Electronic Supporting Information

Heteropolyacids and Ruthenium on Covalent Triazine Frameworks – A Bifunctional Catalyst System for Bio-based Tandemsystems

Lea Hombach^a, Fabian Müller^b, Fulvio Varamo^c, Charles Otieno Ogolla^c, Benjamin Butz^c, Renée Hoffmann^d, Jonas Frohne^c, Holger Schönherr^d, Regina Palkovits^b, Anna Katharina Beine^{a,c*}

^{a.} Max Planck Institute for Chemical Energy Conversion, Stiftstr. 34–36,45470 Mülheim an der Ruhr (Germany)

^{b.} Institute of Technical and Macromolecular Chemistry RWTH Aachen University Worringerweg 2, 52074 Aachen (Germany)

^c Department of Mechanical Engineering, University of Siegen, Paul-Bonatz-Str. 9-11, 57076, Siegen (Germany) *E-mail: katharina.beine@uni-siegen.de*

Content

1	Expe	erimental	3
2	Recy	ycling of PTA/AC in Tandemsystem	5
3	N ₂ -F	Physisorption	5
4	FT-I	R Spectroscopy	6
5	N ₂ -Physisorption of recyceled PTA/CTF catalysts		6
6	TGA		7
7	FT-I	R Spectroscopy of Ru_PTA/CTF3	7
8 TEM /STEM Analyses		1 /STEM Analyses	8
	8.1	Particle Size Distribution Analysis	8
	8.2	Particle Size Distribution Analysis of Ru_PTA/CTF3 Recycled	10
9	Lite	rature	10

1 Experimental

Chemicals

If not stated otherwise, chemicals were used as delivered. Xylan (>95 %), phosphotungstic acid hydrate, ethanol (≥99.8 %), and potassium bromide were purchased from Carl Roth and Ru/C 5wt% was purchased from Sigma Aldrich. The activated carbon (AC) was provided by Silcarbon Aktivkohle GmbH.

Analytical Methods

Nitrogen physisorption experiments were conducted on a Micromeritics ASAP 2060 instrument. Samples were *in-situ* degassed at 200 °C for 5 h using the MicroPrep device. Static volumetric measurements were carried out at 77 K. The specific surface area of each sample was determined by the Brunauer-Emmet-Teller (BET) method in the range of $0.05 \le p/p_0 \le 0.3$. For the analysis of the total pore volume, the highest relative pressure points $p/p_0 = 0.98$ were used.

TGA analyses were conducted in N2 (50 mL min-1) using a Netzsch STA 449 F5 Jupiter device.

Fourier-transform infrared spectroscopy (FTIR) measurements were conducted over a spectral range of 400-4000 cm⁻¹ using an IR Affinity-1S device of Shimadzu. For measuring of carbon samples, 1 mg of carbon material was pestled with 500 mg of dried KBr and pressed into a pellet.

Aqueous solutions of catalytic reactions were filtered and analyzed by HPLC using a LC-10AD VP Shimadzu system with refractive index detector (column: CS-chromatography organic acid resin, eluent: Trifluoroacetic acid in water (154 μ L/L). Leaching of the immobilized HPA catalysts was investigated by XRF on a Spectro Xepos C. The PTA-loading was determined by means of inductively coupled plasma optical emission spectrometry (ICP-OES) on an Arcos Spectro system.

A Thermo Fisher (FEI) Talos F200X transmission electron microscope (TEM) was utilized to collect the bright-field (BFTEM), high-angle annular dark-field (HAADF) scanning TEM (STEM) (HAADF-STEM) images, STEM tomograms as well as energy-dispersive X-Ray (EDX) spectra. The microscope was operated at an acceleration voltage of 200 kV. STEM-HAADF images, used for particle size distribution analyses were analyzed using the open-source software FIJI¹ (for detailed description see 8.1). STEM-EDXS analyses were performed using Thermo Fisher Velox[®] software to calculate the element-specific net intensities (Ru, W, P, C) while 3D-tomographic SIRT-reconstruction was carried out using Thermo Fishers Inspect3D[®] software.

Preparation of CTF1-3

CTFs were prepared under ionothermal conditions in molten ZnCl₂ with a molar ZnCl₂/monomer ratio of 5:1. The salt/monomer mixture was sequentially heated in sealed quartz ampules at 400 °C (10 h; 10 °C min⁻¹) and 600 °C (10h; 10 °C min⁻¹). The obtained monolith was washed according to Bavykina et al..² The CTFs were ballmilled at 30 Hz for 5 min using a Fritsch Pulverisette 23 (15 mL jar & 1x 15 mm ball; hardened stainless steel).

Immobilization of PTA on CTF1-3

1.3 g of phosphotungstic acid was diluted in 8 mL of a 1:1 volumetric EtOH:H2O solution. Then, 1 g of CTF support was added and the mixture was stirred at 60 °C for 16 h. The PTA-loaded carbon was separated by centrifugation and washed until pH 7 and dried at 90 °C for 24 h.

Immobilization of Ruthenium on PTA/CTF3

RuCl₃·xH₂O (0.032 mmol, 6.71 mg) and 400 mg of CTF3 (400 mg) were dispersed in 100 mL ethanol. The suspension stirred at 60 °C. After 16 h the solvent was evaporated using a rotation evaporator and the catalyst was dried at 80 °C. Catalyst reduction under hydrogen took place for 3 h at 250 °C (6 L h⁻¹) using a heating rate of 8 K min⁻¹.

Catalysis

The hydrolytic hydrogention of xylan was performed in 10 mL stainless steel autoclaves equipped with a glas inlet. In a typical experiment, the autoclave was charged with the CTF supported catalyst ($c(PTA) = \ddot{o}4.35 \text{ mmolL}^{-1}$) and 5wt% Ru/C (25 mg). Then a solution of 115 mg xylan in 5 mL H2O was added and the autoclave was pressurized with 50 bar H₂. Standard experiments were performed at 130 °C for 2 h while stirring with a magnetic stirring bar at 750 rpm. After the reaction mixture was cooled down, the autoclave was depressurized and the reaction mixture it was filtered through a syringe filter and analyzed by HPLC.

For recycling experiments, the catalyst was recovered by centrifugation and washed with H_2O (4 x 5 mL). To start a recycling run, new substrate-solution was added (115 mg xylan in 5 mL H2O) and the procedure was repeated.



2 Recycling of PTA/AC in Tandemsystem

Fig. S1 Blind experiments to the recycling of PTA/AC in the hydrolytic hydrogenation of xylan (conditions: 130 °C, 2 h, 50 bar H₂, 750 rpm, m(Xylan) = 0.115 g, c(HPA) = 4.35 mmol/L, m(Ru/C 5wt%), V(H₂O) = 5 mL)

3 N₂-Physisorption



Fig. S2 N₂-Physisorption isotherms of AC and CTF1-3.

4 FT-IR Spectroscopy

Fig. S3 FT-IR Spectroscopy of PTA/CTF1-3 before and after recycling.



5 N₂-Physisorption of recyceled PTA/CTF catalysts



Fig. S4 $\mathsf{N}_2\text{-}\mathsf{Physisorption}$ isotherms of PTA/CTF1-3 after recycling.





Fig. S5 TGA of PTA/CTF1-3 before and after recycling.

7 FT-IR Spectroscopy of Ru_PTA/CTF3

Fig. S6 FT-IR spectroscopy of Ru_PTA/CTF3 after reduction at 250 °C.







Fig. S7: XPS analysis of fresh Ru_PTA/CTF3.

9 Substrate Scope – cellobiose



Fig. S8: Cellobiose conversion *X*, sorbitol yield *Y*, glucose yield *Y* and PTA-Leaching in the reaction of Ru_PTA/CTF3 in the hydrolytic hydrogenation of cellobiose (conditions: 130 °C, 4 h, 50 bar H₂, 750 rpm, m(cellobiose) = 29 mg, $m(Ru_PTA/CTF3) = 25 \text{ mg}, V(H_2O) = 1 \text{ mL})$.

10 TEM /STEM Analyses

10.1 Particle Size Distribution Analysis Ru_PTA/CTF3



Fig. S9: Particle size distribution analysis steps; a.) Scaling; b. - c.) ROI segment selection; d.) Bandpass filter to flatten intensity inhomogeneities; e.) thresholding; f.) Particle detection; g.) Overlay of detected particles on threshold image; h.) Particle size distribution analysis histogram with normal distribution curve

The open source software, FIJI was used to carry out the particle size distribution analysis and involved the following steps (c.f Fig. S7):

a.) Image was first calibrated and scaled

b-c.) A representative region of interest was selected and cropped

- d.) A bandpass filter was applied to flatten the image intensities
- e.) A threshold was applied to the grayscale image

f.) The particle sizes were then measured by applying an adapted circularity value thereby defining the ellipticity and perimeter of the detected particles, a value subsequently used to calculate particle diameter.

g.) The quality of edge detection was tested by overlaying the detected particles in (v) by the threshold image in (iv)

h.) A histogram of the particle size diameter calculated from the circumference of the particles in (iv) was plotted and a normal distribution curve overlayed. The mean particle size distribution and standard deviation parameter values were then extracted from these plots.

10.2 Particle Size Distribution Analysis of Ru_PTA/CTF3 Recycled



Fig. S10: Particle Size Distribution analyses of Ru_PTA/CTF3; Top) HAADF-STEM micrograph and corresponding histogram and normal distribution plot (left) for analyses of majority, narrowly distributed Ru particles with average particle diameter of 1.3 nm; Bottom) HAADF-STEM image used for particle size analyses of large coalesced particles with mean diameters even up to 5.5 nm with corresponding particle size distribution histogram and a normal distribution curve overlayed.

10.3 EDX mapping of Ru_PTA/CTF3 Recycled



Fig. S11: HAADF-STEM image (a) and (b) corresponding energy-dispersive X-ray spectroscopy (EDXS) analyses (net intensity distributions of Ru, W, P and Ru+W color map) after recycling.

10.4 Particle Size Distribution Analysis of Ru_C Recycled



Fig. S12: Particle size distribution analyses of recycled Ru_C; a - c) Overview HAADF-STEM micrographs and corresponding histogram and normal distribution plot; d) for analyses of majority, narrowly distributed Ru particles with average particle diameter of 1.3 nm.



11 XPS Analysis – spent catalyst

Fig. S13: XPS analysis of spent Ru_PTA/CTF3 after 6 recycling experiments.

12 Literature

- 1 J. Schindelin, I. Arganda-Carreras, E. Frise, V. Kaynig, M. Longair, T. Pietzsch, S. Preibisch, C. Rueden, S. Saalfeld, B. Schmid, J.-Y. Tinevez, D. J. White, V. Hartenstein, K. Eliceiri, P. Tomancak and A. Cardona, *Nature Methods*, 2012, **9**, 676-682.
- 2 A. V. Bavykina, M. G. Goesten, F. Kapteijn, M. Makkee and J. Gascon, *ChemSusChem*, 2015, **8**, 809-812.