Isosorbide Synthesis from Cellulose with Efficient and Recyclable Ruthenium Catalyst

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Contents

General experimental details

Materials: Microcrystalline cellulose (MCC), Ru/C (5 w-% of Ru), glucose and sorbitol were purchased from Sigma Aldrich and used as received. 1,4-Sorbitan, 2,5-sorbitan and 1,5-sorbitan were purchased from Carbosynth and used as received. Bagasse pulp (BP, 95.37 w-% of cellulose and 4.63 w-% of lignin) and dissolving pulp (DP) were obtained from Stora Enso.

General procedure for isosorbide synthesis from cellulose: Cellulosic substrate (1.18 mmol of cellulose, using M=162.145 g/mol as the molar mass of the cellulose) and Ru-catalyst (5 w-% of Ru, 0.02 mmol of Ru) were weighed and placed into a glass insert. If the Ru-catalyst was recycled it was ground to powder before the use. The aqueous solution of sulfuric acid with desired concentration (30 ml) was added to the glass insert. Next, the glass insert was placed into an autoclave, which was closed and placed into a heating mantle. The autoclave was pressurised with appropriate gas with vigorous magnetic stirring. The heating was turned on and the autoclave was heated for chosen time at chosen temperature. After desired time, the autoclave was cooled to room temperature, the pressure gas was released and opened. The reaction solution was filtered with glass filter to separate the catalyst and the products. The second step of the reaction was conducted with the gathered filtrate after the catalyst separation. Generally the reaction solutions were analysed with the following procedure: the reaction solution was diluted to 50 ml with milli-q water. An aliquot of 1 ml of the solution and the internal standard (citric acid) was diluted to 10 ml with milli-q water. From this solution 2 ml was taken and filtered through ion exchange resin (Phenomenex, Strata-C-X 33u Polymeric Strong Cation 30 mg/1 ml) and analysed with high-performance liquid chromatography (HPLC).

HPLC Analysis: The reaction product yields were determined with HPLC using refractive index detector (RID) using citric acid as an internal standard. The analysis was conducted with Agilent Technologies 1200 Series HPLC equipped with Phenomenex Rezex ROA – Organic Acid H+ (8%) (300×7.80 mm) column using 5 mM H_2SO_4 aqueous solution as an eluent with the flow rate of 0.35 ml/min. The yields and concentrations of the analytes were determined using a five point calibration curves.

Synthesis of the catalysts: The activated carbon support was sulfonated with the procedure described by Foo *et al.*[1] First 3 g of activated carbon (Norit SX, Sigma Aldrich) was weighed and placed into a 50 ml round bottom flask. To this flask 37.5 ml of H_2SO_4 (10 M or concentrated) was added. The flask was heated at 110 °C for 30 minutes or 3 hours. After the heating the sulfonated carbon was filtered and washed with milli-q water until the water was neutral. The sulfonated carbon was then dried for 16 hours at 80 °C. The dried carbon was ground to fine powder and placed into a glass insert of Roth S30. To the glass insert 40 ml of milli-q water was added, and the insert was placed into an autoclave, which was then heated at 200 °C for 16 hours. After the heating the washed sulfonated carbon was filtered and washed with water until the washing solution was neutral. Then the sulfonated carbon was dried in oven at 80 °C.

The ruthenium was added by impregnation as described by Komanoya *et al.*[2] One gram of the sulfonated carbon was weighed and mixed with 20 ml of milli-q water. 105.9 mg of $RuCl_3 \bullet xH_2O$ (Sigma Aldrich, 47.22 w-% of ruthenium; 5 w-% of Ru on the sulfonated carbon) was dissolved into 5 ml of milli-q water, which was then added dropwise to the sulfonated carbon mixture. This mixture was then mixed at room temperature for 18 hours. After the mixing the water was evaporated using rotary evaporator and further dried *in vacuo* overnight. The precatalysts were treated in oven under reductive or oxidative conditions follows:

i) Reduction of ruthenium(III) to ruthenium (0) resulted in metallic Ru/C catalysts when heated at 400 °C for 2 h under forming gas atmosphere (5% H_2 / 95% N_2). After the required time the oven was cooled to room temperature under forming gas atmosphere.

ii) Partially oxidized RuO_x/C catalysts were acquired by heating the precatalyst 2 h at 400 °C under forming gas, after which the oven was cooled to 290 °C and the atmosphere was changed to air and cooled to room temperature.

TEM analysis: TEM micrographs were obtained with JEM-2800 operated at 200 kV acceleration voltage in bright field mode. TEM samples were prepared by grounding the catalyst as a fine powder, which was dispersed in acetone, followed by dropcasting 0.1 mg/mL dispersion (5 µL) of the sample on Quantifoil R 2/1 Holey carbon film (Cu 200 Mesh). The excess solvent was blotted with filter paper and let to evaporate to dry. The TEM-pictures were processed using Gatan Microscopy Suite Software, to obtain the data for the mean particle analysis.

XRD analysis: X-ray diffractograms were measured with PANalytical X'Pert Pro MPD diffractometer in Bragg-Brentano geometry using programmable slit optics and PIXcel detector in 1D mode. ICDD reference cards 6-663 (Ru) and 40-1290 (RuO_2) were used to qualitatively evaluate the Ru and RuO_2 content in the samples.

Boehm-titration: The acid types and concentrations were determined with Boehm-titration. The titrations were conducted by first adding 375 mg of sulfonated sample into 12.5 ml of 0.025 M NaOH(aq) and $NaHCO_3$(aq). The slurries were stirred for 24 hours, after which the sulfonated carbon was filtered. An aliquot of 10 ml was collected from the filtrate. Then 20 ml of 0.025 M HCl(aq) was added to the collected aliquot. The solutions were back titrated to end point of pH 7.00 with 0.05 M NaOH(aq) solution using Metrohm 907 Titrando machine equipped with Metrohm 800 Dosino dosing device.

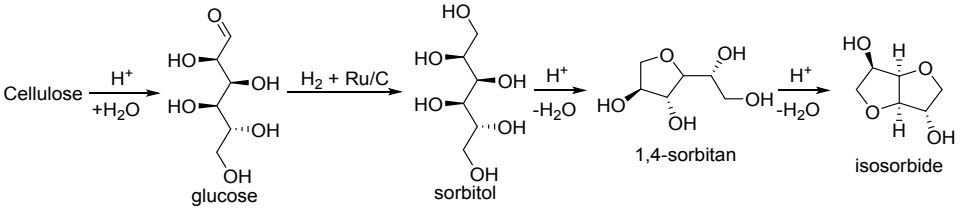
XPS analysis: X-ray photoelectron spectroscopy was performed using an Argus Spectrometer (Omicron NanoTechnology GmbH, Taunusstein, Germany) operating at a pass energy of 20 eV. Samples were prepared by molding catalyst powders onto ultra-high vacuum compatible aluminized polyimide adhesive tape. Measurements were done in a vacuum chamber with a base pressure below $1 \cdot 10^{-10}$ mbar, by illuminating the samples with X-rays emitted from a standard Mg source (K alpha line) at a photon energy of 1253.6 eV. Binding energies were calibrated using the main C 1s peaks associated with C-C/C-H and C-O states (284.8 and 286.6 eV), and peak fitting was done using the CasaXPS software (www.casaxps.com).

SEM analysis: SEM-EDS measurements were done with an INCA 350 energy dispersive X-ray spectrometer (EDS) connected with a Hitachi S-4800 field emission scanning electron microscope (FESEM).

The amount of sulfur in the RuO_x/C_{10M3h} catalyst was studied using XPS and SEM-EDS. However, the amount of sulfur was below the detection limits of these analysis methods. The low amount of sulfur in the RuO_x/C_{10M3h} catalyst indicates that the majority of the sulfonic acids functionalities are decomposed during the heating (400 °C, 2 h, under forming gas) of the catalyst.

Optimization of one-step reactions

Table S1: *Major results from the optimization of the one-pot reactions.[a] The yields were determined with HPLC-RID.*



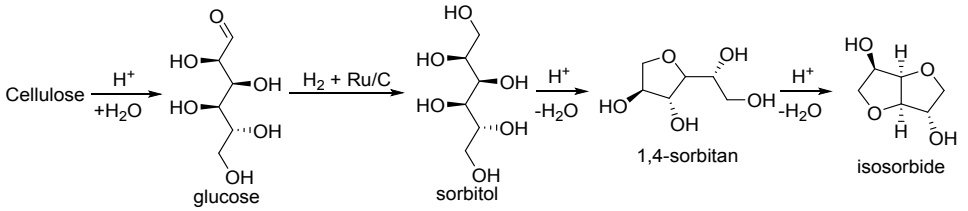
Entry #	Substrate	Acid	c(Acid) [mol/l]	Temp. [°C]	Time [h]	Catalyst	Isosorbide yield [%]
1	BP	H_2SO_4	0.5	220	2	Ru/C	50
2	BP	H_2SO_4	0.25	220	2	Ru/C	40
3	BP	H_2SO_4	0.1	220	2	Ru/C	26
4	BP	H_2SO_4	0.5	190	2	Ru/C	46
5	BP	H_2SO_4	0.5	170	2	Ru/C	20
6	BP	H_2SO_4	0.5	220	1	Ru/C	41
7	BP	H_2SO_4	0.5	220	4	Ru/C	47
8	BP	HOTf (Triflic acid)	0.5	220	2	Ru/C	29
9	BP	HCl	0.5	220	2	Ru/C	6
10	BP	TFA (Trifluoro acetic acid)	0.5	220	2	Ru/C	19
11	BP	Amberlyst-38	0.5	220	2	Ru/C	8
12	BP	HNO_3	0.5	220	2	Ru/C	0
13	MCC	H_2SO_4	0.5	220	2	Ru/C	51
14	DP	H_2SO_4	0.5	220	2	Ru/C	50
15	Glucose	H_2SO_4	0.5	220	2	Ru/C	60
16	Sorbitol	H_2SO_4	0.5	220	2	Ru/C	67
17 [b]	BP	H_2SO_4	0.5	220	2	2nd run Ru/C	0
18 [b]	MCC	H_2SO_4	0.5	220	2	2nd run Ru/C	0
19 [b]	DP	H_2SO_4	0.5	220	2	2nd run Ru/C	0
20 [c]	BP	H_2SO_4	0.5	220	2	Pt/C	0
21 [c]	BP	H_2SO_4	0.5	220	2	Pd/C	4
22 [c]	BP	H_2SO_4	0.5	220	2	Rh/C	4
23 [d]	Isosorbide	H_2SO_4	0.5	220	2	-	98
24 [d]	Isosorbide	H_2SO_4	0.5	220	4	-	95
25 [d]	Isosorbide	H_2SO_4	0.5	170	4	-	>99

[a] Reaction conditions: 40 bars of H_2, 30 ml of the acid solutions, 1.18 mmol of cellulose, 0.02 mmol of Ru (5 w-% Ru/C); [b] Reactions were conducted with the once used filtered Ru/C to see the recyclability of the catalyst, large quantities of levulinic acid and formic acid were detected with HPLC; [c] 0.02 mmol of metals (5 w-% metal/C) were used as hydrogenation catalysts; [d] 1.18 mmol of isosorbide.

Optimization of two-step reactions

First step studies

Table S2: *Major results from the optimization of the first step of the two-step reactions.[a] The yields were determined with HPLC-RID.*

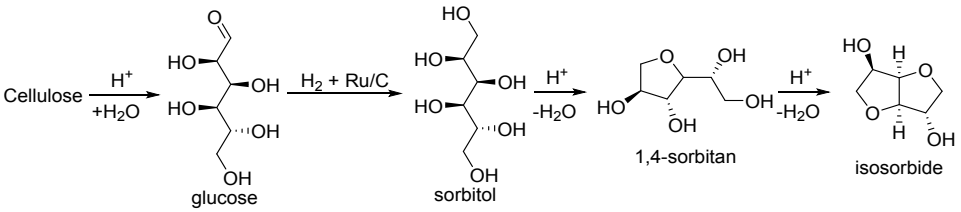


Entry #	Temp. [°C]	Time [h]	Substrate	Catalysts	H_2 pressure [bar]	1,4-Sorbitan + Sorbitol yield [%][b]	Isosorbide yield [%]	Glucose yield [%]
1	170	2	BP	Ru/C + 0.5 M H_2SO_4	20	55	4	0
2	170	2	BP	Ru/C + 0.5 M H_2SO_4	40	52	10	0
3	170	2	BP	Ru/C + 0.5 M H_2SO_4	10	40	5	11
4	170	2	BP	Ru/C + 0.5 M H_2SO_4	5	12	0	25
5	160 [c]	2	BP	Ru/C + 0.5 M H_2SO_4	20	47	0	0
6	170 [c]	2	BP	Ru/C + 0.5 M H_2SO_4	20	66	6	0
7	180 [c]	2	BP	Ru/C + 0.5 M H_2SO_4	20	51	17	0
8	190 [c]	2	BP	Ru/C + 0.5 M H_2SO_4	20	45	19	0
9	170	1	BP	Ru/C + 0.5 M H_2SO_4	20	30	0	0
10	170	4	BP	Ru/C + 0.5 M H_2SO_4	20	53	9	0
11	170	6	BP	Ru/C + 0.5 M H_2SO_4	20	39	20	0
12	170	1	BP	Ru/C + 0.25 M H_2SO_4	20	20	0	0
13	170	2	BP	Ru/C + 0.25 M H_2SO_4	20	44	0	0
14	170	4	BP	Ru/C + 0.25 M H_2SO_4	20	46	8	0
15	170	6	BP	Ru/C + 0.25 M H_2SO_4	20	47	11	0
16	170	1	BP	Ru/C + 0.1 M H_2SO_4	20	11	0	0
17	170	2	BP	Ru/C + 0.1 M H_2SO_4	20	19	0	0
18	170	4	BP	Ru/C + 0.1 M H_2SO_4	20	38	3	0
19	170	6	BP	Ru/C + 0.1 M H_2SO_4	20	46	5	0

[a] Reaction conditions: 1.18 mmol of cellulose, 30 ml of H_2SO_4 aqueous solution, 0.02 mmol of Ru (5 w-% Ru/C); [b] The signals of 1,4-sorbitan and sorbitol could not be separated with HPLC, the yield presented is the average of the calculated yields for pure 1,4-sorbitan and sorbitol; [c] Conducted using 2nd use Ru/C (0.02 mmol of Ru).

Second step studies

Table S3: *Major results from the optimization of the second step of the two-step reactions.[a] Prior to all of the second step reactions the first step was conducted under the optimized reaction conditions (170 °C, 0.5 M H_2SO_4, 20 bar H_2, 2h, using the 50mg of the 2nd Ru/C catalyst) The yields were determined with HPLC-RID.*

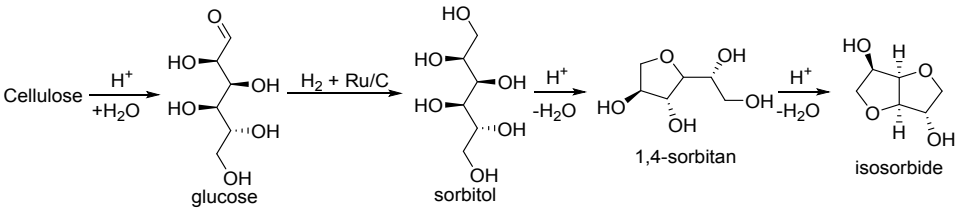


Entry #	Temp. [°C]	Time [h]	Substrate	Catalysts	H_2 pressure [bar][c]	1,4-Sorbitan + Sorbitol yield [%][b]	Isosorbide yield [%]
1	200	1	BP	Ru/C + 0.5 M H_2SO_4	40	62	7
2	200	2	BP	Ru/C + 0.5 M H_2SO_4	40	37	27
3	200	4	BP	Ru/C + 0.5 M H_2SO_4	40	20	41
4	200	5	BP	Ru/C + 0.5 M H_2SO_4	40	8	53
5	200	6	BP	Ru/C + 0.5 M H_2SO_4	40	4	54
6	220	1	BP	Ru/C + 0.5 M H_2SO_4	40	43	12
7	220	2	BP	Ru/C + 0.5 M H_2SO_4	40	5	44
8	220	4	BP	Ru/C + 0.5 M H_2SO_4	40	2	48
9	220	6	BP	Ru/C + 0.25 M H_2SO_4	40	2	36
10	240	1	BP	Ru/C + 0.25 M H_2SO_4	40	35	22
11	240	2	BP	Ru/C + 0.25 M H_2SO_4	40	0	47
12	260	1	BP	Ru/C + 0.25 M H_2SO_4	40	3	43
13	260	2	BP	Ru/C + 0.1 M H_2SO_4	40	0	37

[a] Reaction conditions: 1.18 mmol of cellulose, 30 ml of H_2SO_4 aqueous solution, 0.02 mmol of Ru (5 w-% Ru/C); [b] The signals of 1,4-sorbitan and sorbitol could not be separated with HPLC, the yield presented is the average of the calculated yields for pure 1,4-sorbitan and sorbitol; [c] Pressure was added to prevent the evaporation of the water from the used glass insert.

Ru/C recycling studies

Table S4: *Major results from the Ru/C recycling reactions.[a] The yields were determined with HPLC-RID.*



Entry #	Use of the Catalyst	Substrate	1,4-Sorbit. + Sorbitol yield [%][b]	Isosorbide yield [%]	1,5-Sorbit. yield [%]	2,5-Sorbit. yield [%]	Glucose yield [%]	Levulinic acid yield [%]
1	1st Ru/C	BP	55	4	3	7	0	0
2	2nd Ru/C	BP	66	6	3	8	3	0
3	3rd Ru/C	BP	20	7	2	0	15	0
4	4th Ru/C	BP	0	0	0	0	21	9
5	5th Ru/C	BP	0	0	0	0	16	29
6	1st Ru/C	MCC	52	6	5	6	0	0
7	2nd Ru/C	MCC	66	8	4	8	0	0
8	3rd Ru/C	MCC	69	7	4	7	0	0
9	4th Ru/C	MCC	66	8	4	8	0	0
10	5th Ru/C	MCC	68	8	4	8	0	0
11	1st Ru/C	DP	53	6	4	6	0	0
12	2nd Ru/C	DP	65	5	3	6	0	0
13	3rd Ru/C	DP	67	6	3	6	3	0
14	4th Ru/C	DP	67	5	3	6	4	0
15	5th Ru/C	DP	60	6	2	5	6	0
16	2nd Ru/C	-	3	0	0	0	0	0

[a] Reaction conditions: 1.18 mmol of cellulose, 30 ml of 0.5 M H_2SO_4 aqueous solution, 0.02 mmol of Ru (5 w-% Ru/C), 170°C, 20 bar H_2, 2 hours; [b] The signals of 1,4-sorbitan and sorbitol could not be separated with HPLC, the yield presented is the average of the calculated yields for pure 1,4-sorbitan and sorbitol.

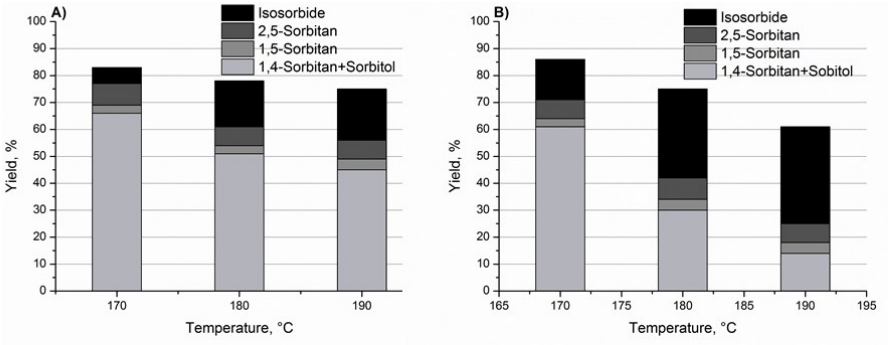


Figure S1: *The effect of reaction temperature and reaction time (**A)** 2 hours and **B)** 4 hours) on the product distribution in the first step using 2nd run Ru/C as catalyst and BP as a substrate.*

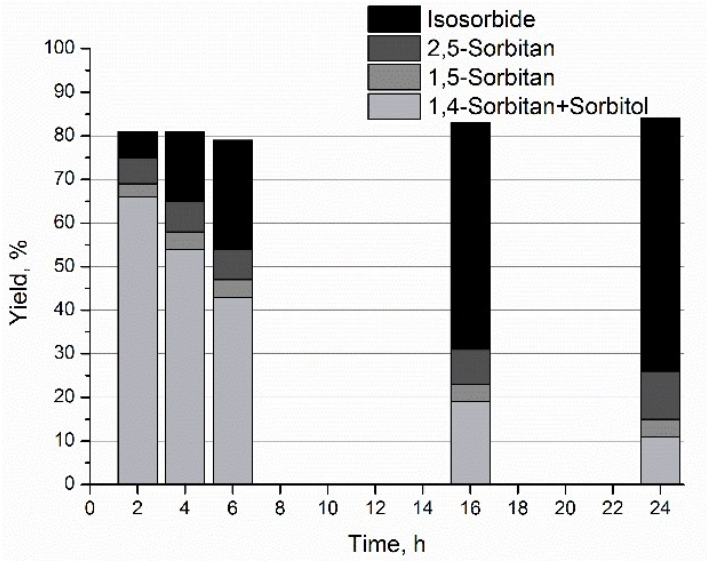
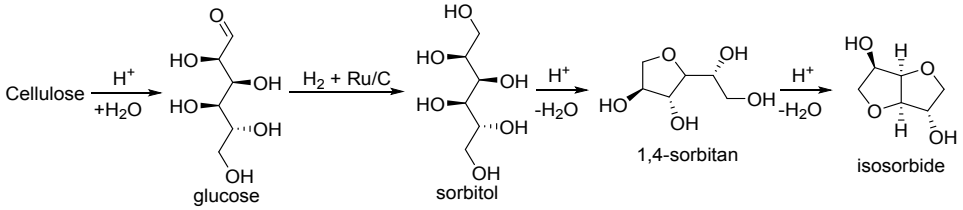


Figure S2: *The effect of reaction time on the product distribution at 170 °C (50 mg of 2nd use Ru/C (0.02 mmol of Ru), 30ml of 0.5 M H_2SO_4). BP used as a substrate. 2nd use catalyst was once used in the 2 hour 170 °C first step reaction.*

Table S5: *Major results from the 24 h reaction time Ru/C recycling reactions.[a] The yields were determined with HPLC-RID.*



Entry #	Use of the Catalyst	Substrate	1,4-Sorbit. + Sorbitol yield [%][b]	Isosorbide yield [%]	1,5-Sorbit. yield [%]	2,5-Sorbit. yield [%]	Glucose yield [%]	Levulinic acid yield [%]
1	1st Ru/C	BP	10	39	4	8	0	0
2	2nd Ru/C	BP	5	32	3	6	0	0
3	3rd Ru/C	BP	0	0	0	0	0	22
4	1st Ru/C	MCC	16	33	4	9	0	0
5	2nd Ru/C	MCC	11	30	3	6	0	0
6	3rd Ru/C	MCC	0	0	0	0	0	13
7	1st Ru/C	DP	11	36	4	6	0	0
8	2nd Ru/C	DP	5	29	3	6	0	0
9	3rd Ru/C	DP	0	0	0	0	0	17

[a] Reaction conditions: 1.18 mmol of cellulose, 30 ml of 0.5 M H_2SO_4 aqueous solution, fresh catalyst 0.02 mmol of Ru (5 w-% Ru/C), 170°C, 40 bar H_2, 24 hours; [b] The signals of 1,4-sorbitan and sorbitol could not be separated with HPLC, the yield presented is the average of the calculated yields for pure 1,4-sorbitan and sorbitol.

Catalyst Characterization

TEM-studies

Table S6: *Data obtained from TEM measurements.*

Sample	Average Particle Size	Number of particles measured	Minimum Particle Size	Maximum Particle Size
Ru/C (fresh commercial)	2.66	51	0.93	4.71
Ru/C (after first run BP)	3.10	53	1.53	5.95
Ru/C (after fifth run MCC)	2.98	64	1.31	8.73
$RuO_x/C_{10M30min}$ (fresh)	2.48	52	0.68	8.66
$RuO_x/C_{10M30min}$ (after fourth run BP)	4.87	41	3.06	9.89
$RuO_x/C_{10M30min}$ (after fourth run MCC)	4.84	44	1.41	7.70

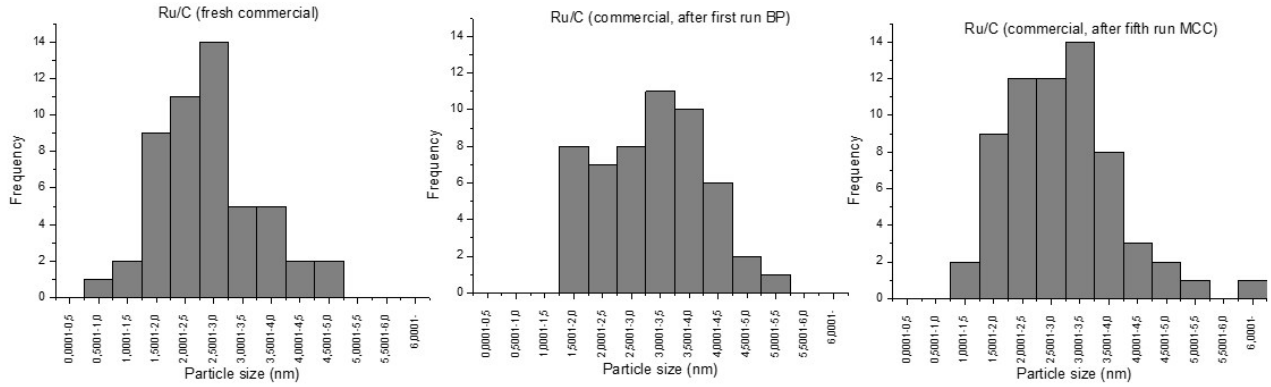


Figure S3: *Particle size distribution of commercial Ru/C.*

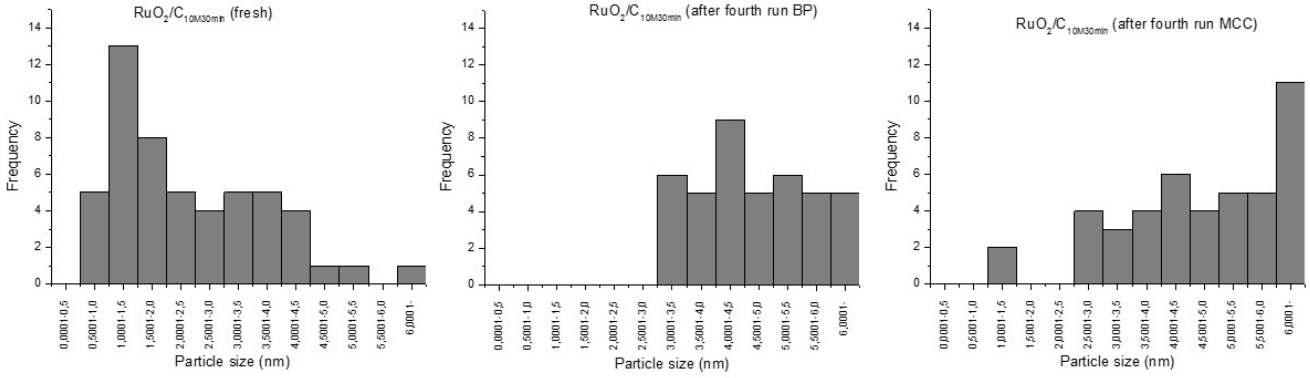


Figure S4: *Particle size distribution of $RuO_x/C_{10M30min}$.*

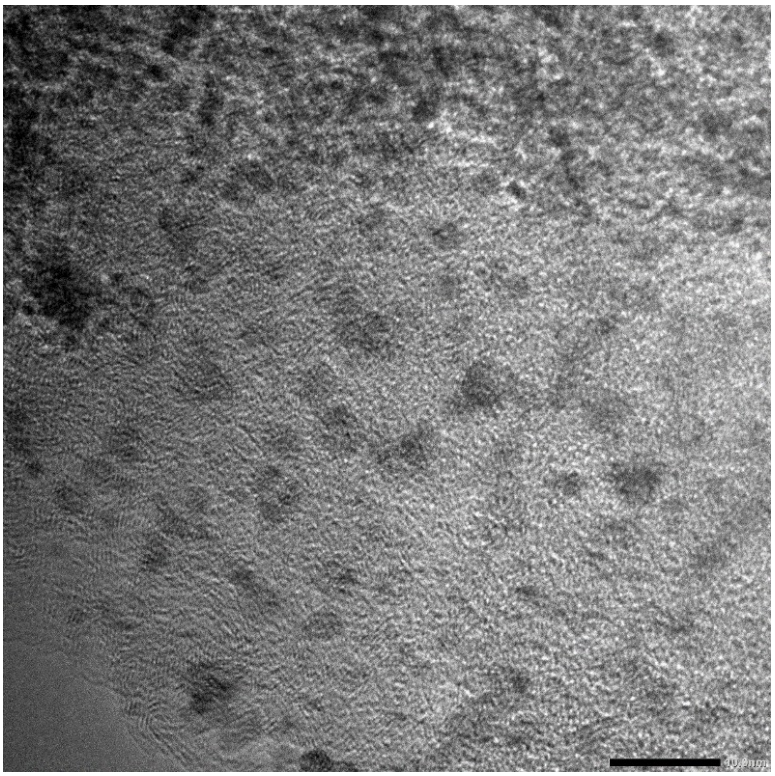


Figure S5: *TEM-image of the fresh commercial Ru/C. Scale bar 10 nm.*

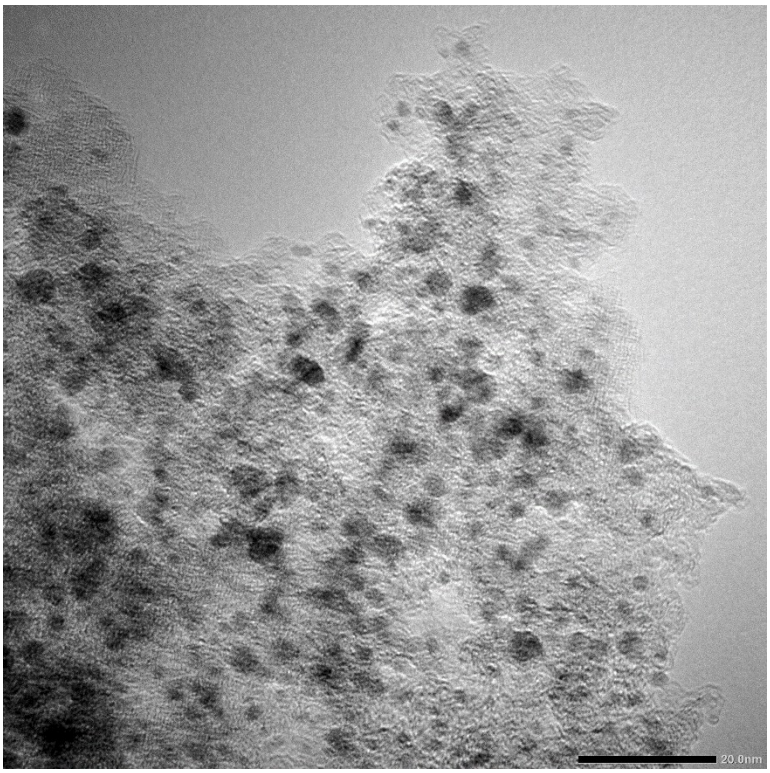


Figure S6: *TEM-image of the commercial Ru/C (after first run BP). Scale bar 20 nm.*

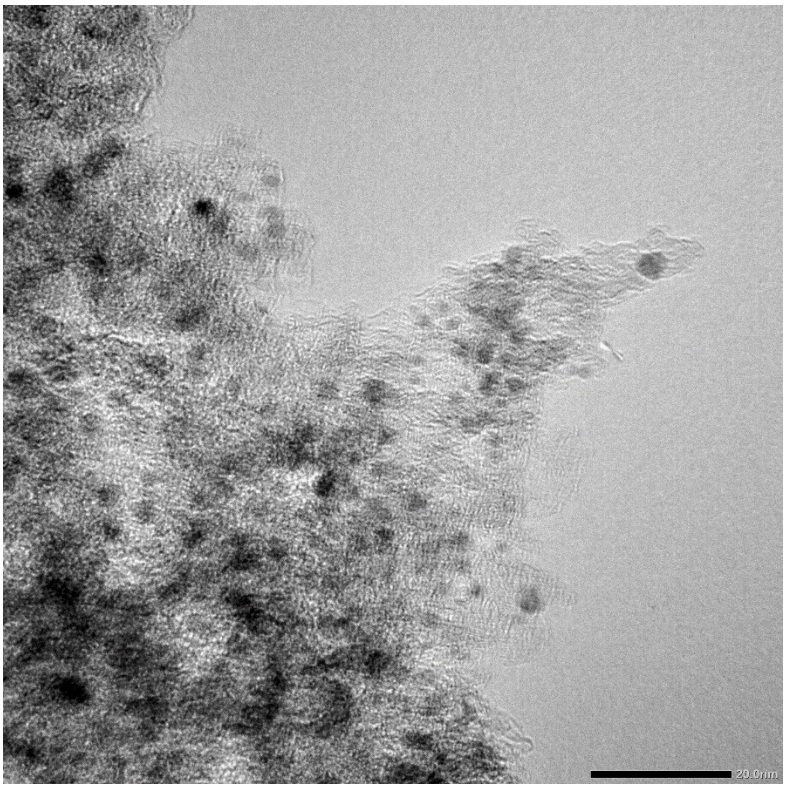


Figure S7: *TEM-image of the commercial Ru/C (after fifth run MCC). Scale bar 20 nm.*

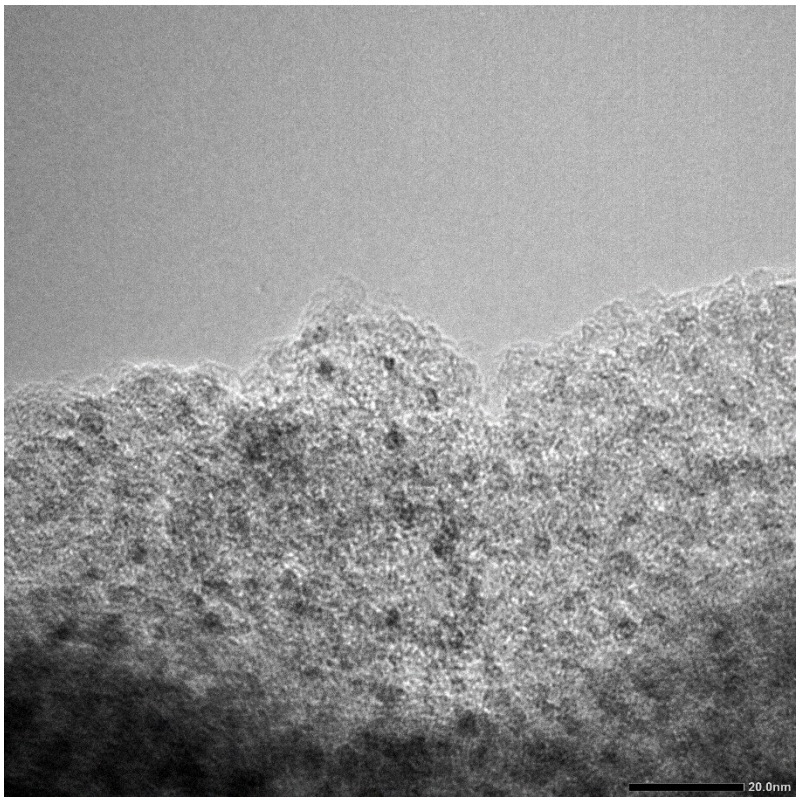


Figure S8: *TEM-image of the fresh $RuO_x/C_{10M30min}$. Scale bar 20 nm.*

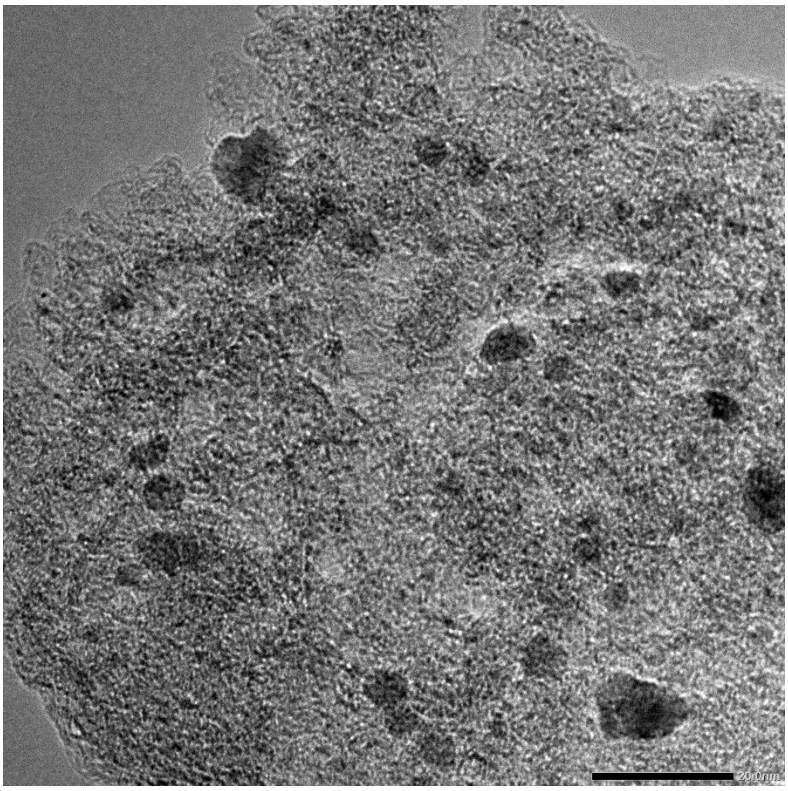


Figure S9: *TEM-image of the $RuO_x/C_{10M30min}$ (after fourth run BP). Scale bar 20 nm.*

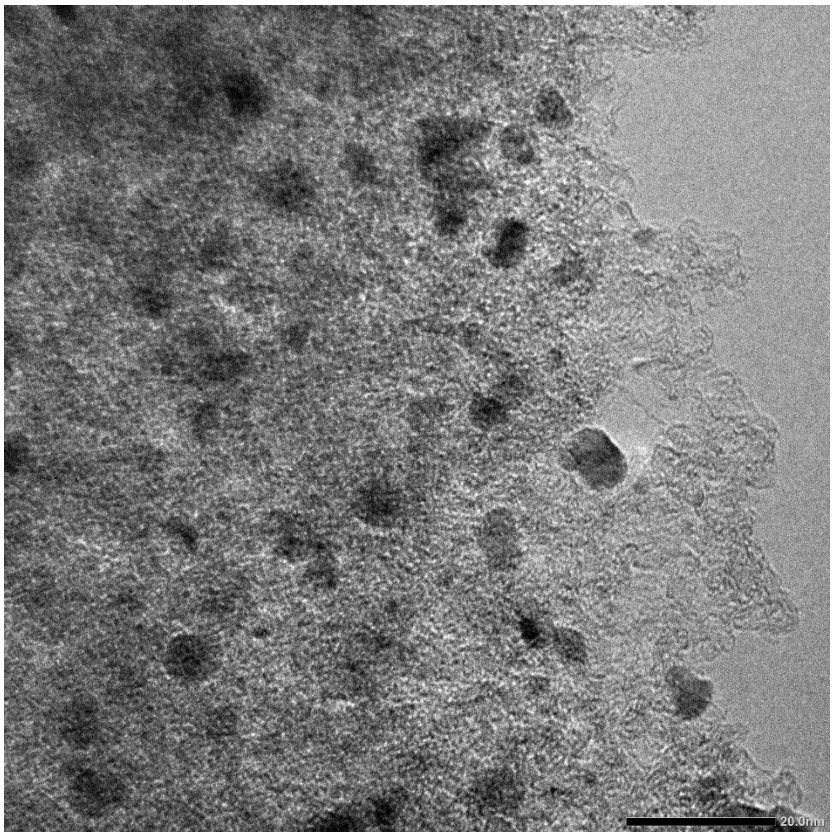


Figure S10: *TEM-image of the $RuO_x/C_{10M30min}$ (after fourth run MCC). Scale bar 20 nm.*

XRD- and XPS-analysis

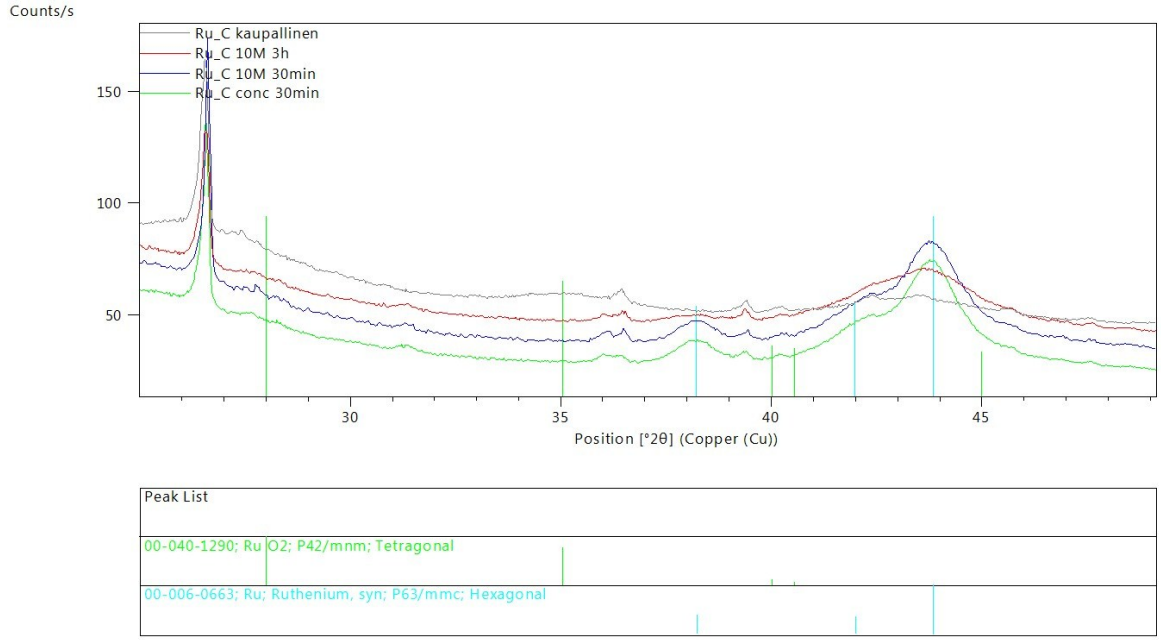


Figure S11: *XRD-diffractograms of the $Ru/C_{sulfonated}$ and commercial Ru/C catalysts. Commercial Ru/C (top), Ru/C_{10M3h} (second from the top), $Ru/C_{10M30min}$ (second from the bottom) and $Ru/C_{conc30min}$ (bottom).*

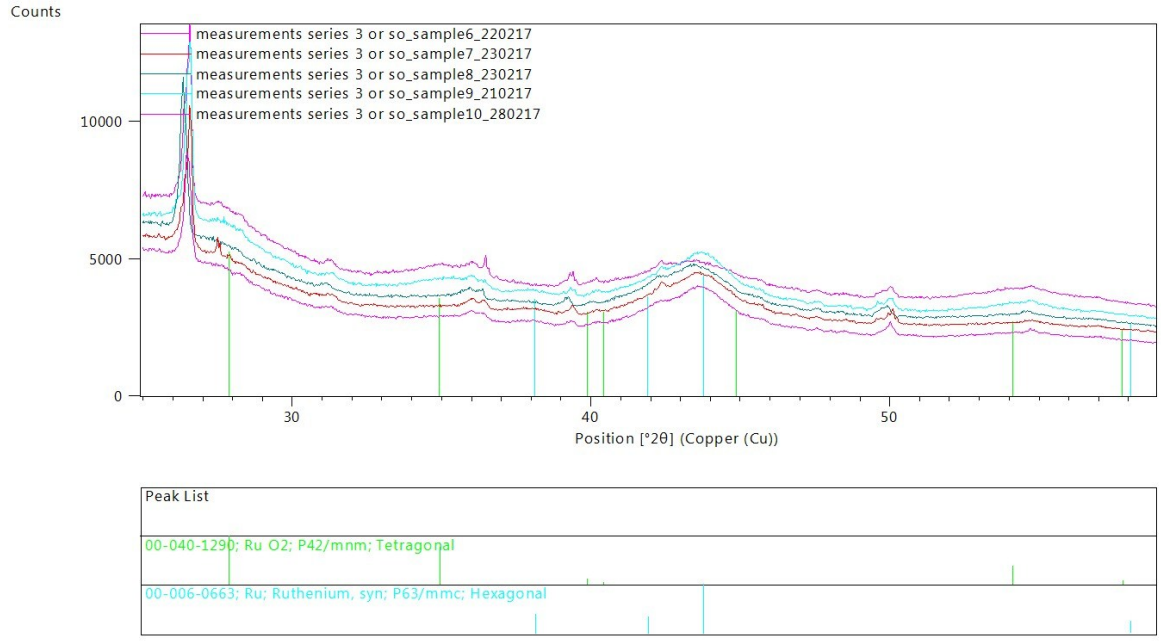


Figure S12: *XRD-diffractograms of the $RuO_x/C_{sulfonated}$ catalysts. Sample6 = $RuO_x/C_{conc30min}$ (top), Sample7 = RuO_x/C_{10M3h} (second from the top), Sample8 = RuO_x/C_{conc3h} (middle), Sample9 = $RuO_x/C_{NoritSX}$ (second from the bottom) and Sample10 = $RuO_x/C_{10M30min}$ (bottom)*

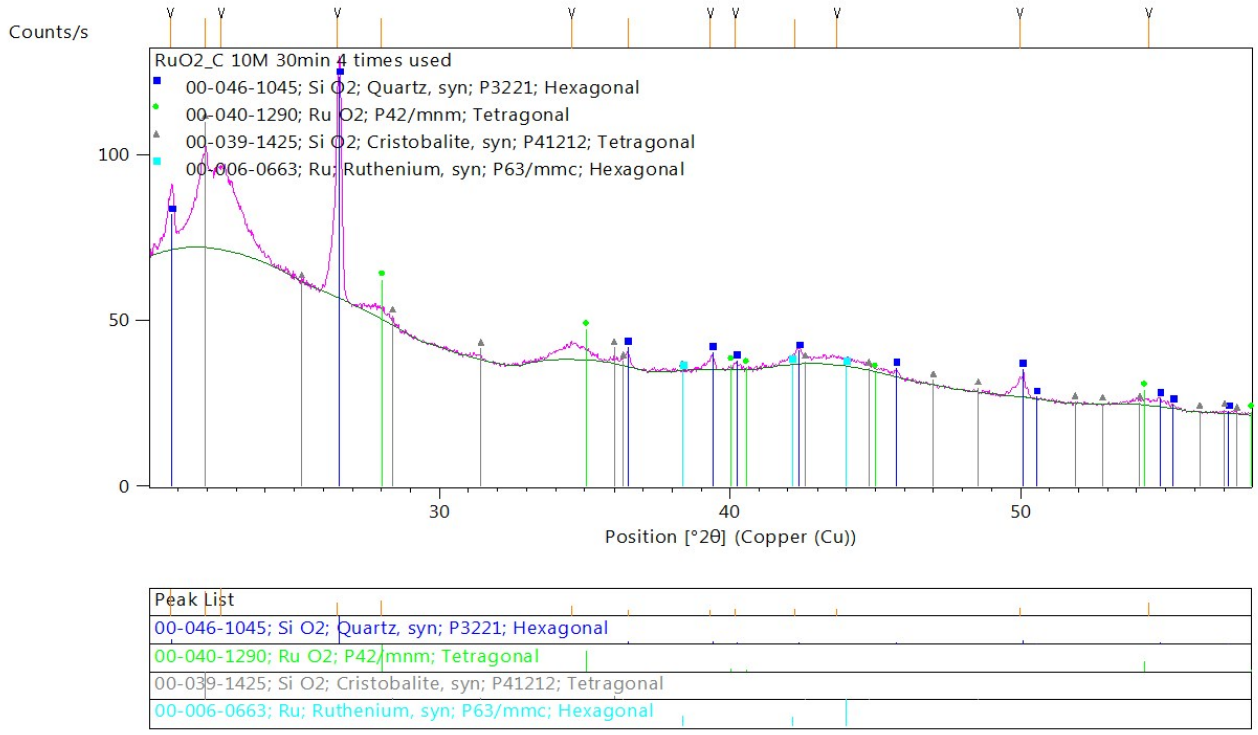


Figure S13: *XRD-diffractogram of four times used $RuO_x/C_{10M30min}$. Unknown substance visible at ~23°.*

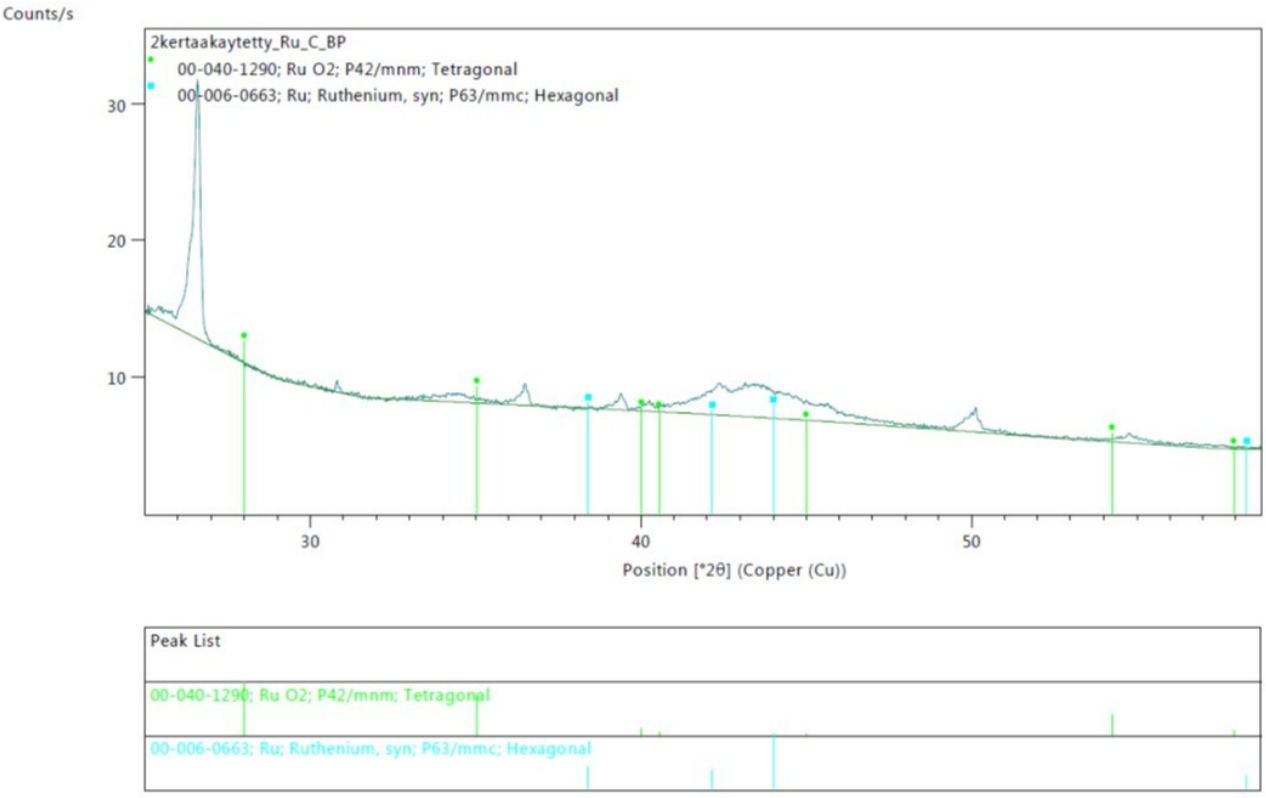


Figure S14: *XRD-diffractogram of two times used (BP as substrate) commercial Ru/C.*

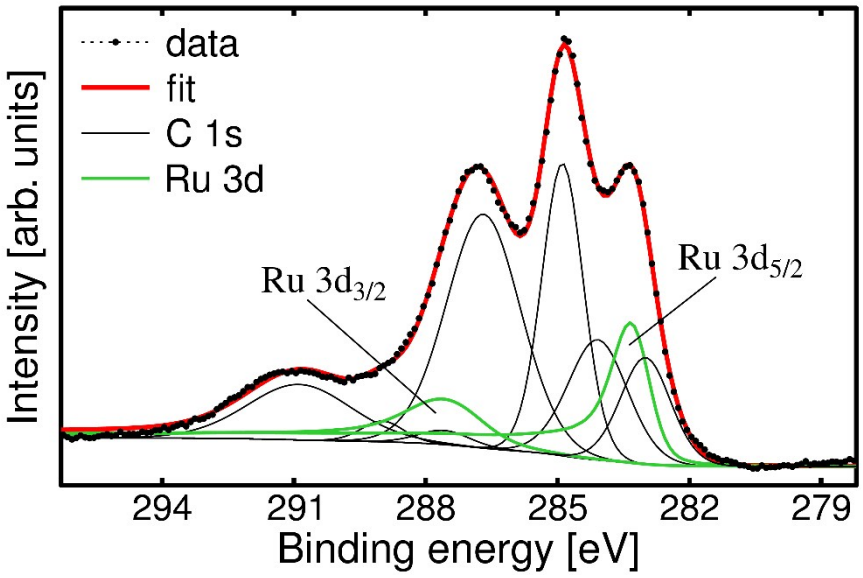


Figure S15: *XPS-spectrum of RuO_x/C_{10M3h}.*

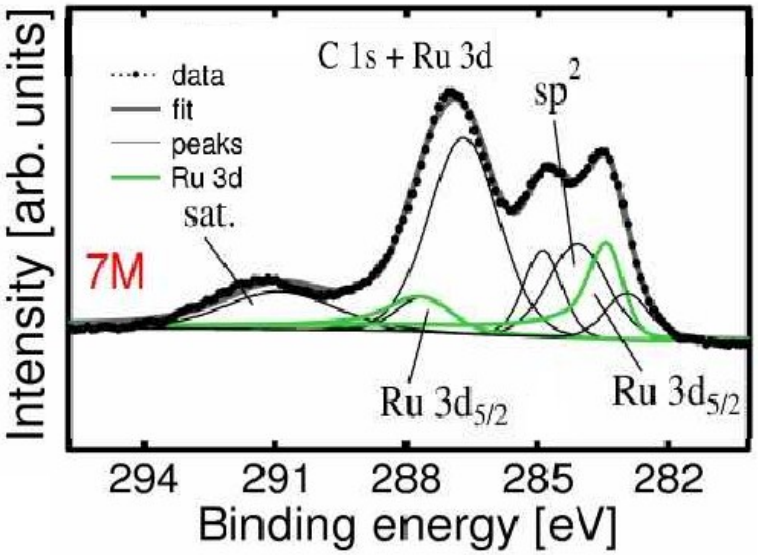


Figure S16: *XPS-spectrum of Ru/C_{10M3h}.*

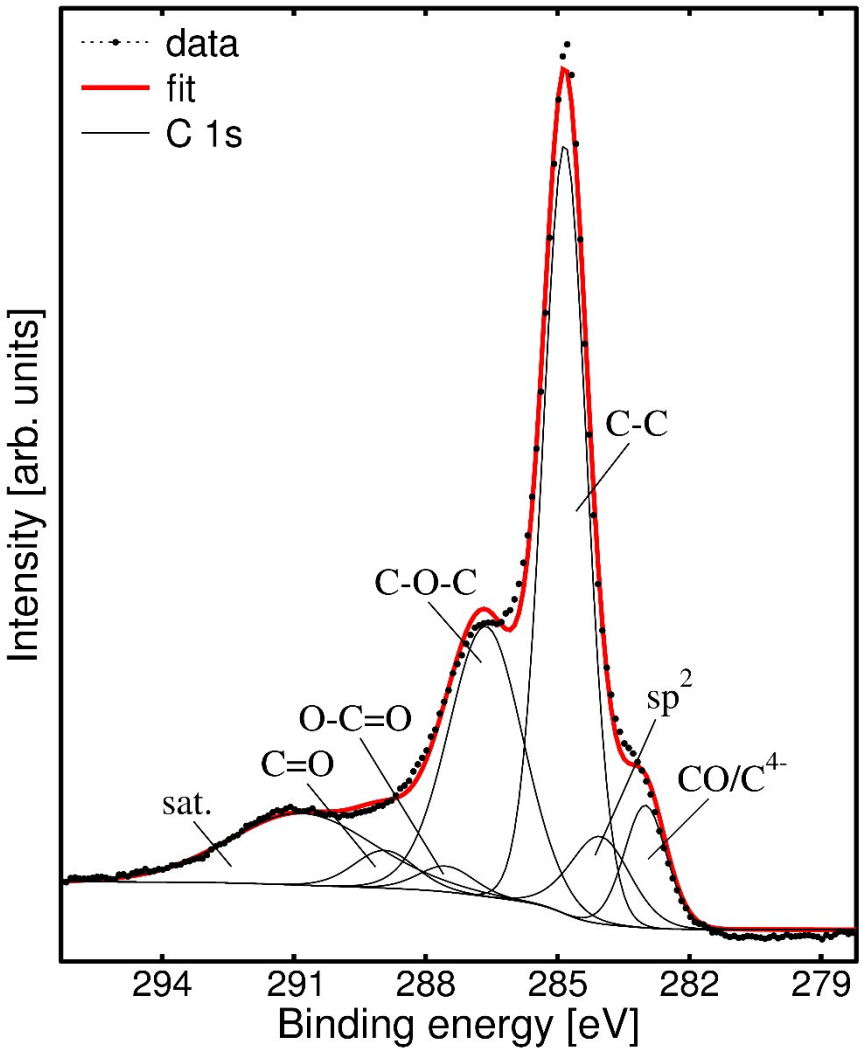


Figure S17: *XPS-spectrum of C_{10M3h}.*

Table S7: *Carbon bonding and the relative amounts of the functionalities.*

Sample	C-C (%)	C-O-C (%)	O-C=O (%)	C=O (%)	sp^2 (%)	sat. (%)	CO/C^{4-} (%)
RuO_x/C_{10M3h}	24.55	35.24	1.76	1.47	14.49	11.69	10.80
Ru/C_{10M3h}	10.60	44.36	0.82	6.11	18.00	13.51	6.61
C_{10M3h}	43.19	25.64	2.92	1.81	6.62	13.23	6.58

Table S8: *Oxygen bonding and the relative amounts of the functionalities.*

Sample	O^{2-} (%)	OH^-/C-O (%)	O-C=O (%)	H_2O (%)
RuO_x/C_{10M3h}	1.78	55.92	39.31	2.99
Ru/C_{10M3h}	1.25	60.62	34.29	3.84
C_{10M3h}	2.26	60.40	33.97	3.37

Boehm-titrations

Table S9: *The amount of strong acid sites of different carbon support material and catalysts.*

Sample	Strong acid sites (µmol/g)
Ru/C	285
once used Ru/C (BP as substrate)	530
twice used Ru/C (BP as substrate)	408
$C_{10M30min}$	314
C_{10M3h}	438
$C_{conc30min}$	447
C_{conc3h}	447
$C_{NoritSX}$	47
$Ru/C_{10M30min}$	233
Ru/C_{10M3h}	253
$Ru/C_{conc30min}$	333
$RuO_x/C_{10M30min}$	349
RuO_x/C_{10M3h}	408
RuO_x/C_{conc3h}	425
$RuO_x/C_{conc30min}$	419
$RuO_x/C_{NoritSX}$	325

Catalysts on sulfonated carbon

Table S10: *The effect of different catalysts on recyclability of the hydrogenation catalyst using cellulosic substrates.[a] The yields were determined with HPLC-RID.*

Entry #	Use of the Catalyst	Subst.	1,4-Sorbit. + Sorbitol yield [%][b]	Isosorbide yield [%]	1,5-Sorbit. yield [%]	2,5-Sorbit. yield [%]	Glucose yield [%]	Levulinic acid yield [%]
1	1st $Ru/C_{10M30min}$	BP	16	4	3	2	20	0
2	2nd $Ru/C_{10M30min}$	BP	0	0	0	0	0	22
3	1st Ru/C_{10M3h}	BP	56	4	3	6	6	0
4	2nd Ru/C_{10M3h}	BP	30	0	0	0	19	0
5	1st $Ru/C_{conc30min}$	BP	24	4	3	4	11	0
6	2nd $Ru/C_{conc30min}$	BP	3	0	0	0	16	13
7	1st $RuO_x/C_{NoritSX}$	BP	66	6	3	7	0	0
8	2nd $RuO_x/C_{NoritSX}$	BP	68	8	3	7	3	0
9	3rd $RuO_x/C_{NoritSX}$	BP	52	7	3	6	5	0
10	4th $RuO_x/C_{NoritSX}$	BP	25	5	0	3	10	0
11	1st $RuO_x/C_{10M30min}$	BP	67	7	4	7	0	0
12	2nd $RuO_x/C_{10M30min}$	BP	69	8	3	7	0	0
13	3rd $RuO_x/C_{10M30min}$	BP	67	7	3	6	2	0
14	4th $RuO_x/C_{10M30min}$	BP	53	9	3	6	2	0
15	1st RuO_x/C_{10M3h}	BP	67	8	3	7	0	0
16	2nd RuO_x/C_{10M3h}	BP	69	8	3	7	0	0
17	3rd RuO_x/C_{10M3h}	BP	71	7	3	7	0	0
18	4th RuO_x/C_{10M3h}	BP	67	8	3	7	3	0
19	1st $RuO_x/C_{conc30min}$	BP	66	8	3	8	0	0
20	2nd $RuO_x/C_{conc30min}$	BP	66	10	3	8	0	0
21	3rd $RuO_x/C_{conc30min}$	BP	42	9	3	6	3	0
22	4th $RuO_x/C_{conc30min}$	BP	21	5	2	3	7	0
23	1st RuO_x/C_{conc3h}	BP	68	6	3	7	0	0
24	2nd RuO_x/C_{conc3h}	BP	70	7	3	7	2	0
25	3rd RuO_x/C_{conc3h}	BP	62	7	6	6	4	0
26	4th RuO_x/C_{conc3h}	BP	38	6	3	4	9	0
27	1st $RuO_x/C_{NoritSX}$	DP	59	6	3	6	4	0
28	2nd $RuO_x/C_{NoritSX}$	DP	69	7	3	7	3	0
29	3rd $RuO_x/C_{NoritSX}$	DP	63	6	3	6	4	0
30	4th $RuO_x/C_{NoritSX}$	DP	62	6	3	6	5	0
31	1st $RuO_x/C_{10M30min}$	DP	64	6	3	7	0	0
32	2nd $RuO_x/C_{10M30min}$	DP	71	7	4	8	0	0
33	3rd $RuO_x/C_{10M30min}$	DP	69	7	3	7	0	0
34	4th $RuO_x/C_{10M30min}$	DP	71	8	4	7	0	0
35	1st RuO_x/C_{10M3h}	DP	63	10	3	5	0	0
36	2nd RuO_x/C_{10M3h}	DP	70	8	3	7	3	0
37	3rd RuO_x/C_{10M3h}	DP	71	7	3	7	2	0
38	4th RuO_x/C_{10M3h}	DP	71	7	4	7	3	0
39	1st $RuO_x/C_{conc30min}$	DP	61	10	3	6	0	0
40	2nd $RuO_x/C_{conc30min}$	DP	65	9	3	6	3	0
41	3rd $RuO_x/C_{conc30min}$	DP	65	8	3	7	4	0
42	4th $RuO_x/C_{conc30min}$	DP	66	8	3	6	4	0
43	1st RuO_x/C_{conc3h}	DP	63	5	3	6	3	0
44	2nd RuO_x/C_{conc3h}	DP	70	9	4	7	2	0
45	3rd RuO_x/C_{conc3h}	DP	67	6	3	6	3	0
46	4th RuO_x/C_{conc3h}	DP	69	7	3	7	3	0
47	RuO_2	DP	49	5	3	4	4	0
48	1st $RuO_x/C_{10M30min}$	MCC	63	7	4	6	0	0
49	2nd $RuO_x/C_{10M30min}$	MCC	63	6	4	6	0	0
50	3rd $RuO_x/C_{10M30min}$	MCC	70	8	4	7	0	0
51	4th $RuO_x/C_{10M30min}$	MCC	64	9	4	8	0	0
52[c]	RuO_x/C_{10M3h}	BP	0	0	0	0	0	0

[a] Reaction conditions: 1.18 mmol of cellulose BP as a substrate, 30 ml of 0.5 M H_2SO_4 aqueous solution, 0.02 mmol of Ru (5 w-% Ru/C), 170°C, 20 bar H_2, 2 hours; [b] The signals of 1,4-sorbitan and sorbitol could not be separated with HPLC, the yield presented is the average of the calculated yields for pure 1,4-sorbitan and sorbitol.; [c] experiment conducted in 30 ml water without H_2SO_4.

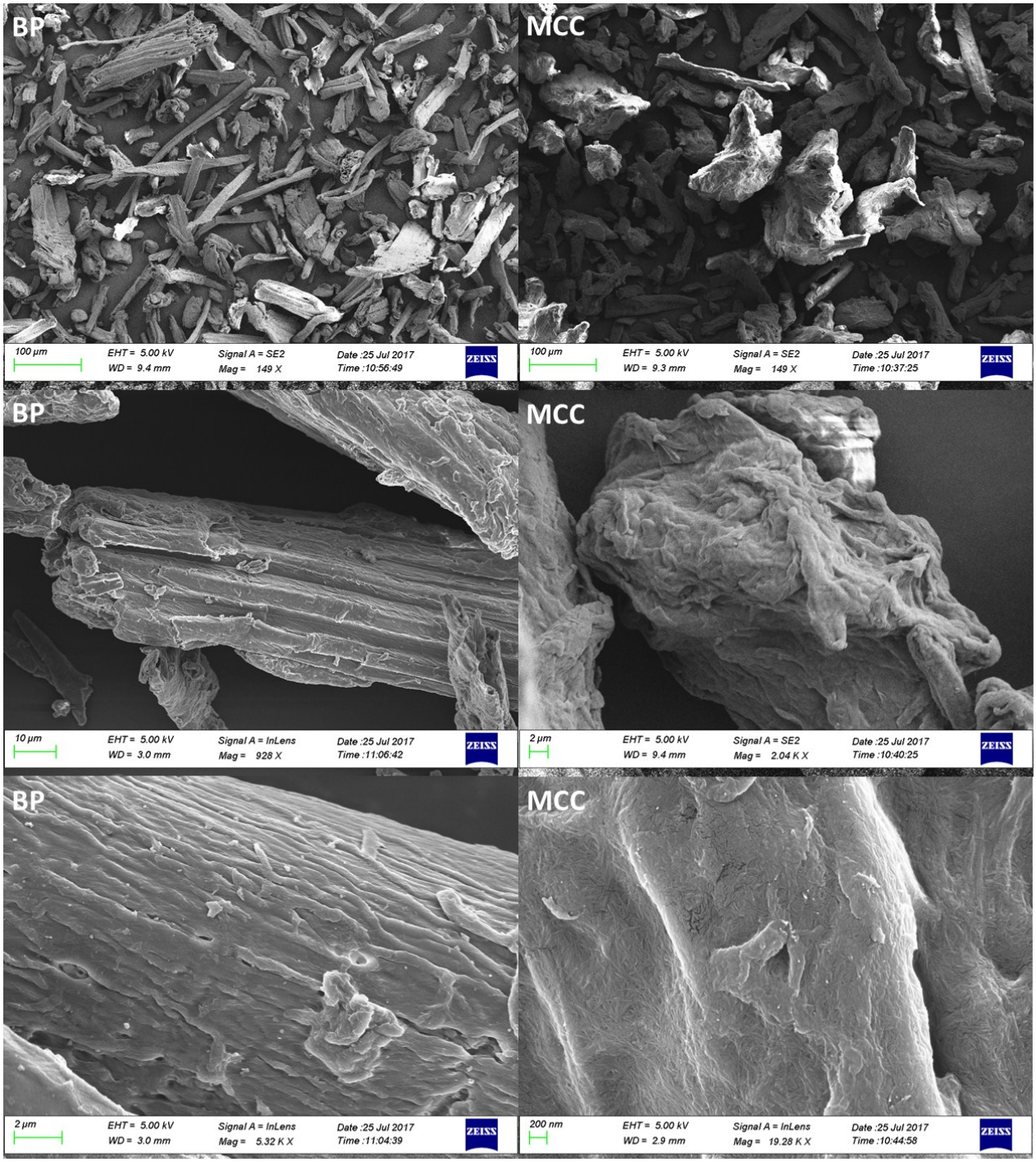


Figure S18: *SEM-images of bagasse pulp (BP, left column)and microcrystalline cellulose (MCC, right column).*

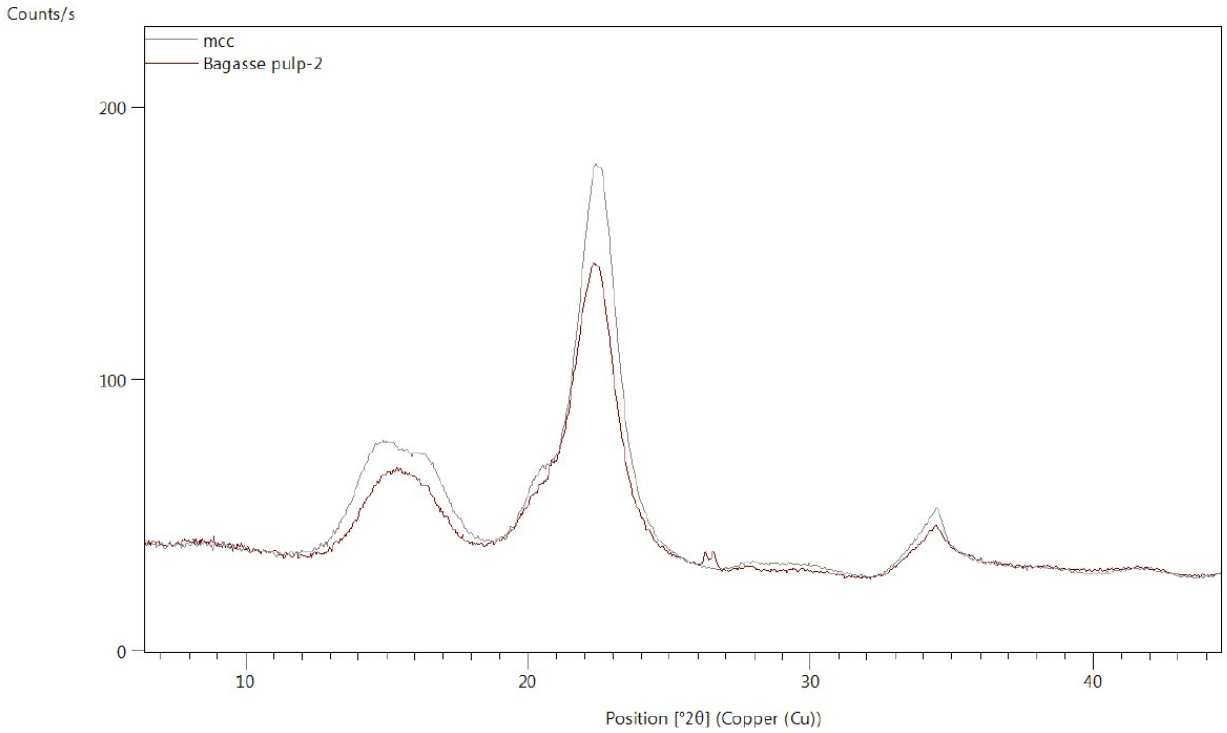


Figure S19: *Diffractograms of MCC (gray) and BP (red) measured with XRD.*

References

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2 T. Komanoya, H. Kobayashi, K. Hara, W. J. Chun and A. Fukuoka, *Appl. Catal. A Gen.*, 2011, **407**, 188–194.