Supporting Information for

Selective catalytic oxidation of humins to carboxylic acids using the H₄[PVMo₁₁O₄₀] Keggin-type polyoxometalate enhanced by alcohol doping and solubilizer

Tobias Esserᵃ, André Wassenbergᵃ, Dorothea Voßᵃ and Jakob Albertᵃ*

ᵃ Institute of Technical and Macromolecular Chemistry, Universität Hamburg, Bundesstraße 45, 20146 Hamburg, Germany

*e-mail: jakob.albert@uni-hamburg.de

This document contains 1 Table and 15 Figures on 10 pages.
SCO of humins using the H₄[PVMo₁₁O₄₀] Keggin-type polyoxometalate

**Figure S1:** Exemplary ¹H-NMR spectra (600 MHz, D₂O) for the liquid product phase of the selective catalytic oxidation of humin using H₄[PVMo₁₁O₄₀] catalyst (HPA-1) in aqueous phase. *Experimental conditions:* 3-fold reaction system, 90 °C, 30 bar O₂, 30 h, 1000 rpm, 830 mmol of vanadium (V) for substitution in 30 mL water.

**Figure S2:** Exemplary ¹³C-NMR spectra (600 MHz, D₂O) for the liquid product phase of the selective catalytic oxidation of humin using HPA-1 as catalyst in aqueous phase. *Experimental conditions:* 3-fold reaction system, 90 °C, 30 bar O₂, 30 h, 1000 rpm, 83 mmol of vanadium (V) for substitution in 30 mL water.
Figure S3: Exemplary HSQC spectra (600 MHz, D$_2$O) for the liquid product phase of the selective catalytic oxidation of humin using HPA-1 as catalyst in aqueous phase. Experimental conditions: 3-fold reaction system, 90 °C, 30 bar O$_2$, 30 h, 1000 rpm, 83 mmol of vanadium (V) for substitution in 30 mL water.

Figure S4: Exemplary HMBC spectra (600 MHz, D$_2$O) for the liquid product phase of the selective catalytic oxidation of humin using HPA-1 as catalyst in aqueous phase. Experimental conditions: 3-fold reaction system, 90 °C, 30 bar O$_2$, 30 h, 1000 rpm, 83 mmol of vanadium (V) for substitution in 30 mL water.
Table S1: Comparison of quantification via $^1$H-NMR and HPLC for the selective catalytic oxidation of humins using HPA-1 as catalyst in aqueous phase.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Total Yield / %</th>
<th>Combined Yield / % (FA + AA)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$^1$H-NMR$^b$</td>
<td>HPLC$^c$</td>
</tr>
<tr>
<td>1$^a$</td>
<td>Blank</td>
<td>11.2</td>
<td>11.3</td>
</tr>
<tr>
<td>2$^a$</td>
<td>$\text{H}<em>4[\text{PVMo}</em>{11}\text{O}_{40}]$</td>
<td>30.1</td>
<td>29.8</td>
</tr>
</tbody>
</table>

*Experimental Conditions:* a) 3-fold reaction system, 90 °C, 30 bar $\text{O}_2$, 30 h, 1000 rpm, 300 mg solid humin (16.20 mmol carbon), 0.83 mmol of vanadium (V) for substitution (20 mol$^{-1}$$_{\text{Carbon}}$) in 30 mL water, b) determined with quantitative $^1$H-NMR and tert.-butanol as standard, c) determined with HPLC according to the corresponding section of the experimental part.

Selection of a suitable additive for the suppression of CO$_2$ formation in SCO of humins

Figure S5: $^1$H-NMR spectra (600 MHz, D$_2$O) for the liquid product phase of the additive stability experiments using HPA-1 as catalyst in alcohol-doped aqueous phase. *Experimental conditions:* 3-fold reaction system, 90 °C, 30 bar $\text{O}_2$, 30 h, 1000 rpm, 83 mmol of vanadium (V) for substitution in 30 mL of 10-vol.% aqueous solution of the respective alcohol.
Figure S6: Chromatograms for the liquid product phase of the additive stability experiments using HPA-1 as catalyst in alcohol-doped aqueous phase. **Experimental conditions:** 3-fold reaction system, 90 °C, 30 bar O₂, 30 h, 1000 rpm, 0.83 mmol of vanadium (V) for substitution in 30 mL of 10-vol.% aqueous solution of the respective alcohol.

### The effect of para-toluene sulfonic acid as solubilizer on the SCO of humins

![Figure S7: 1H-NMR spectra (600 MHz, D₂O) for the liquid product phase of the pTSA stability experiment using HPA-1 as catalyst in aqueous phase. **Experimental conditions:** 3-fold reaction system, 90 °C, 30 bar O₂, 30 h, 1000 rpm, 0.83 mmol of vanadium (V) for substitution and 3.0 mmol pTSA in 30 mL aqueous phase.](image-url)
**Figure S8:** Chromatogram for the liquid product phase of the pTSA stability experiment using HPA-1 as catalyst in aqueous phase. *Experimental conditions:* 3-fold reaction system, 90 °C, 30 bar O₂, 30 h, 1000 rpm, 0.83 mmol of vanadium (V) for substitution and 3.0 mmol pTSA in 30 mL aqueous phase.

**Figure S9:** $^{51}$V-NMR spectra (600 MHz, D₂O) for the reduced HPA-1 catalyst in aqueous phase.
**Figure S 10:** $^1$H-NMR spectra (600 MHz, D$_2$O) for the liquid product phase of the pTSA stability experiment using fully reduced HPA-1 blue as catalyst in aqueous phase. *Experimental conditions:* 3-fold reaction system, 90 °C, 30 bar O$_2$, 30 h, 1000 rpm, 0.83 mmol of vanadium (V) for substitution and 3.0 mmol pTSA in 30 mL aqueous phase.

**Figure S 11:** Chromatogram for the liquid product phase of the pTSA stability experiment using fully reduced HPA-1 blue as catalyst in aqueous phase. *Experimental conditions:* 3-fold reaction system, 90 °C, 30 bar O$_2$, 30 h, 1000 rpm, 0.83 mmol of vanadium (V) for substitution and 3.0 mmol pTSA in 30 mL aqueous phase.
Optimization of SCO of humins by synergetic combination of MeOH and pTSA

![Graph showing the optimization of SCO of humins.]

**Figure S12:** Reproduction for selective catalytic oxidation of humin using HPA-1 as catalyst in aqueous methanol solution with pTSA (combined system). *Experimental conditions:* 3-fold reaction system, 120 °C, 30 bar O\(_2\), 30 h, 1000 rpm, 300 mg solid solid humin (16.20 mmol carbon), 0.83 mmol of vanadium (V) for substitution (20 mol\(_{\text{Carbon}}\)mol\(^{-1}\text{V}\)) in 5 vol.-% methanol with 1.5 mmol pTSA.

**Catalyst characterization**

![Graph showing the FT-IR (ATR) spectrum of the H\(_4\)PVMo\(_{11}\)O\(_{40}\) POM-catalyst.]

**Figure S13:** FT-IR (ATR) spectrum of the H\(_4\)PVMo\(_{11}\)O\(_{40}\) POM-catalyst. Vibration modes: 1055 cm\(^{-1}\) (P-O), 958 cm\(^{-1}\) (M=O\(_t\)), 877 cm\(^{-1}\) ((M-O-M)\(_\text{vertex}\)), 756 cm\(^{-1}\) ((M-O-M)\(_\text{edge}\)). \(^1\)
Figure S14: $^{51}$V NMR spectrum of the H$_4$[PVMo$_{11}$O$_{40}$] POM-catalyst in a mixture of 90 % H$_2$O (pH 1) and 10 % acetone-d$_6$. NaVO$_3$ was used as external standard.

Figure S15: $^{31}$P NMR spectrum of the H$_4$[PVMo$_{11}$O$_{40}$] POM-catalyst in a mixture of 90 % H$_2$O (pH 1) and 10 % acetone-d$_6$. 85 % H$_3$PO$_4$ was used as external standard.
References