Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

Supporting Information for

Selective catalytic oxidation of humins to carboxylic acids using the $H_4[PVMo_{11}O_{40}]$ Keggin-type polyoxometalate enhanced by alcohol doping and solubilizer

Tobias Esser[a], André Wassenberg[a], Dorothea Voß[a] and Jakob Albert[a]*

[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 $H_4[PVMo_{11}O_{40}]$ Keggin-type polyoxometalate

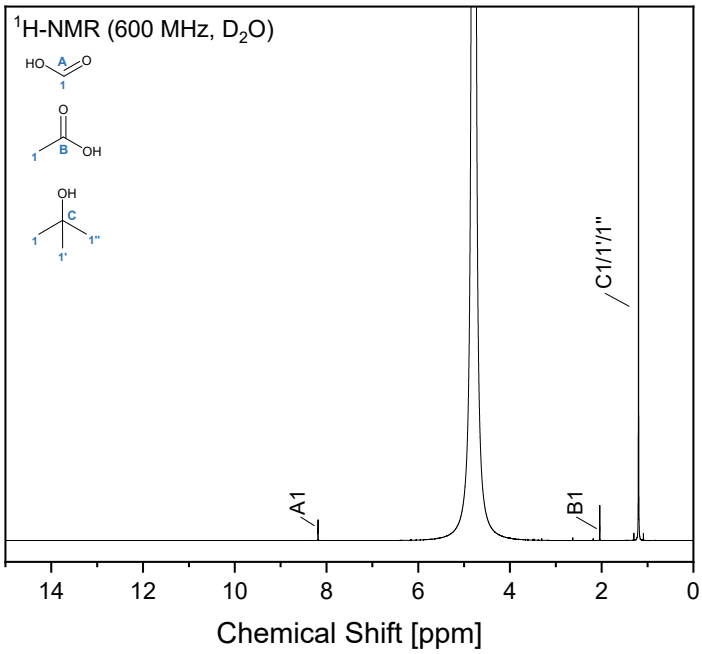

Figure S1: Exemplary ^{1}H-NMR spectra (600 MHz, D_2O) for the liquid product phase of the selective catalytic oxidation of humin using $H_4[PVMo_{11}O_{40}]$ catalyst (HPA-1) in aqueous phase. *Experimental conditions:* 3-fold reaction system, 90 °C, 30 bar O_2, 30 h, 1000 rpm, 830 mmol of vanadium (V) for substitution in 30 mL water.

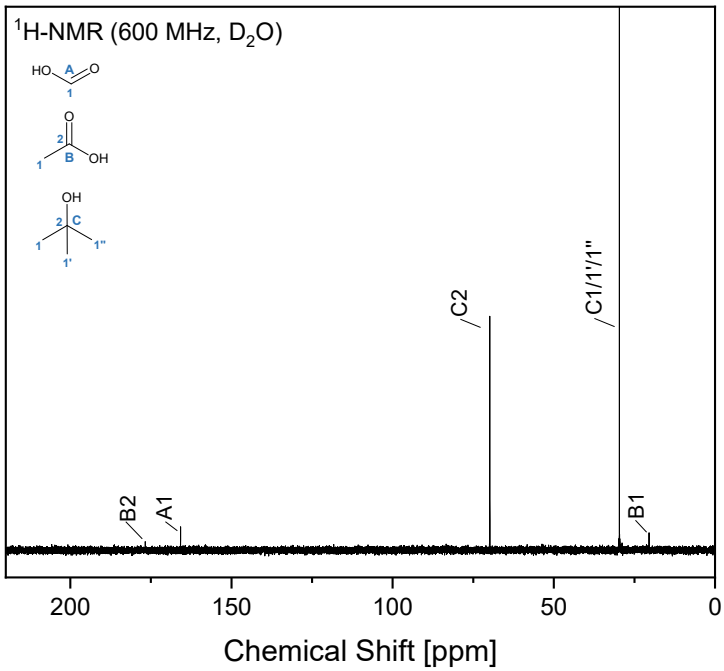

Figure S2: Exemplary ^{13}C-NMR spectra (600 MHz, D_2O) for the liquid product phase of the selective catalytic oxidation of humin using HPA-1 as catalyst in aqueous phase. *Experimental conditions:* 3-fold reaction system, 90 °C, 30 bar O_2, 30 h, 1000 rpm, 83 mmol of vanadium (V) for substitution in 30 mL water.

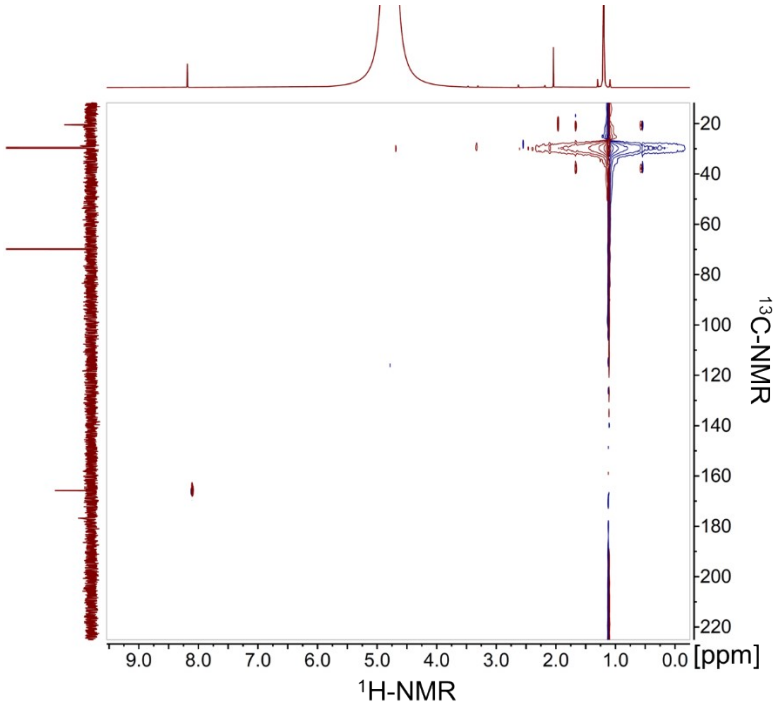

Figure S3: Exemplary HSQC spectra (600 MHz, D_2O) for the liquid product phase of the selective catalytic oxidation of humin using HPA-1 as catalyst in aqueous phase. *Experimental conditions:* 3-fold reaction system, 90 °C, 30 bar O_2, 30 h, 1000 rpm, 83 mmol of vanadium (V) for substitution in 30 mL water.

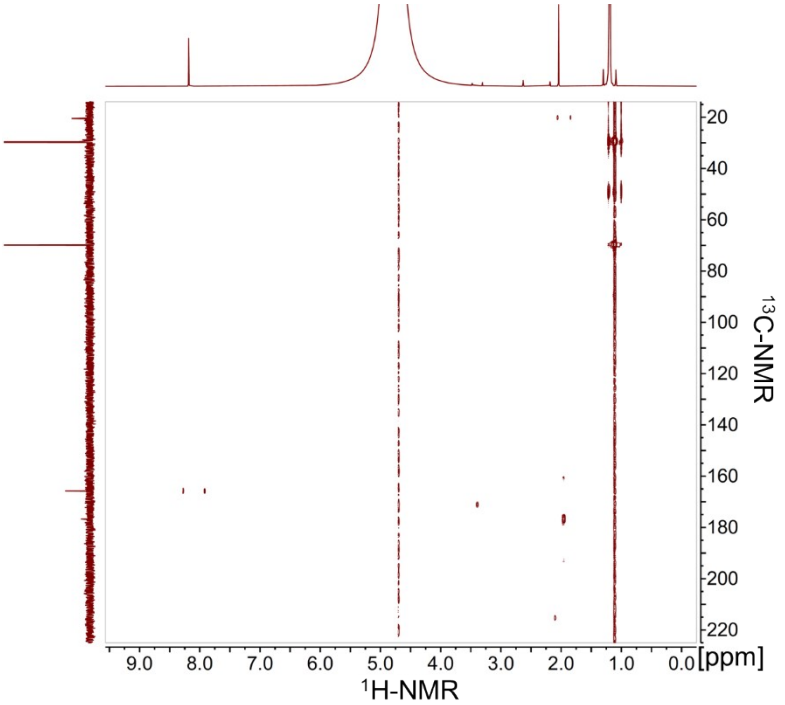

Figure S4: Exemplary HMBC spectra (600 MHz, D_2O) for the liquid product phase of the selective catalytic oxidation of humin using HPA-1 as catalyst in aqueous phase. *Experimental conditions:* 3-fold reaction system, 90 °C, 30 bar O_2, 30 h, 1000 rpm, 83 mmol of vanadium (V) for substitution in 30 mL 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.

Entry	Catalyst	Total Yield / %		Combined Yield / % (FA + AA)	
		^{1}H-NMR[b]	HPLC[c]	^{1}H-NMR[b]	HPLC[c]
1[a]	Blank	11.2	11.3	3.2	3.3
2[a]	$H_4[PVMo_{11}O_{40}]$	30.1	29.8	10.9	10.6

Experimental Conditions: a) 3-fold reaction system, 90 °C, 30 bar O_2, 30 h, 1000 rpm, 300 mg solid humin (16.20 mmol carbon), 0.83 mmol of vanadium (V) for substitution (20 mol_{Carbon} mol^{-1}_{V}) 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

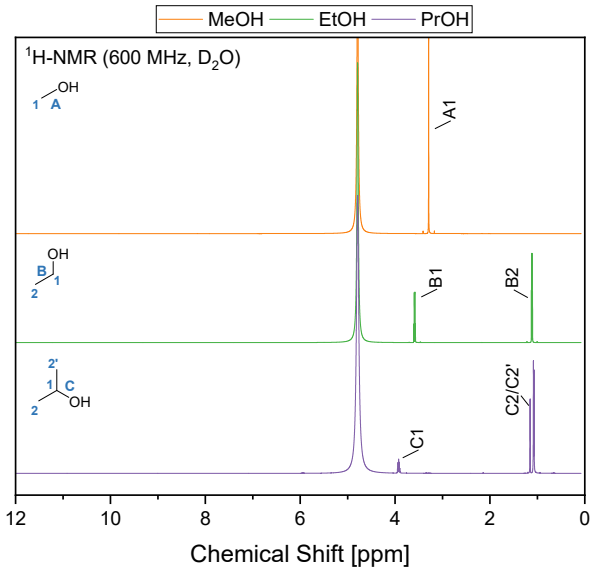

Figure S5: ^{1}H-NMR spectra (600 MHz, D_2O) for the liquid product phase of the additive stability experiments using HPA-1 as catalyst in alcohol-doped aqueous phase. *Experimental conditions:* 3-fold reaction system, 90 °C, 30 bar O_2, 30 h, 1000 rpm, 83 mmol of vanadium (V) for substitution in 30 mL of 10-vol.% aqueous solution of the respective alcohol.

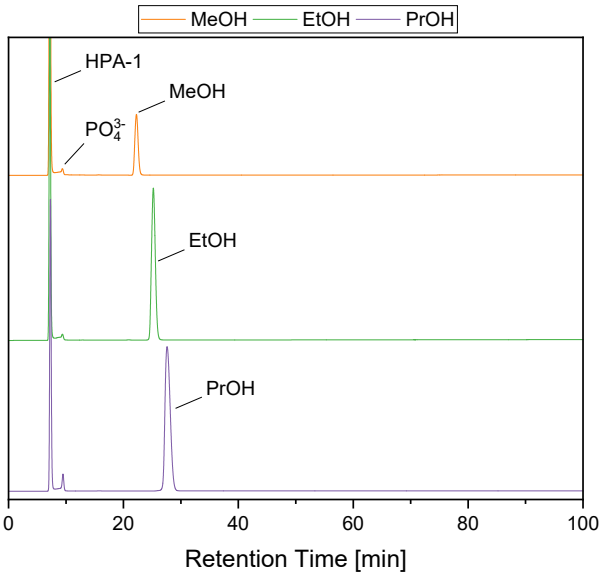

Figure S6: Chromatograms for the liquid product phase of the additive stability experiments using HPA-1 as catalyst in alcohol-doped aqueous phase. *Experimental conditions:* 3-fold reaction system, 90 °C, 30 bar O_2, 30 h, 1000 rpm, 0.83 mmol of vanadium (V) for substitution in 30 mL of 10-vol.% aqueous solution of the respective alcohol.

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

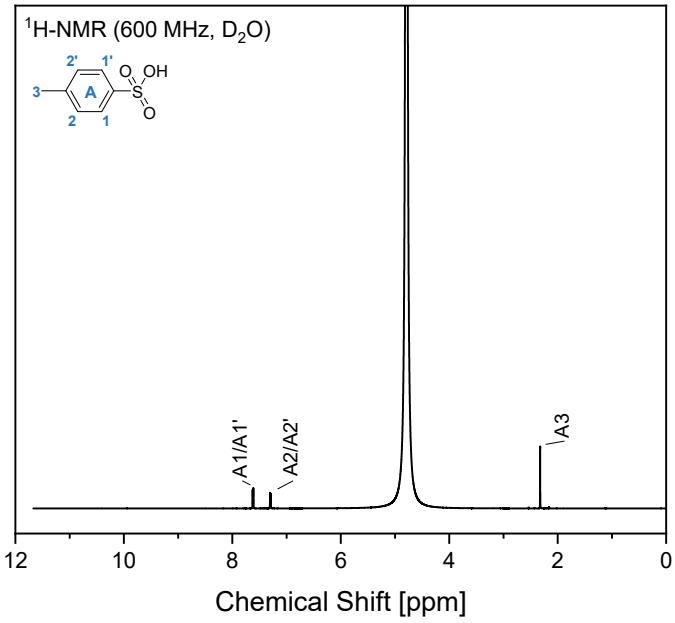

Figure S7: ^{1}H-NMR spectra (600 MHz, D_2O) for the liquid product phase of the pTSA stability experiment using HPA-1 as catalyst in aqueous phase. *Experimental conditions:* 3-fold reaction system, 90 °C, 30 bar O_2, 30 h, 1000 rpm, 0.83 mmol of vanadium (V) for substitution and 3.0 mmol pTSA in 30 mL aqueous phase.

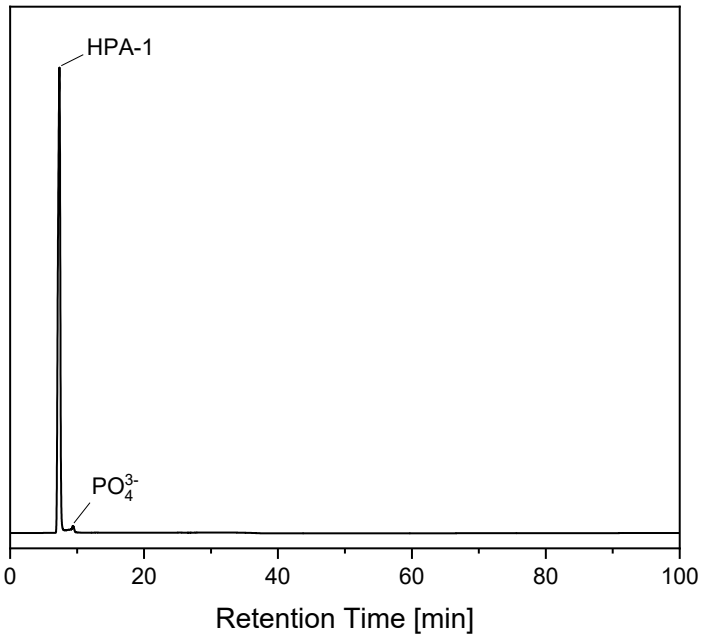

Figure S8: Chromatogram for the liquid product phase of the pTSA stability experiment using HPA-1 as catalyst in aqueous phase. *Experimental conditions:* 3-fold reaction system, 90 °C, 30 bar O_2, 30 h, 1000 rpm, 0.83 mmol of vanadium (V) for substitution and 3.0 mmol pTSA in 30 mL aqueous phase.

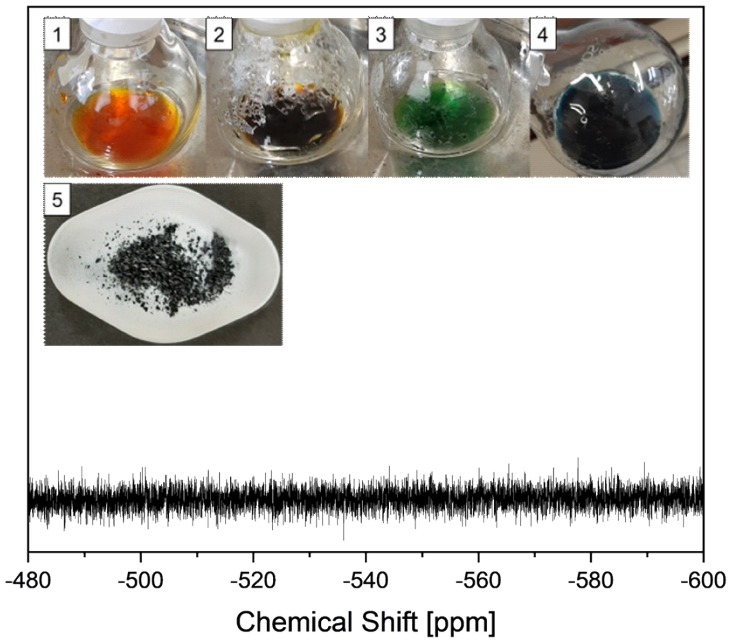

Figure S9: ^{51}V-NMR spectra (600 MHz, D_2O) for the reduced HPA-1 catalyst in aqueous phase.

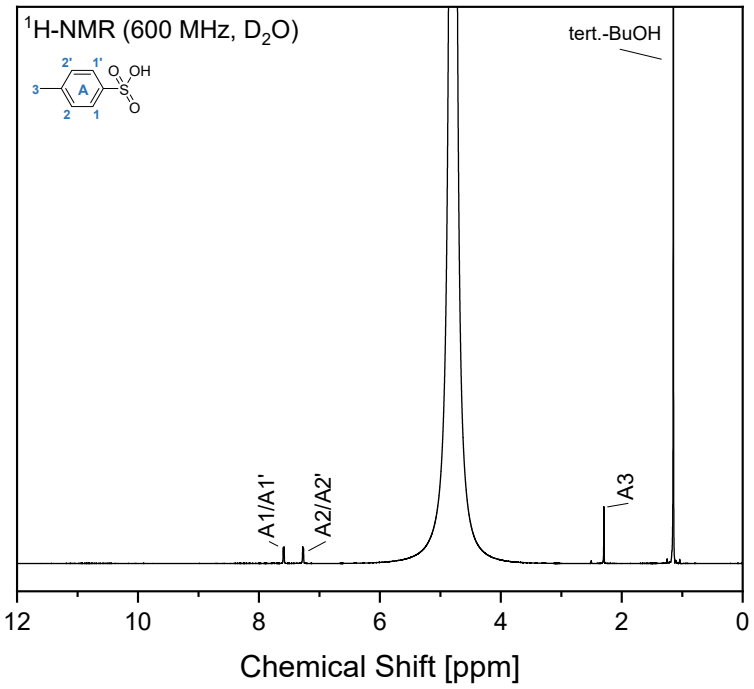

Figure S 10: ^{1}H-NMR spectra (600 MHz, D_2O) for the liquid product phase of the pTSA stability experiment using fully reduced HPA-1 blue as catalyst in aqueous phase. *Experimental conditions:* 3-fold reaction system, 90 °C, 30 bar O_2, 30 h, 1000 rpm, 0.83 mmol of vanadium (V) for substitution and 3.0 mmol pTSA in 30 mL aqueous phase.

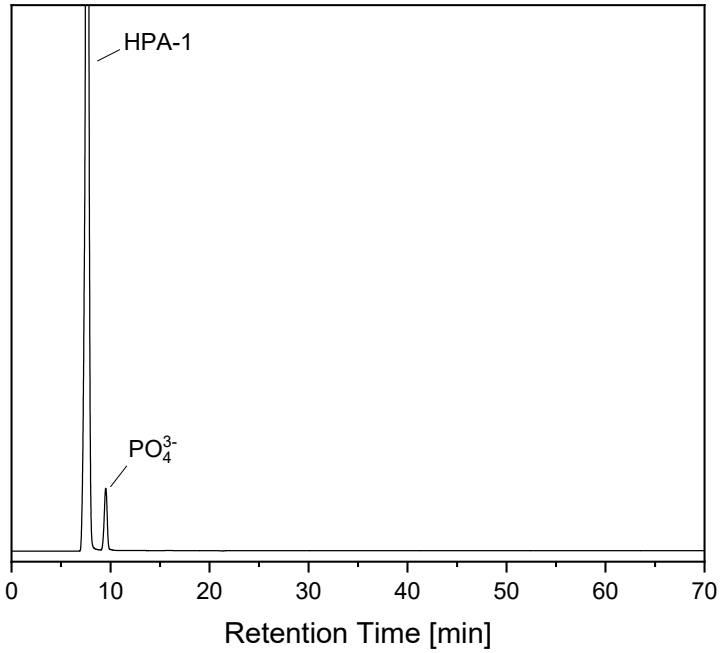

Figure S 11: Chromatogram for the liquid product phase of the pTSA stability experiment using fully reduced HPA-1 blue as catalyst in aqueous phase. *Experimental conditions:* 3-fold reaction system, 90 °C, 30 bar O_2, 30 h, 1000 rpm, 0.83 mmol of vanadium (V) for substitution and 3.0 mmol pTSA in 30 mL aqueous phase.

Optimization of SCO of humins by synergetic combination of MeOH and pTSA

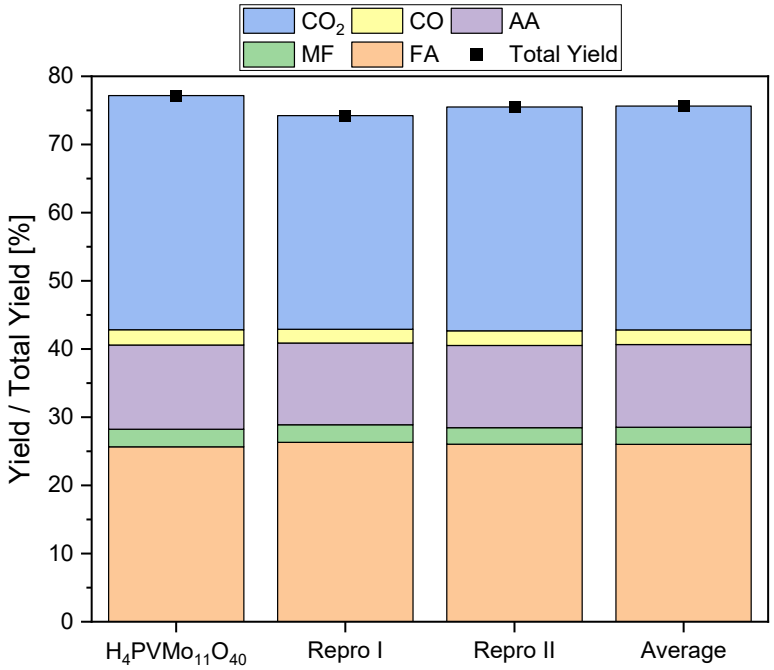

Figure S12: Reproduction for selective catalytic oxidation of humin using HPA-1 as catalyst in aqueous methanol solution with pTSA (combined system). *Experimental conditions:* 3-fold reaction system, 120 °C, 30 bar O_2, 30 h, 1000 rpm, 300 mg solid solid humin (16.20 mmol carbon), 0.83 mmol of vanadium (V) for substitution (20 $mol_{Carbon}\,mol^{-1}{}_{V}$) in 5 vol.-% methanol with 1.5 mmol pTSA.

Catalyst characterization

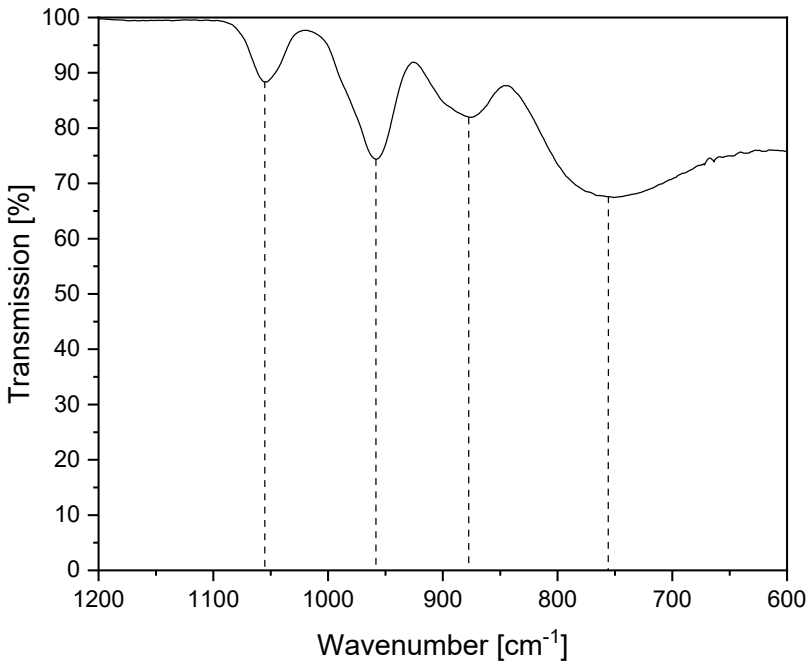

Figure S13: FT-IR (ATR) spectrum of the $H_4[PVMo_{11}O_{40}]$ POM-catalyst. Vibration modes: 1055 cm^{-1} (P-O), 958 cm^{-1} (M=O_t), 877 cm^{-1} ((M-O-M)$_{vertex}$), 756 cm^{-1} ((M-O-M)$_{edge}$).[1]

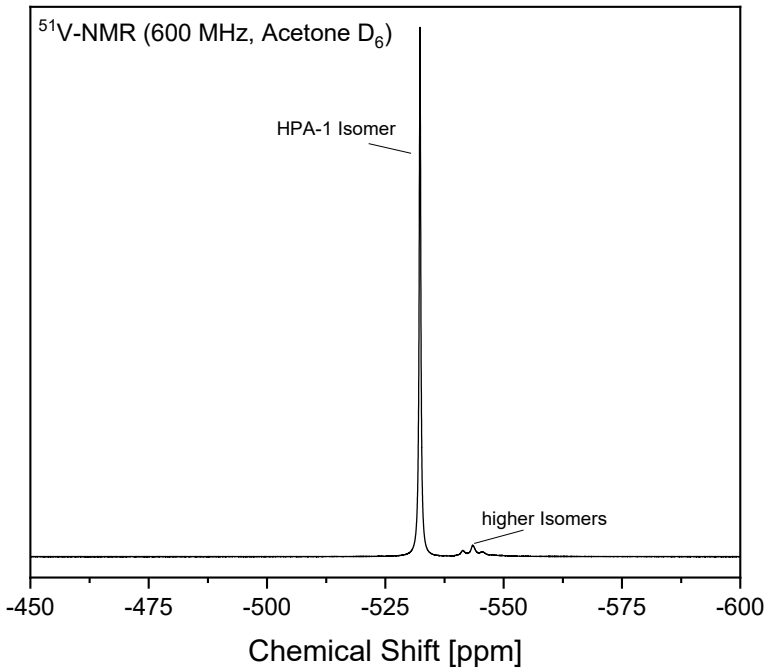

Figure S14: ^{51}V NMR spectrum of the $H_4[PVMo_{11}O_{40}]$ POM-catalyst in a mixture of 90 % H_2O (pH 1) and 10 % acetone-*d*6. $NaVO_3$ was used as external standard.

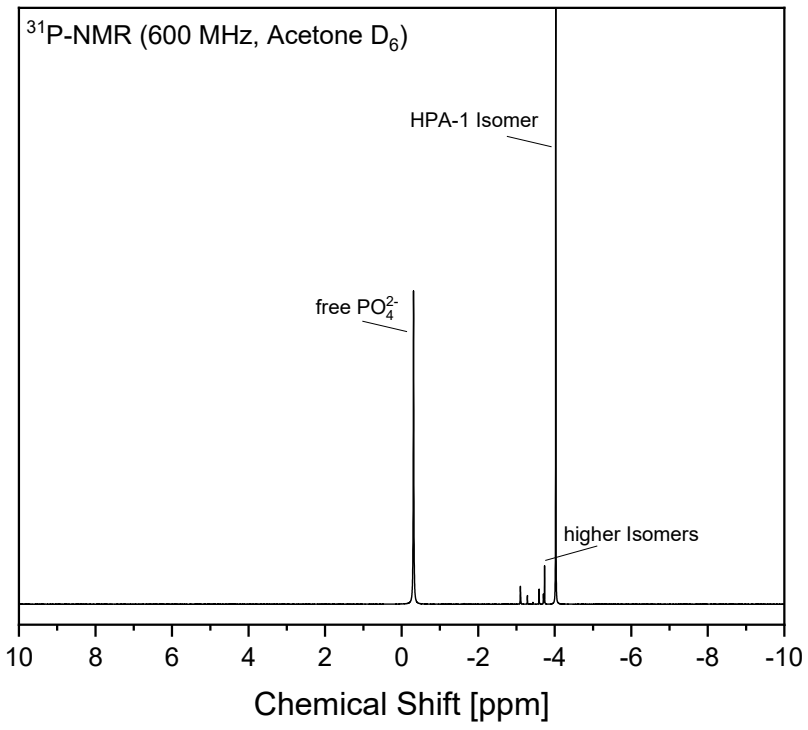

Figure S15: ^{31}P NMR spectrum of the $H_4[PVMo_{11}O_{40}]$ POM-catalyst in a mixture of 90 % H_2O (pH 1) and 10 % acetone-*d*6. 85 % H_3PO_4 was used as external standard.

References

1 J. K. Lee, J. Melsheimer, S. Berndt, G. Mestl, R. Schlögl and K. Köhler, *Applied Catalysis A: General*, 2001, **214**, 125–148.