Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information for

Combining autoclave and LCWM reactor studies to shed light on the kinetics of glucose oxidation catalyzed by doped molybdenum-based heteropoly acids

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(This document contains 15 pages with 18 Figures and 1 Table.)

Characterization of polyoxometalate catalysts

All three synthesized polyoxometalate catalysts were characterized by different analytical methods.

FTIR:

Infrared spectroscopy was carried out to confirm the presence of Keggin species (Figure S1) [6, 10]. Intense IR bands are found that we assigned to the characteristic stretching vibrations of the Keggin oxoanion observed at 1051 cm^{-1} (ν_{as} P-O_a), 951 cm^{-1} (ν_{as} M-O_d), 877 cm^{-1} (ν_{as} M-O_b-M) and a broad band at 766 cm^{-1} (ν_{as} M-O_c-M), respectively (M=Mo, V).

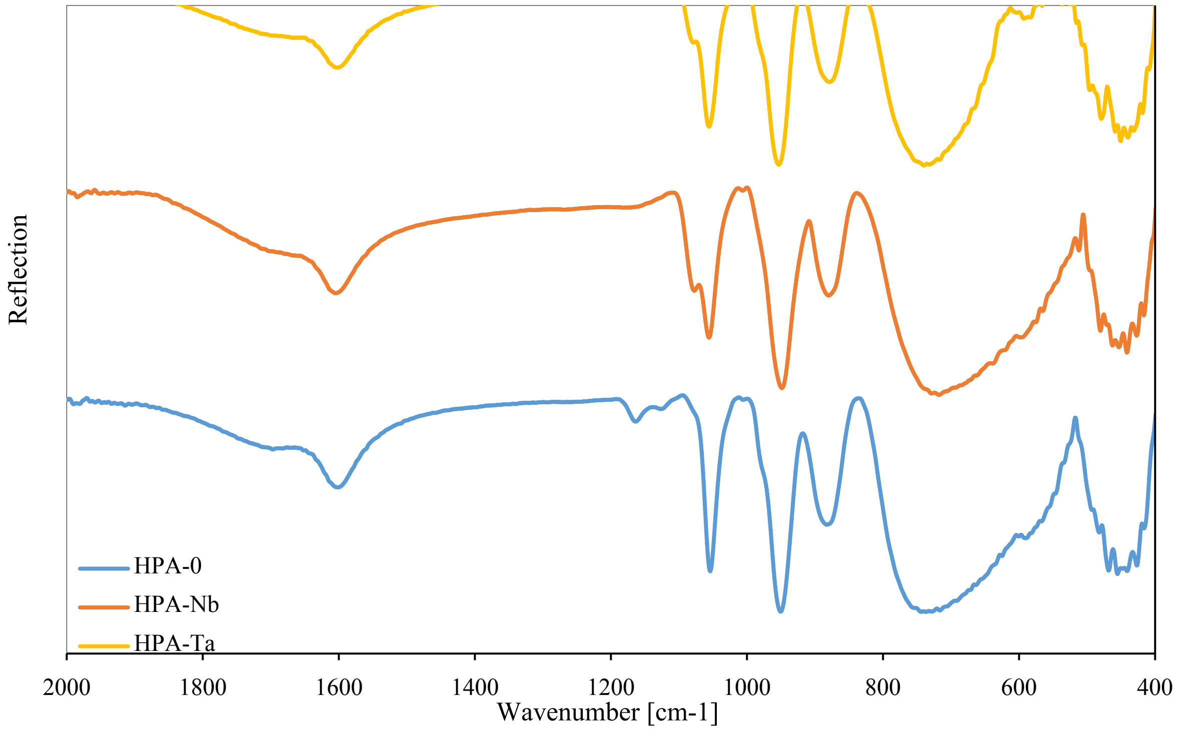


Figure S1: FTIR-spectra of the synthesized catalysts HPA-Mo, HPA-Nb and HPA-Ta.

^{31}P-NMR:

^{31}P-NMR spectra of HPA-Mo, HPA-Ta and HPA-Nb (Figures S2-S4) showed the same chemical shifts according to the literature [6, 28]. They show the signals of all positional isomers at the appropriate shifts and, in addition, the peak for the free $[PO_4]^{3-}$ anion at +0.1 ppm.

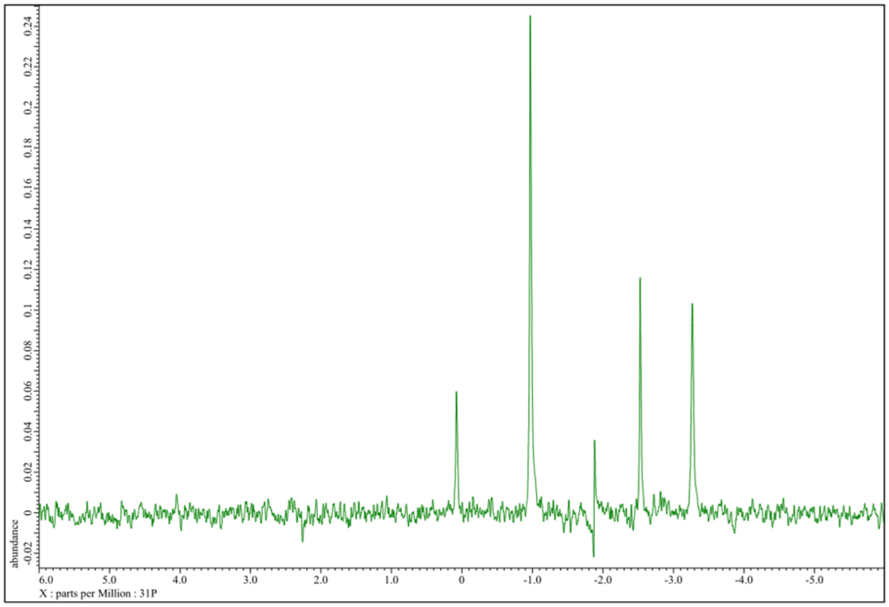


Figure S2: ^{31}P-NMR of the synthesized catalyst HPA-Mo.

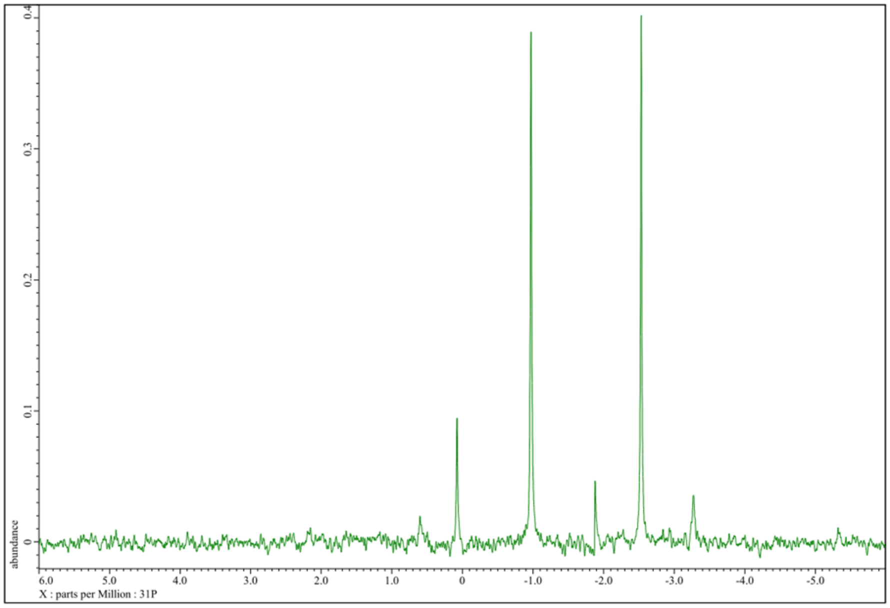


Figure S3: ^{31}P-NMR of the synthesized catalyst HPA-Ta.

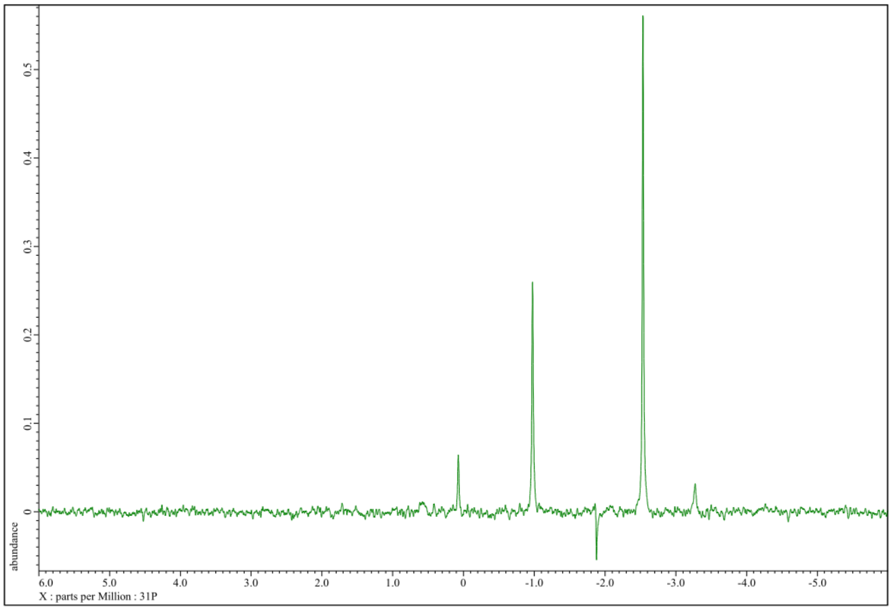


Figure S4: ^{31}P-NMR of the synthesized catalyst HPA-Nb.

Raman:

Raman spectroscopy for all applied catalysts was conducted using a laser Raman microscope (Bruker Senterra 1, NDYAG laser) at a wavelength of 532 nm. All catalysts show the main bands assigned in literature [30] to heteropoly compounds with a Keggin structure, as depicted in Figure S5. Split bands (M=O groups) 230-250 cm^{-1}, broad band at 625 cm^{-1} (Mo-O$_c$-Mo vibration bands), bands in the region 876-909 cm^{-1} (Mo-O$_b$-Mo and Mo-O-P stretching vibrations), and bands at 984 and 1002 cm^{-1} (Mo-O$_d$ stretching bands). The partial variation, and principally the disappearance of the second peak of the broad band at 625 cm^{-1}, implies that the Keggin structure was partially damaged by the substitution of Nb and Ta in the structure (Figures S5).

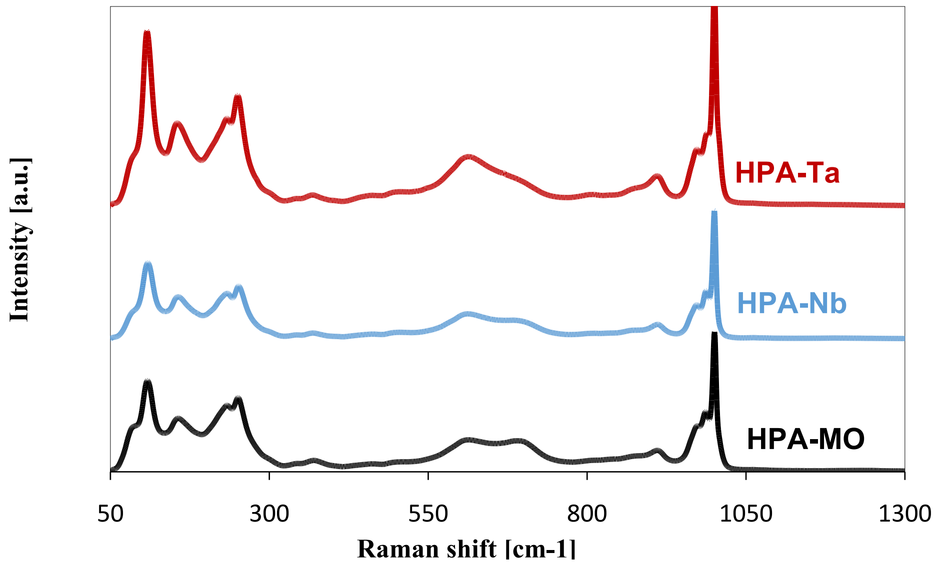


Figure S5: Raman spectra of HPA-n (n= 0, Nb, Ta) powder catalysts.

XRD:

Powder X-ray diffraction was performed to confirm the presence of Keggin structures (STADIP Stoe & Cie GmbH). All measurements were carried out on a flat sample holder in transmission geometry (4–60°/2θ, λ=1,54060 Å, Ge[111]-monochromator), detector: Mythen1K (Dectris, Baden, Switzerland). The experimental X-ray patterns of the three compounds look very similar to each other (Figures S6). Here, reflections of the compound $H_3PMo_{12}O_{40}\cdot 8\ H_2O$ are present, but additional reflections at about ~6.6, ~8.5, and ~9.9°/2θ cannot be assigned unambiguously without further information about the samples.

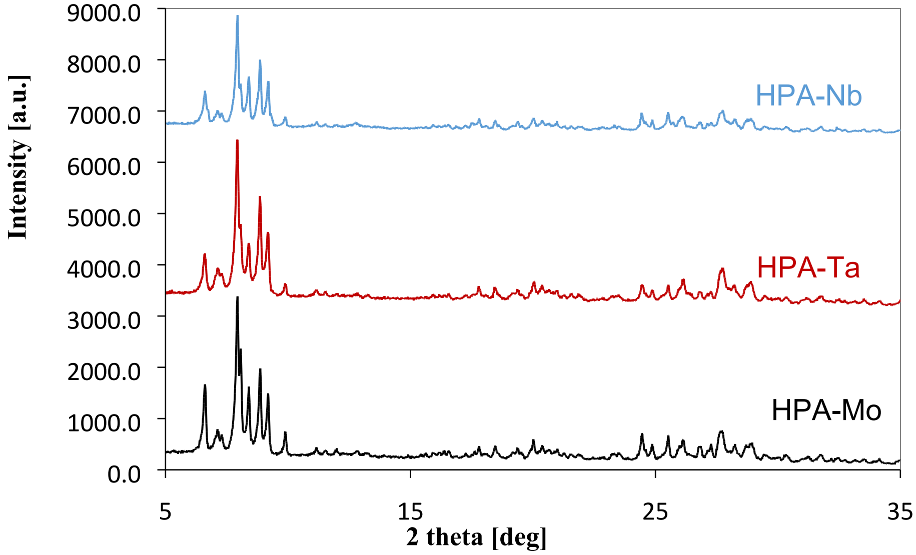
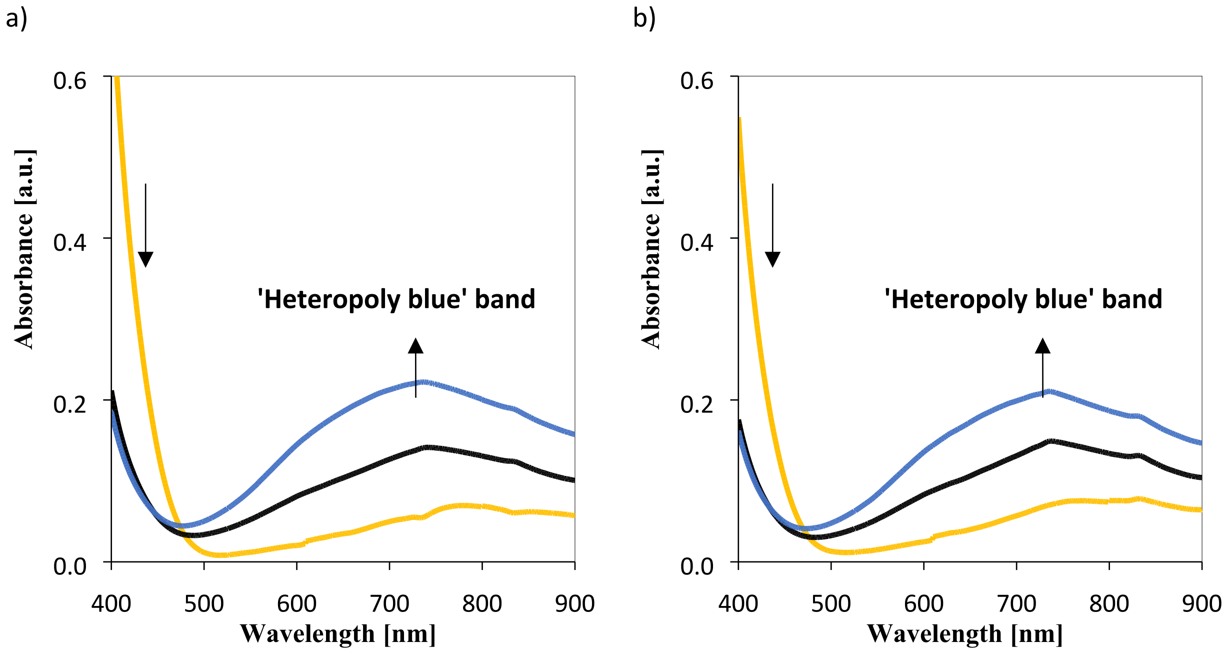


Figure S6: Powder XRD diffraction measurements in different HPA-n (n=Mo, Nb, Ta) catalysts.

Reduction experiments within LCWM microreactor



c)

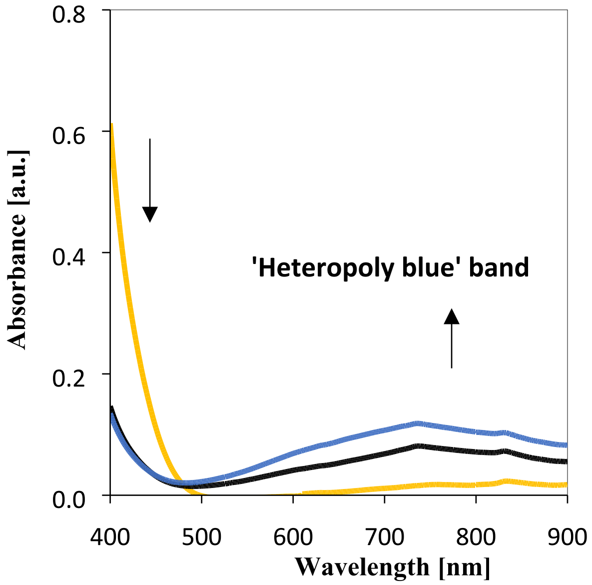


Figure S7: Example absorption spectra of the partial reduction of HPA-Nb (a), HPA-Ta (b), and HPA-Mo (c) within the LCWM reactor (yellow, black, and blue spectra represent the fully oxidized, partial reduced, and reduced forms respectively). *Reaction conditions*: 130 °C, 2 bar N_2 saturation, 40 µM HPA initial concentration, 0.75 mmol L^{-1} glucose, LCWM reactor.

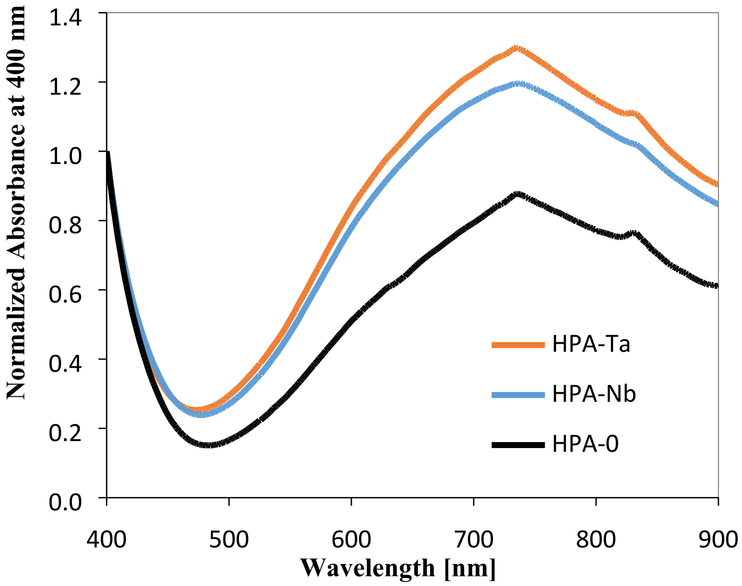


Figure S8: Normalized absorption spectra (at 400 nm) of the three different reduced catalysts at t=70 min. *Reaction conditions*: 130 °C, 2 bar N_2 saturation, 40 µM HPA initial concentration, 0.75 mmol L^{-1} glucose, LCWM reactor.

Cyclic voltammetry experiments:

Figure S9 and S10 depict the cyclic voltammograms of HPA-n$_{ox}$ complexes dissolved in a sodium sulfate solution.

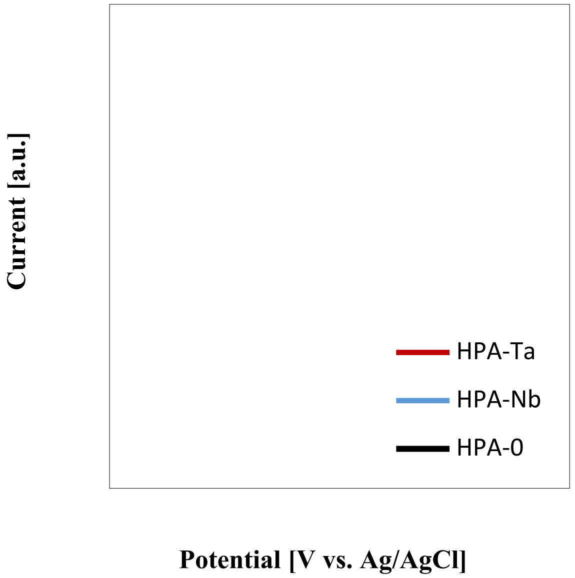


Figure S9: Cyclic voltammograms of the HPA-n (n= Mo, Nb, Ta) catalysts recorded in N$_2$-saturated 0.5 M Na$_2$SO$_4$ aqueous electrolyte solution at a scan rate of 20 mV s^{-1} (pH=3.3).

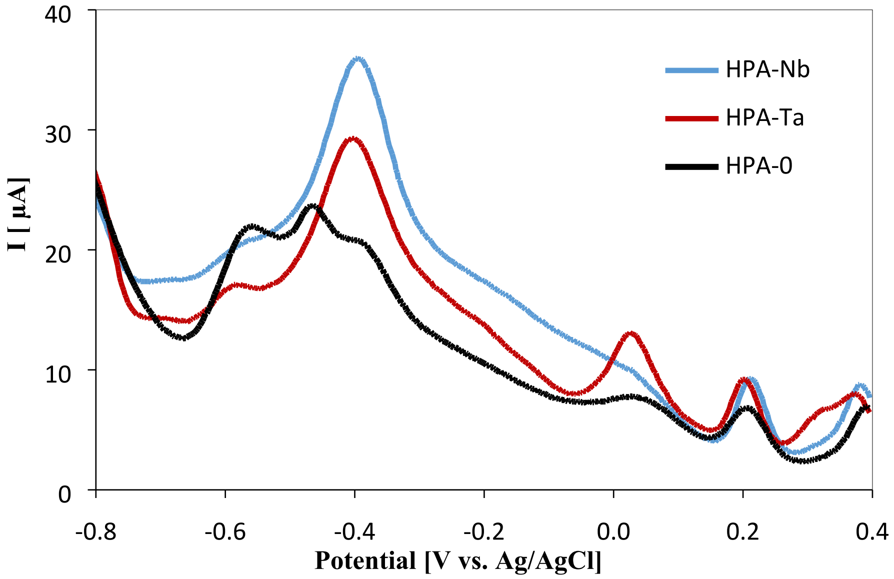


Figure S10: Square wave voltammograms of HPA-n (n=Mo, Nb, Ta) in a recorded in N$_2$-saturated 0.5 M Na$_2$SO$_4$ aqueous electrolyte solution (pH=3.3).

Batch experiments at 80 °C

Table S1: Conversion of glucose using different Keggin-type polyoxometalate catalysts in batch mode at 80 °C. *Reaction conditions:* 250 mmol L^{-1} glucose, 1 mmol catalyst, 100 g water as solvent, 80 °C, 60 bar oxygen pressure, 1000 rpm stirrer speed, 8 hours reaction time

Entry	Catalyst	FA-Yield [%]	GA-Yield [%]	CO_2-Yield [%]	Total Carbon Yield [%]
1	HPA-Mo	0.3	0.5	0.0	0.8
2	HPA-Ta	traces	0.0	0.0	0.0
3	HPA-Nb	traces	0.0	0.0	0.0

Substrate oxidation kinetics for HPA-Ta

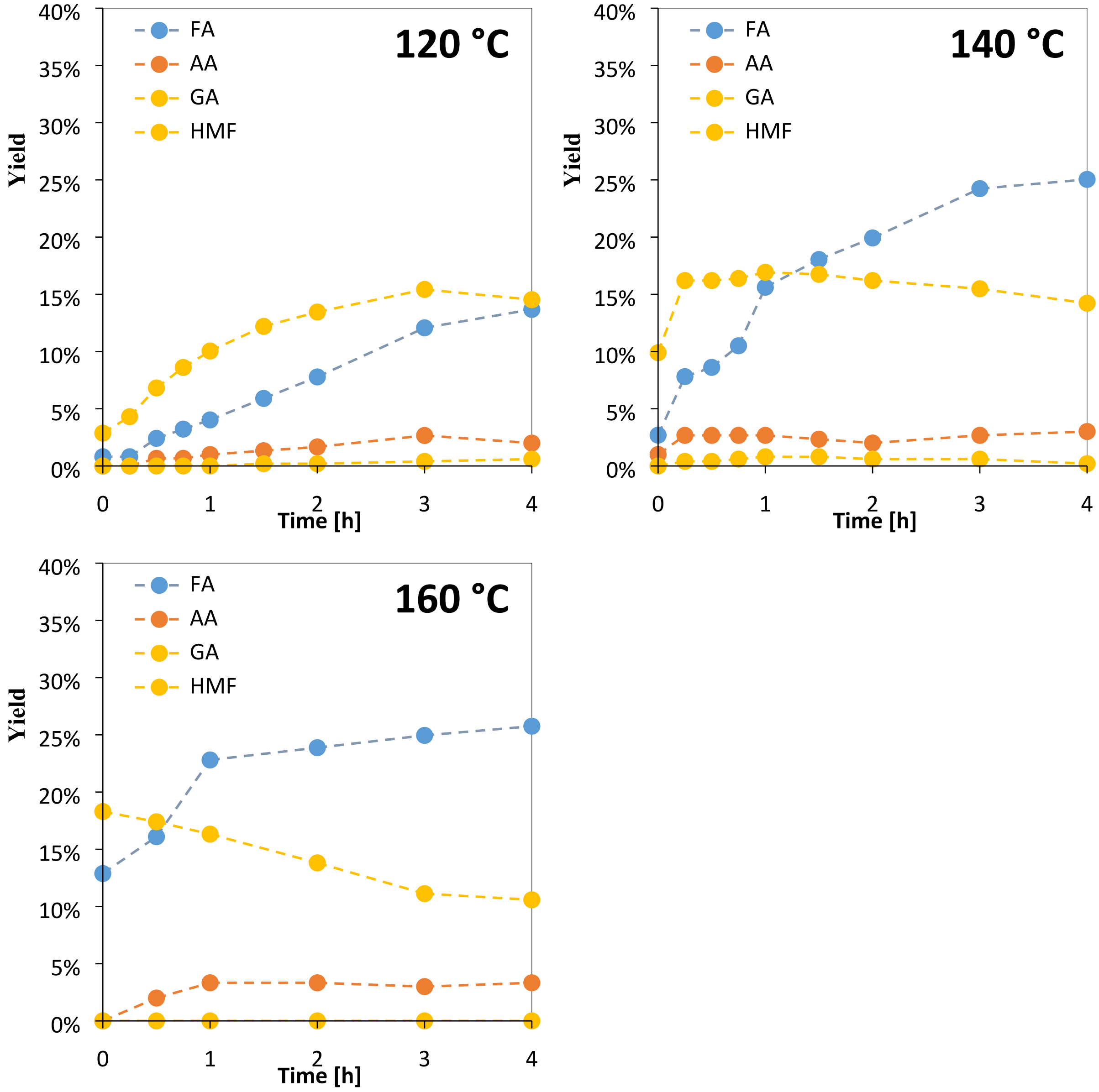


Figure S11: HPA-Ta catalyst: Time depended yield distribution of the liquid products for different reaction temperatures. *Reaction conditions*: 120-160 °C, 60 bar O_2, 1000 rpm, 1 mmol HPA-Ta, 100 g water, 0.25 mol L^{-1} glucose, 4 h fed-batch, and high-pressure autoclave.

Substrate oxidation kinetics for HPA-Mo

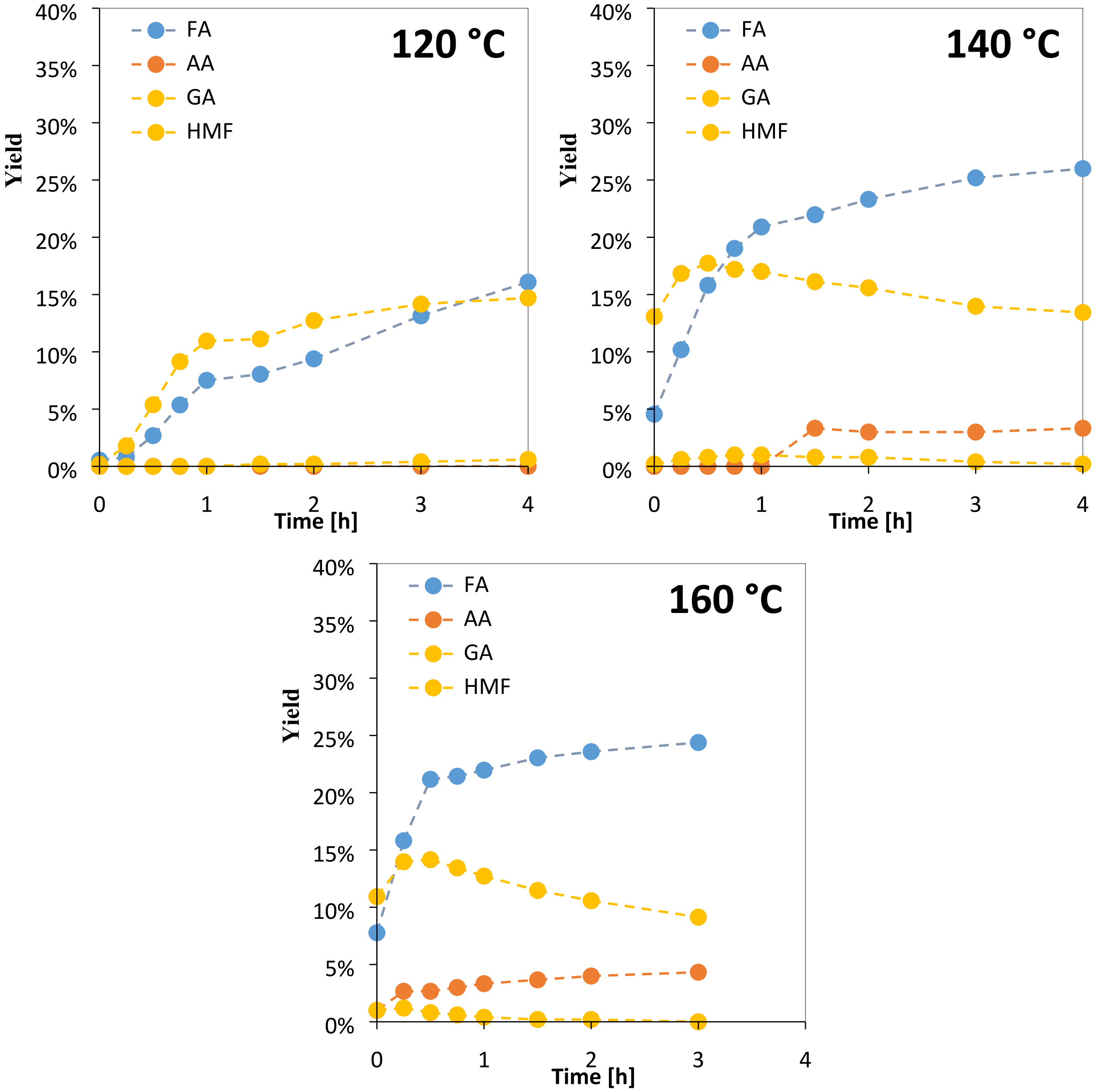


Figure S12: HPA-Mo catalyst: Time depended yield distribution of the liquid products for different reaction temperatures. *Reaction conditions*: 120-160 °C, 60 bar O_2, 1000 rpm, 1 mmol HPA-MO, 100 g water, 0.25 mol L^{-1} glucose, 4 h fed-batch, and high-pressure autoclave.

Normalized concentration-time profiles for HPA-Nb

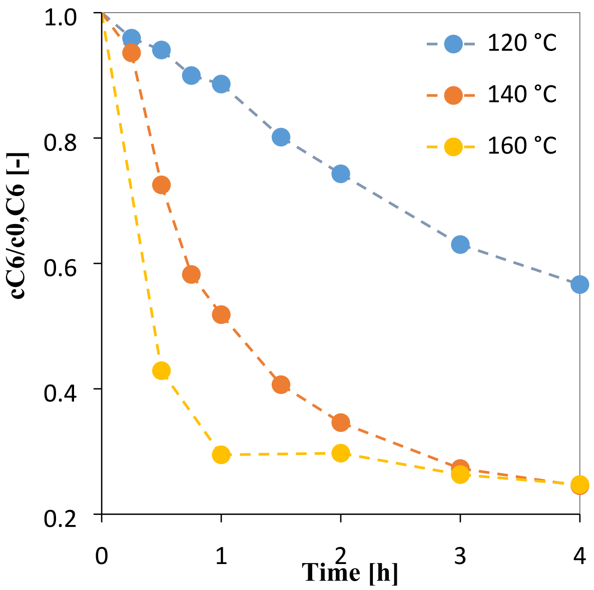


Figure S13: HPA-Nb catalyst: Normalized concentration − time profiles for different reaction temperatures. Reaction conditions: 120-160 °C, 60 bar O2, 1000 rpm, 1 mmol HPA-Nb, 100 g water, 0.25 mol L-1 glucose, 4 h fed-batch, and high-pressure autoclave.

Normalized concentration-time profiles for HPA-Ta

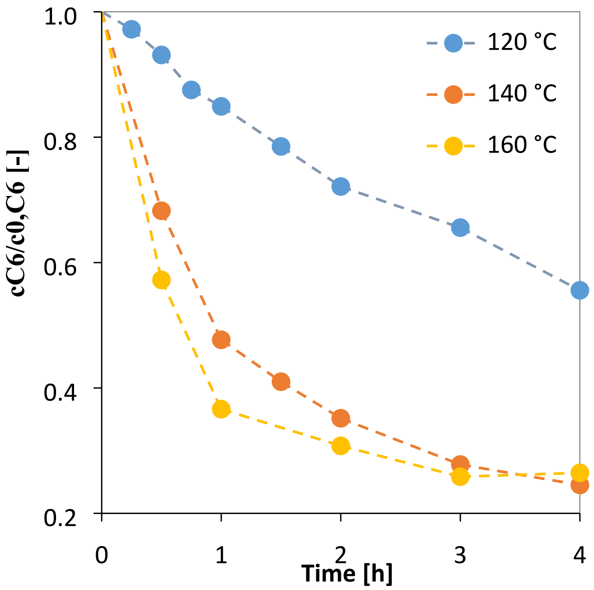


Figure S14: HPA-Ta catalyst: Normalized concentration − time profiles for different reaction temperatures. Reaction conditions: 120-160 °C, 60 bar O2, 1000 rpm, 1 mmol HPA-Ta, 100 g water, 0.25 mol L-1 glucose, 4 h fed-batch, and high-pressure autoclave.

Normalized concentration-time profiles for HPA-Mo

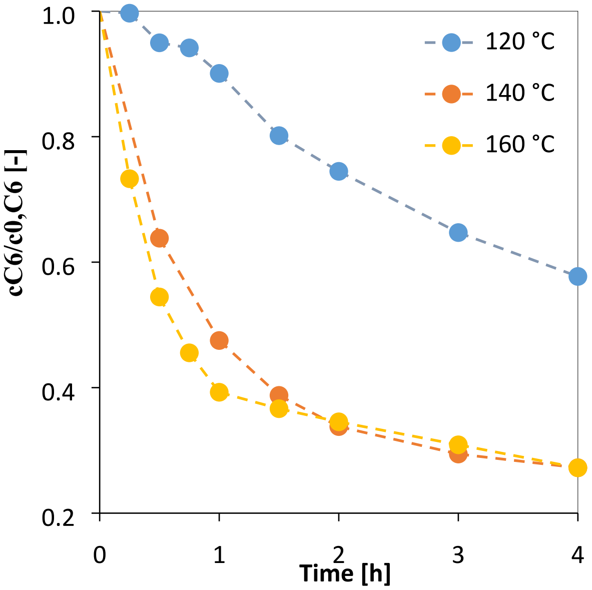


Figure S15: HPA-Mo catalyst: Normalized concentration − time profiles for different reaction temperatures. Reaction conditions: 120-160 °C, 60 bar O2, 1000 rpm, 1 mmol HPA-MO, 100 g water, 0.25 mol L-1 glucose, 4 h fed-batch, and high-pressure autoclave.

Determination of reaction orders

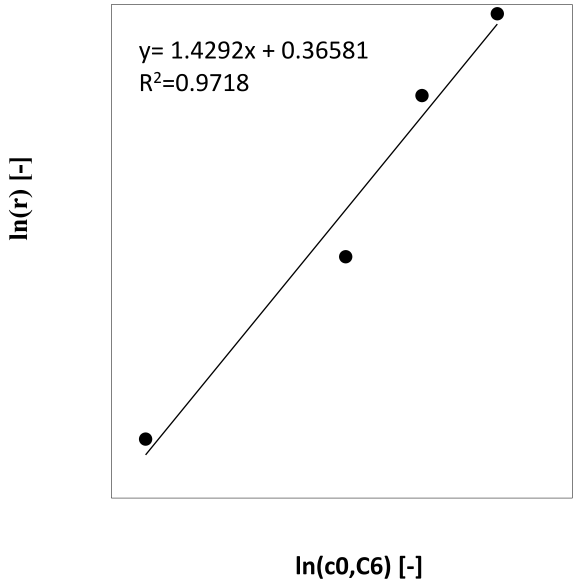


Figure S16: Logarithmic plot of the reaction rate vs the logarithm of the initial glucose concentration for the HPA-Nb catalyst. *Reaction conditions*: 160 °C, 60 bar O_2, 1000 rpm, 1 mmol HPA-Nb, 100 g water, 0.25-1.00 mol L^{-1} glucose, 4 h fed-batch, and high-pressure autoclave.

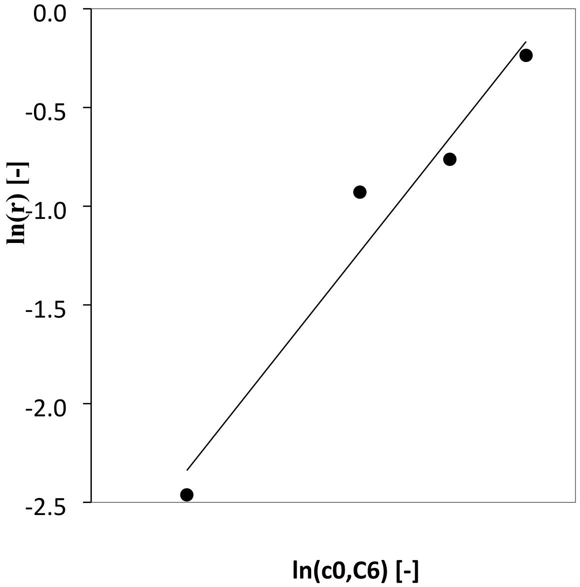


Figure S17: Logarithmic plot of the reaction rate vs the logarithm of the initial glucose concentration for the HPA-Ta catalyst. *Reaction conditions*: 160 °C, 60 bar O_2, 1000 rpm, 1 mmol HPA-Ta, 100 g water, 0.25-1.00 mol L^{-1} glucose, 4 h fed-batch, and high-pressure autoclave.

Reoxidation experiments within LCWM microreactor

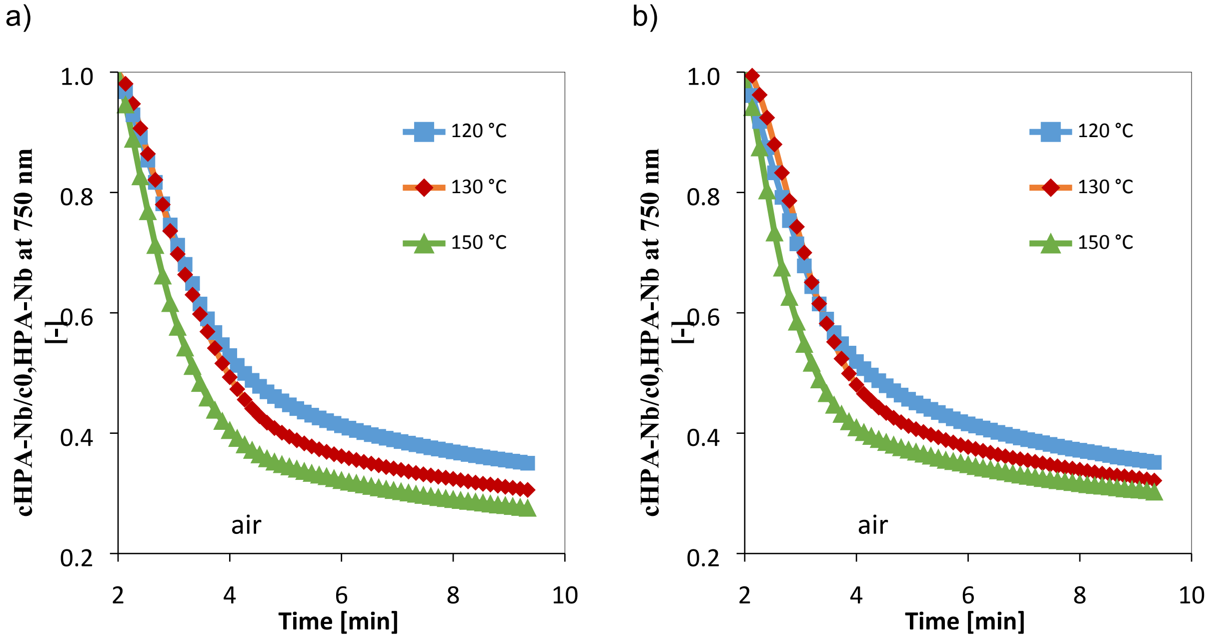


Figure S18: Normalized concentration-time profiles at 750 nm of the reoxidation of pre-reduced HPA-Ta (a) and HPA-Mo (b) catalysts. Reaction conditions: 80-140 °C, 5 bar synthetic air saturation, 11 µM pre-reduced HPA-Nb initial concentration, LCWM reactor.