Supporting Information

Is water a suitable solvent for the catalytic amination of alcohols?

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Experimental

Materials

For catalyst impregnation the following support materials and chemicals were used as received: Activated carbon (Cabot Norit A Supra EUR), titanium dioxide (Saint-Gobain), zirconium dioxide (Saint-Gobain), cerium dioxide (Sigma-Aldrich 99.9 %), ethanol (Chemsolute, 99.5 %), ruthenium(III)chloridehydrate (39 – 42 % Ru; abcr, 99.9 % (Ru)), rhodium(III)chloridetri hydrate (Chempur 99.95 %), palladium(II)chloride (Degussa 99.9 %), gallium(III)nitrate (Chempur, 99.9 %), indium(II)acetate (Sigma-Aldrich, 99.99 %) , iron(III)chloride (Merck 98 %), nickel(II)chloride (abcr, 99.5 %), tin(IV)acetate (Sigma-Aldrich, 95 %), bismuth chloride (Sigma Aldrich, 98%).

Hydroxyapatite was synthesized by the method of S. Wuyts.[1] A solution of ammonia bisulfate solution (125 mL, 7.9 mg $(NH_4)_2HPO_4$ (Sigma-Aldrich, 99.9 %), pH = 11, 10 ml aq. NH_3 25 wt.-%) was added dropwise to a calcium nitrate solution (23.6 mg $Ca(NO_3)_2 \cdot H_2O$ (Fluka, Sigma-Aldrich, 98 %), 50 mL H_2O, 2 mL aq. NH_3 25 wt.-%). The sample was stirred for 2 h at room temperature and additionally heated under reflux for 1 h. The product was centrifuged and re-dispersed in 30 mL of H_2O and freeze dried.

The ion exchange was performed with 1 g of hydroxyapatite and 124.7 mg $RuCl_3 \cdot H_2O$. The compounds were stirred in 45 mL of H_2O. The working up was done via centrifuging and freeze drying.

Catalytic Experiments

The following chemicals for the catalytic experiments were used as received: Aqueous ammonia solution (25 wt-%; Sigma-Aldrich, Reag. Ph. Eur.), isomannide (abcr, 98 %), ethanol (Chemsolute, 99.5 %), cylcohexanol, propane-1,2-diol (Sigma-Aldrich, 99 %), propane-1,3-diol (Sigma-Aldrich 98 %), butane-1,4-diol (Sigma-Aldrich, 99.5 %), butane-2,3-diol (Sigma-Aldrich, 98 %), pentane-1,5-diol (Sigma-Aldirch, 99 %), hexane-1,6-diol (Sigma-Aldrich, 97 %), ruthenium on carbon (5 wt-%; Aldrich)

Analytical Methods

The GC-Method was the same as used by R. Pfützenreuter and M. Rose.[2] 20 µL of the sample and 10 µL of the analytical standard (dodecane) were added to 0.5 mL of pyridine before 10 µL chlorotrimethylsilane (Fluka (Sigma-Aldrich)), 99.0 %) and 0.575 µL N-Methyl-N-(trimethylsilyl)trifluoro acetamide (Sigma-Aldrich, suitable for silylation) were added. For the reaction the sample was heated for 1 h at 80 °C.

GC-Analyses were performed with a Focus GC (Thermo Scientific) and a Rtx-1 Pona column (50 m).

For the inductive coupled plasma optical emission spectroscopy (ICP-OES) the device ICP Spectroflame D from the company Spectro was used. The procedure for investigating the solid ruthenium catalysts is the following: The catalyst (30 mg) is dissolved by digesting it in molten KNO_3 (0.12 g) and KOH (1 g). Afterwards it is dissolved in hydrochloric acid.

Quantitative ^1H-NMR spectra were measured with a Bruker Avance 400 in D_2O (Aldrich, 99.9 %). The conversions X of the hydroxyl groups were calculated via the integrals of $\mathbf{H}_x$-C-O (3.2 – 3.8 ppm) and $\mathbf{H}_x$-C-N (2.3 – 2.8 ppm) according to the following equation:

$$X = 1 - \frac{A\,(H_x - C - O)}{A\left(H_x - C - O\right) \;+\; A\,(H_x - C - N)}$$

Powder X-Ray Diffraction (XRD) patterns were collected using a Siemens D5000 diffractometer with Cu kα rays in the range of 3-90° 2θ.

The XPS measurements were carried out at the DWI Leibniz Institute for Interactive Materials, Aachen.

STEM and EDX measurements were done by the Gemeinschaftslabor für Elektronenmikroskopie GFE of RTWTH Aachen University.

Reference:

1 S. Wuyts, D. E. De Vos, F. Verpoort, D. Depla, R. De Gryse and P. A. Jacobs, *J. Catal.*, 2003, **219**, 417-424.

2 R. Pfützenreuter and M. Rose, *ChemCatChem*, 2016, **8**, 251-255.

Additional Figures

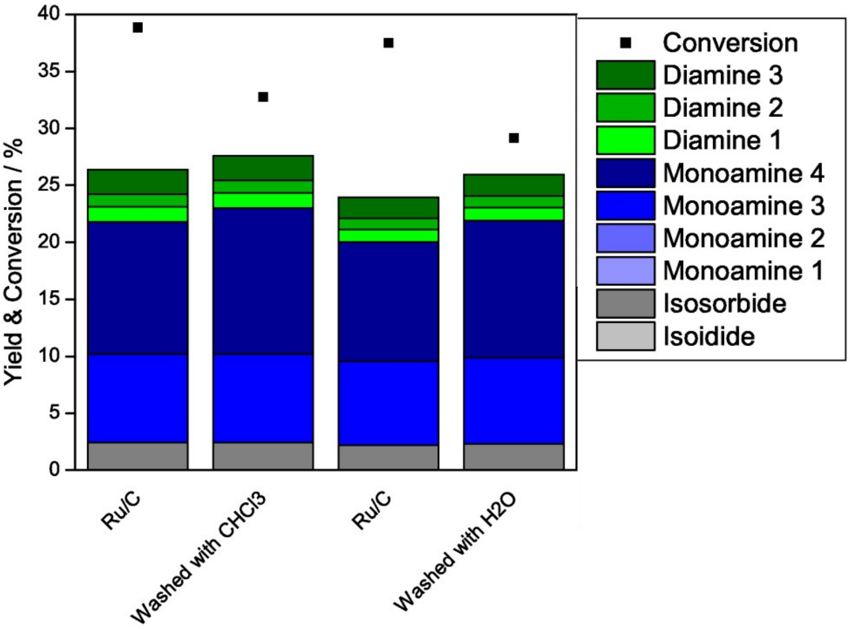

Figure S1 Washing of the spent catalyst by refluxing it for 1 h in water or chloroform, respectively, showed the influence on the incomplete mass balance by adsorbed substrate and product species.

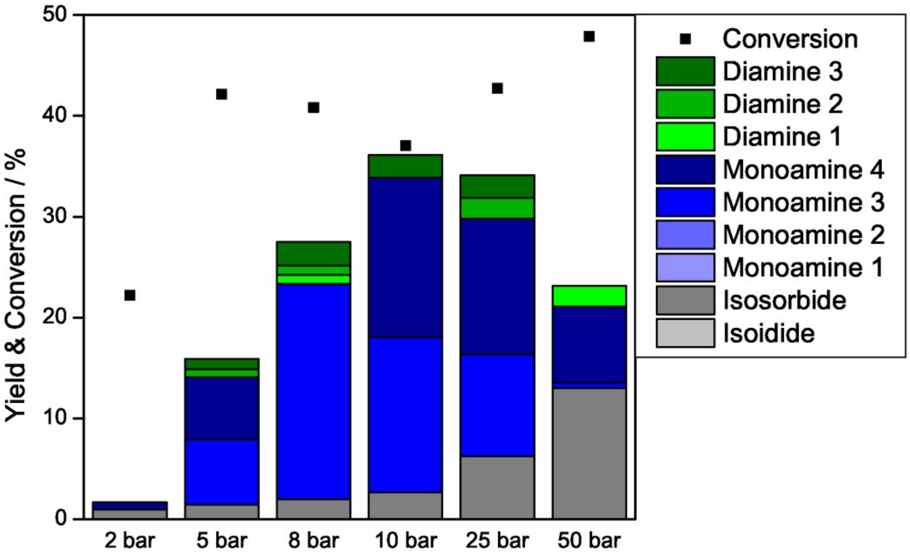

Figure S2 Pressure dependence of the amination reaction catalysed by the commercial Ru/C catalyst.

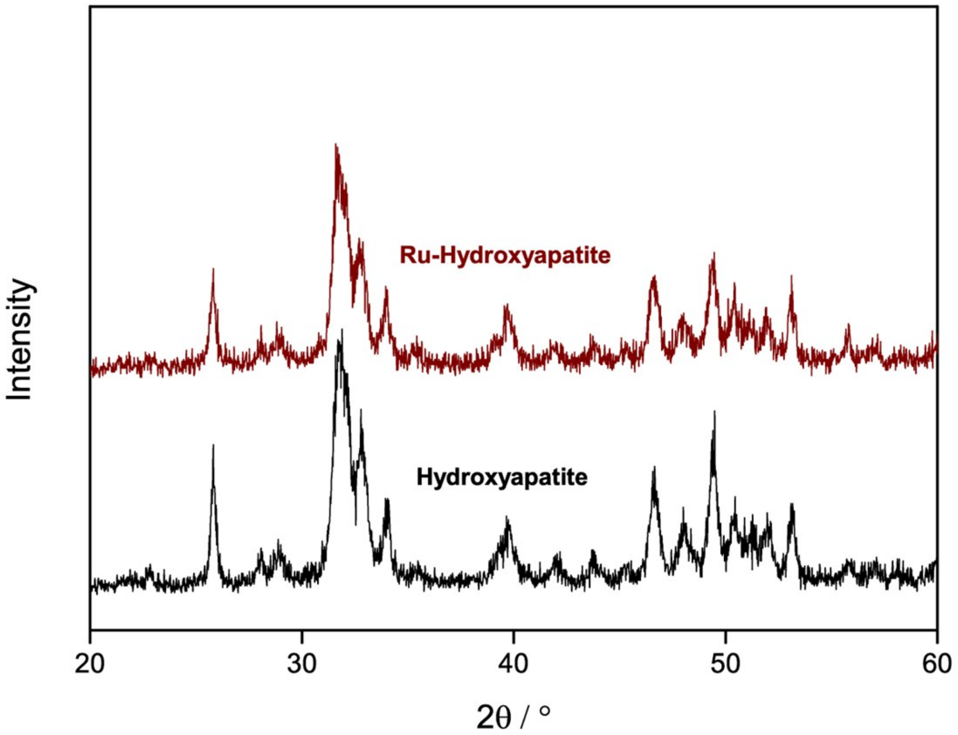

Figure S3 Powder XRD pattern of the synthesized hydroxyapatite (bottom) and the confirmation of the hydroxyapatite structure after the ion exchange with Ru^{3+} (top).

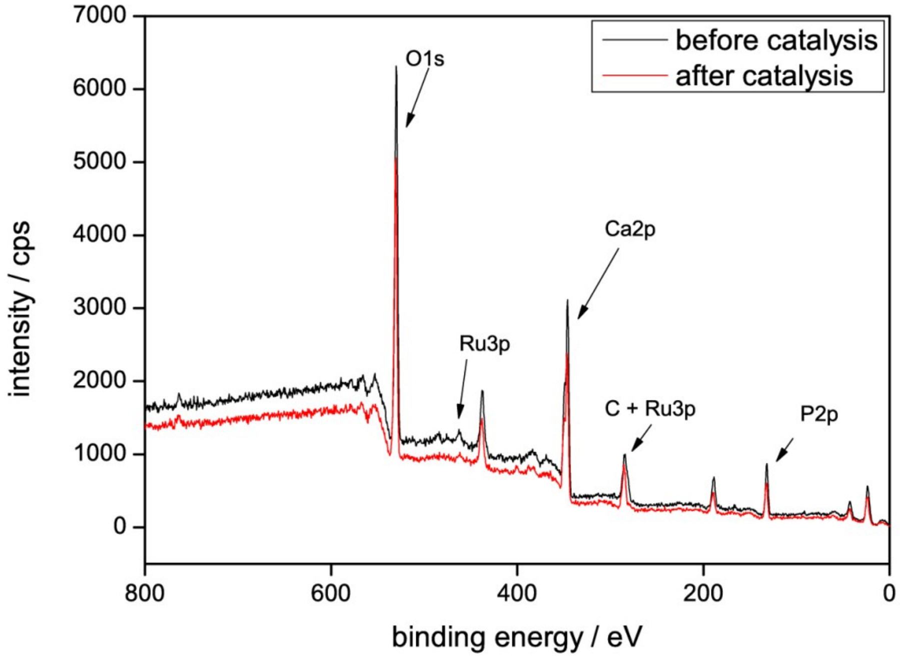

Figure S4 XPS spectra of a Ru/hydroxyapatite catalyst before (black) and after (red) catalysis.

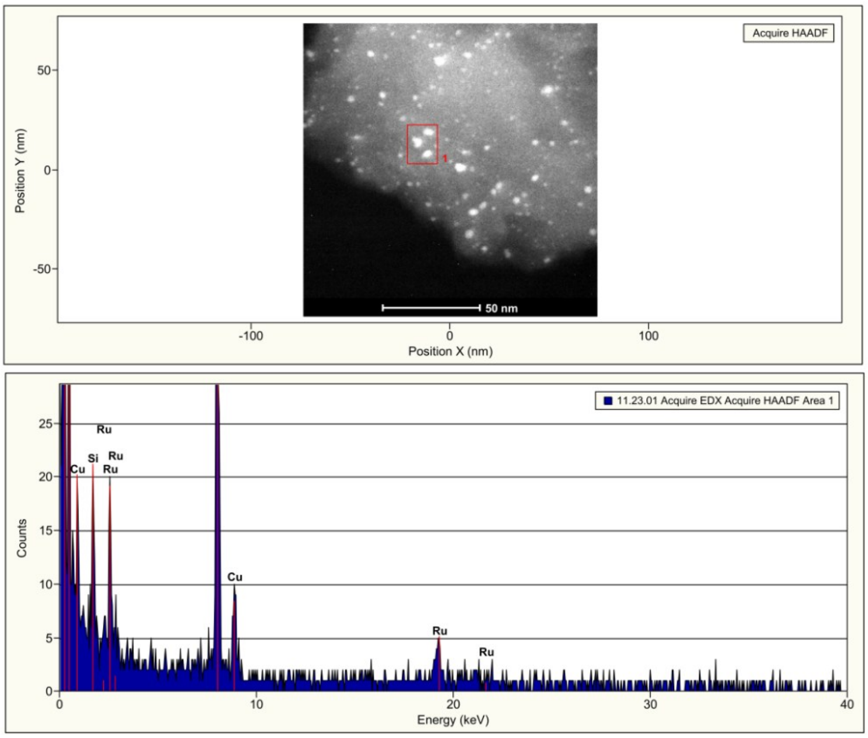

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Figure S5 HAADF-STEM of the Ru(2.4)Pd(2.0)/C catalyst (top) and EDX spectroscopic analysis. Copper signals are an artefact of the Cu grid used as sample support.

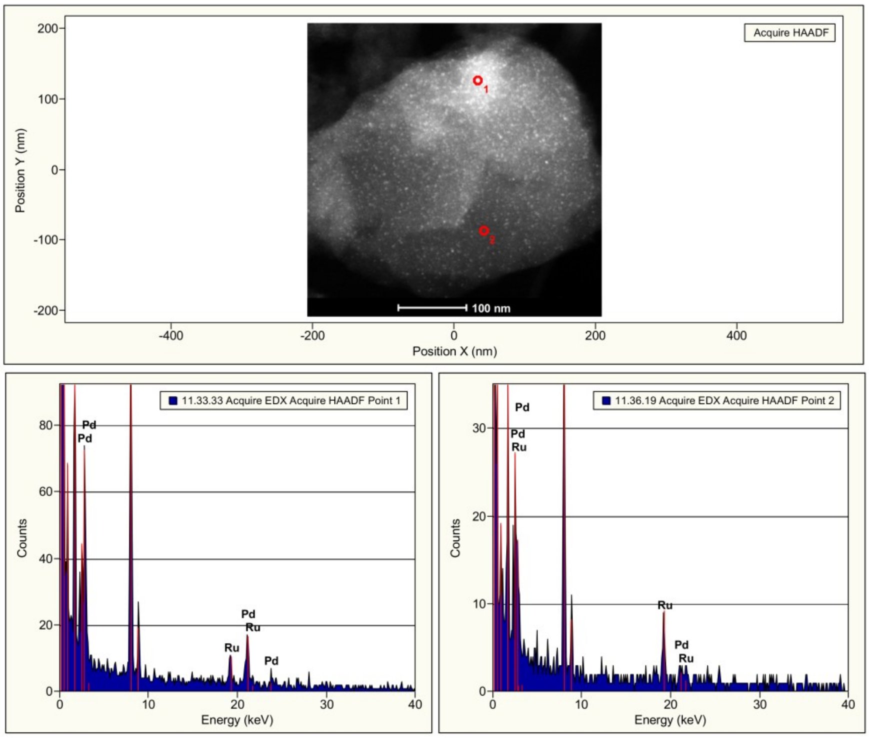

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Figure S6 HAADF-STEM of the Ru(2.4)Pd(2.0)/C catalyst (top) and EDX spectroscopic analysis. Copper signals are an artefact of the Cu grid used as sample support

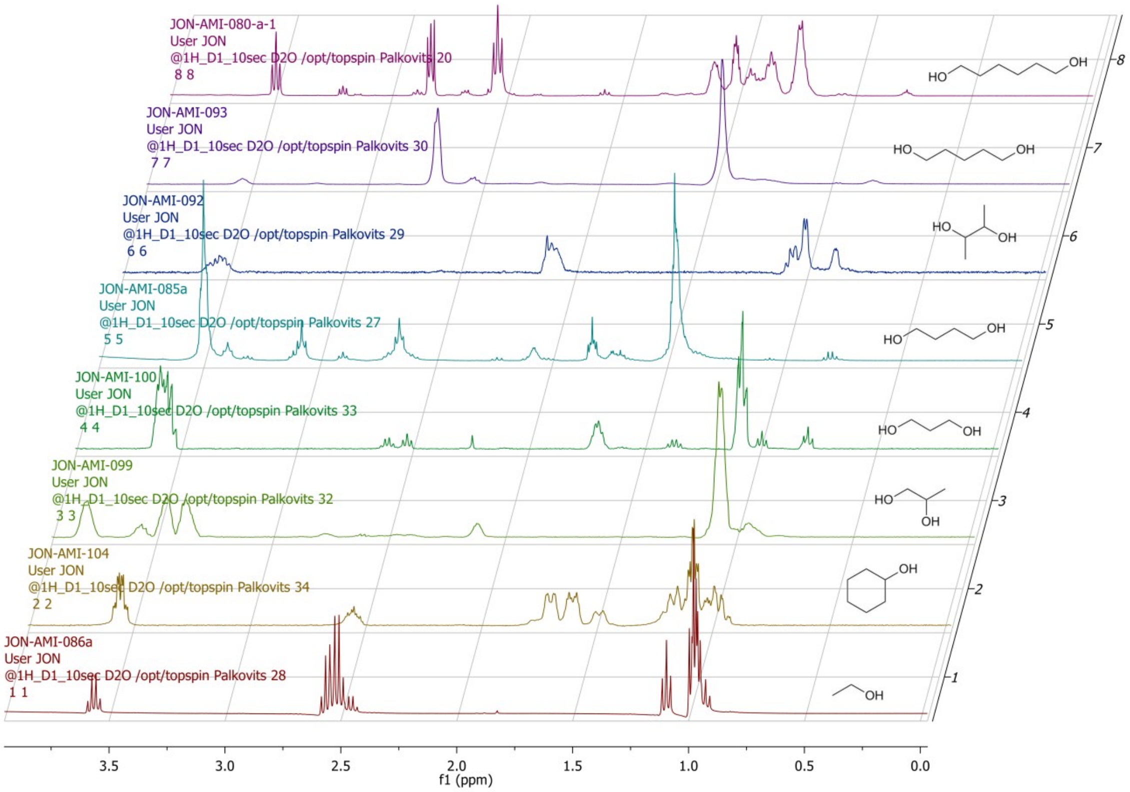

Figure S7 ^{1}H NMR spectra of the amination reaction with various alcohols. $H_{(1,2,3)}$C-OH signals 3.2 – 3.8 ppm and $H_{(1,2,3)}$C-N signals 2.3 – 2.8 ppm (2 mol-% Ru/C, 170 °C, 6 h) .

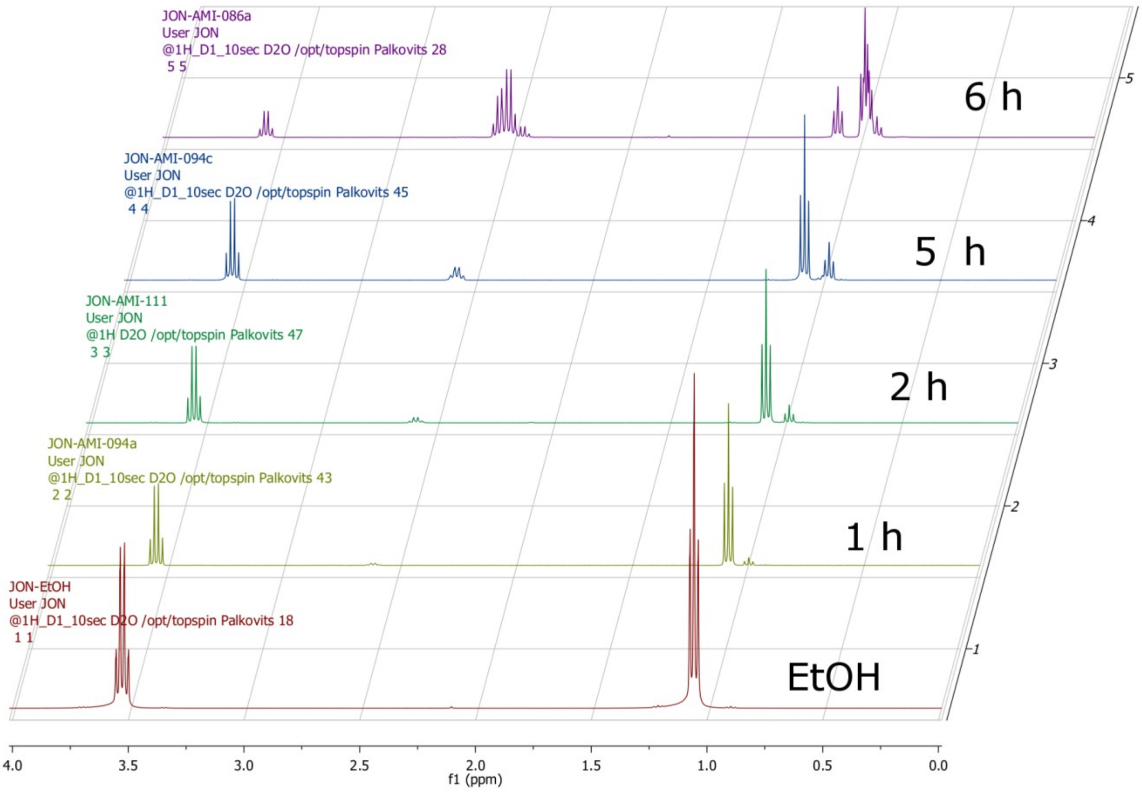

Figure S8 ^{1}H NMR spectra of the amination reaction of EtOH. H_2C-OH signals 3.6 ppm and H_2C-N signals 2.6 ppm.