}=1.3$ and $25\text{ }^\circ\text{C}$ without resolution enhancement.

UV-Vis Spectroscopy

Steady state UV-Vis measurements were performed in a Specord S 600 UV-Vis spectrometer (Analytic Jena) at room temperature in a 10 x 10 mm quartz cuvette.

Figure 8 illustrates the UV-Vis spectrum of $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ (HPA-2) in hydrochloric aqueous solution ($\text{pH}=1.0$) in the spectral range between 200 and 500 nm. The spectrum displays ligand-to-metal charge transfer (LMCT) bands associated to the oxygen- Mo^{6+} transition in octahedral coordination around 217 nm and a broad, weak band around 330 nm which overlaps the second band of the vanadium-free species (HPA-0).

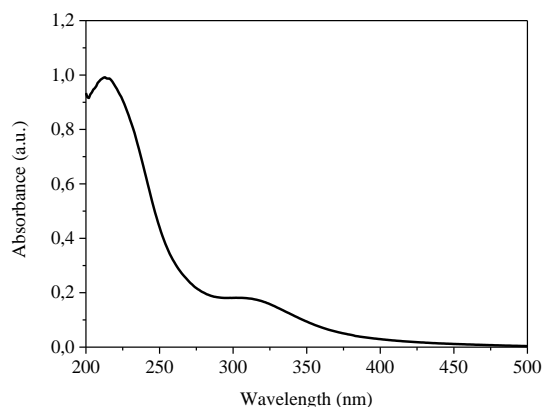


Figure 8: UV-Vis spectrum of LMCT region of $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ (HPA-2) in hydrochloric aqueous solution ($\text{pH}=1.0$).

Electrochemistry

Electrochemical data of the different HPA- n ($n=0-6$) catalysts were obtained by cyclic voltammetry (CV) and square wave voltammetry (SWV) using a FRA 2 $\mu\text{Autolab}$ Typ III Potentiostat/Galvanostat (with impedance unit) (METROM). The usual three-electrode setup consist of a glassy carbon electrode as a working electrode, a Pt wire as a counter electrode and a silver wire as pseudo reference electrode. The measurements were performed under anaerobic conditions in a home-built glass cell in hydrochloric aqueous solution ($\text{pH}=1.0$).

Figure 9 presents the cyclic voltammograms (CVs) of $\text{H}_8[\text{P V}_3\text{Mo}_7\text{O}_{40}]$ (HPA-5) in hydrochloric aqueous solution ($\text{pH}=1.0$) in a potential range of -0.7 to 1.1 V at different scan rates. The different voltammograms show several redox-processes that could be assigned to the reduction of the vanadium as well as to the reduction of Mo. In accordance to the square wave voltammograms the redox peaks in the potential range between -0.12 V and $+0.32$ V belong to the reduction of the different vanadium species and the other peaks in the potential range of $+0.16$ V to -0.6 V to the reduction of molybdenum.

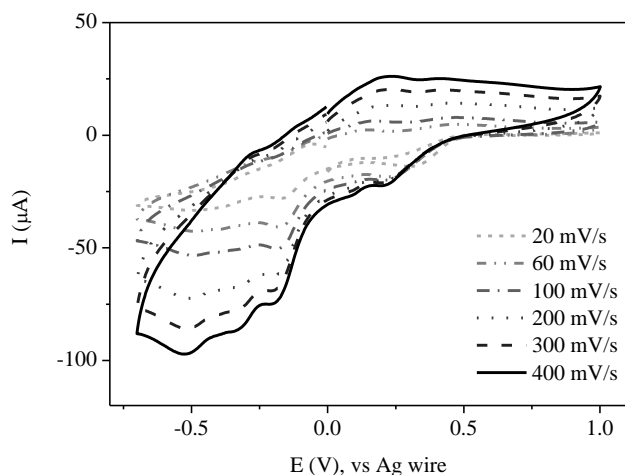


Figure 9: CV of $5.0 \times 10^{-4} \text{ M H}_8[\text{PV}_5\text{Mo}_7\text{O}_{40}]$ (HPA-5) in hydrochloric aqueous solution recorded at different scan rates at room temperature.

in situ UV-Vis Electrochemistry

Spectroelectrochemical experiments were carried out using a METROHM PGSTAT 101 and recorded by a SPECORD S600 Analytic Jena spectrophotometer in hydrochloric aqueous solution under argon atmosphere. The measurements were performed in a quartz glass cuvette with an optical path length of 1.0 mm, containing a three-electrode arrangement: as working electrode served a light-transparent platinum gauze, as pseudo-reference electrode a silver wire and as counter electrode a platinum wire.

Figure 10 and 11 illustrate the results of the spectroelectrochemical measurements of the reduction of HPA-5 in hydrochloric aqueous solution in a potential region of + 0.5 to -0.4 V. The decrease of the absorption bands at around 217 nm and 330 nm as well as the formation of a new absorption band at around 300 nm in the LMCT region demonstrate the reduction of V(V) and Mo(VI) in the heteropolyacid cage as previously described for HPA-2.

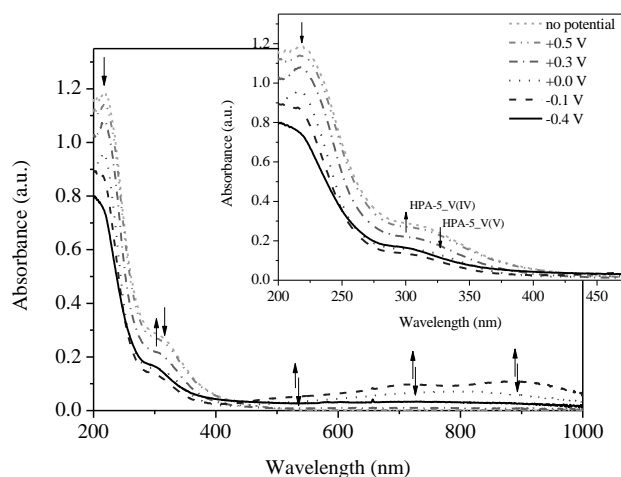


Figure 10: UV-Vis spectra of the Reduction of $\text{H}_8[\text{PV}_5\text{Mo}_7\text{O}_{40}]$ (HPA-5); at (---) no potential; (-••-) +0.5 V; (-•-) +0.3 V; (•••) 0.0 V; (-•) -0.1 V; (—) -0.4 V in hydrochloric aqueous solution (pH=1.0), in a spectral region between 200 and 1000 nm.

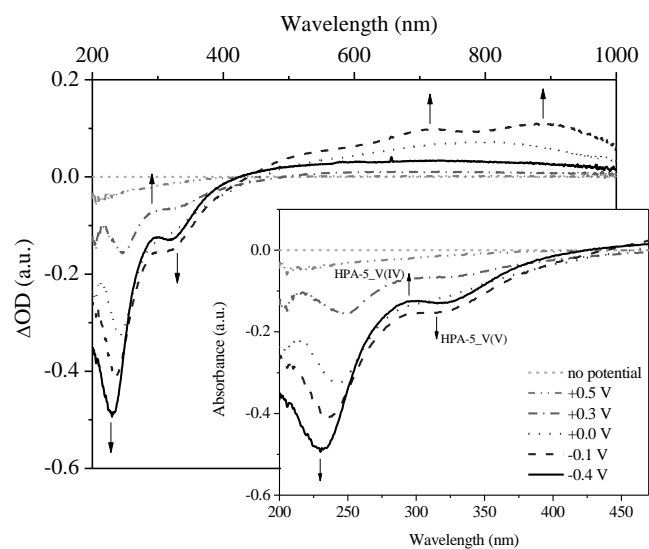


Figure 11: Differential spectra of the *in situ* UV-vis electrochemical measurements (reduction) of $H_8[PV_5Mo_7O_{40}]$ (HPA-5); at (---) no potential; (-●●-) +0.5 V; (-●-) +0.3 V; (●●●) 0.0 V; (- - ●) -0.1 V; (—) -0.4 V in hydrochloric aqueous solution (pH=1), in a spectral region between 200 and 1000 nm; insert: zoom in between 200 and 470 nm.