

## Electronic Supplementary Information (ESI)

# From microcrystalline cellulose to hard- and softwood-based feedstocks: their hydrogenolysis to polyols over a highly efficient ruthenium-tungsten catalyst

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### Supplementary Text

#### Structural features of Ru/W/AC after cellulose hydrogenolysis (curve c of Figs. S1, S2)

Compared to the fresh Ru/W/AC catalyst which showed one TPR peak with a maximum at 360 K allocated to ruthenium dioxide reduction (reduction temperature of polycrystalline RuO<sub>2</sub> = 434 K (39), the two peaks in the low-temperature region of the used catalyst indicates either the reduction of two different oxidized ruthenium species (RuO<sub>x</sub>) formed in hot compressed water or the presence of smaller and larger particles of ruthenium dioxide (39). The hydrogen consumption in the region of 450-600 K is assigned to the reduction of oxygenates adsorbed on the catalyst surface during the reaction. The diffractogram revealed the presence of tungsten and traces of a phase which cannot be identified with the help of reference codes.

XRD reference codes: 00-026-1080, C; 00-032-1393, WO<sub>2</sub>; 98-007-1732, W; 01-073-0471, WC; 98-009-9060, W<sub>2</sub>C (HighScorePlus (version 3.0.d) using data bases PAN ICSD (40) and PDF2 flat file (41)).

39. J. Assmann, PhD Thesis, Ruhr-University Bochum, 2004.

40. ICSD Database FIZ Karlsruhe 2009-2.

41. PDF-2 Release 1999 (ICDD).

Figs. S1 to S4

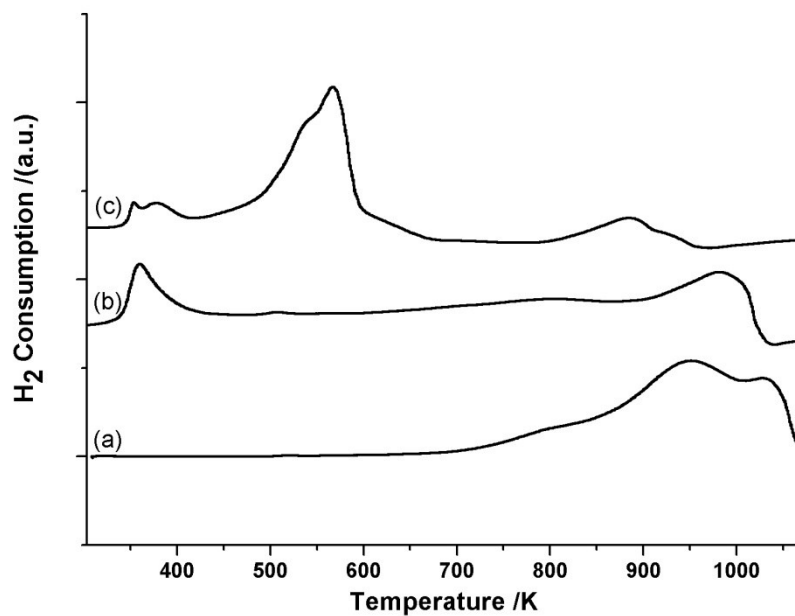


Fig. S1 H<sub>2</sub>-TPR pattern of W/AC (a) and of Ru/W/AC before (b) and after (c) reaction.

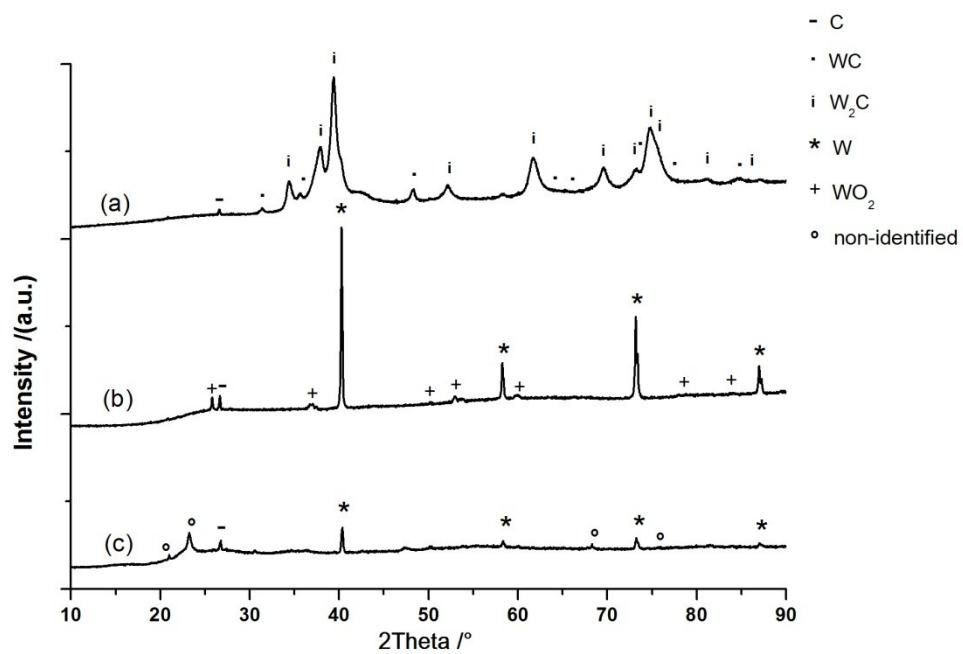


Fig. S2 XRD patterns of W/AC (a) and Ru/W/AC before (b) and after (c) reaction.

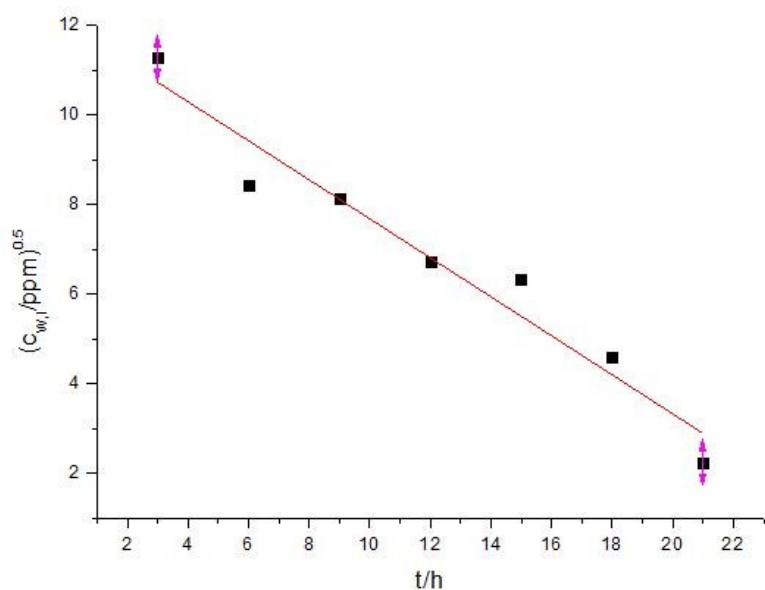


Fig. S3 Kinetics of tungsten leaching.

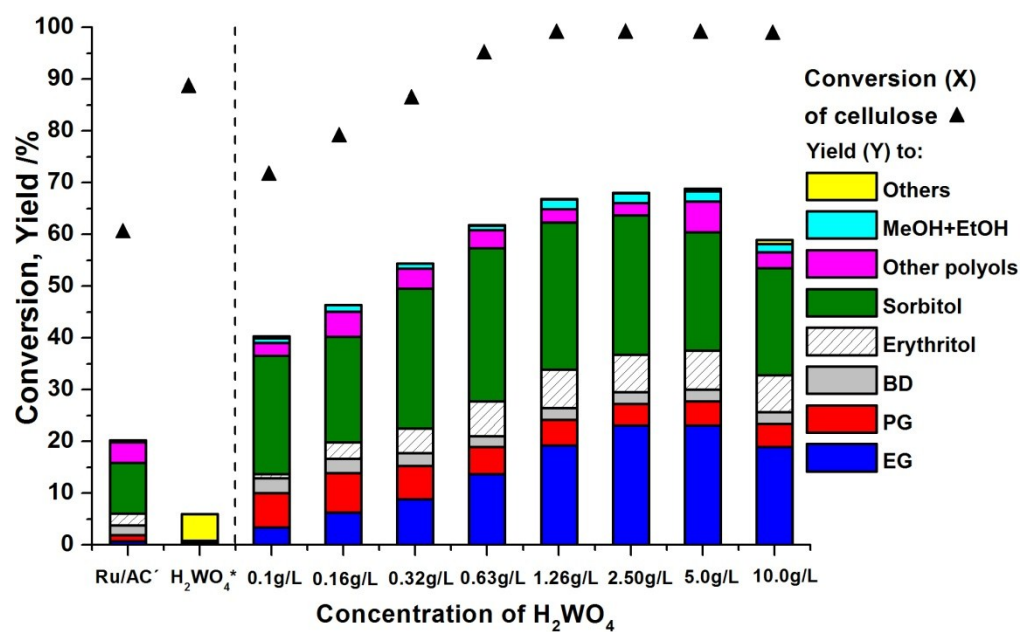


Fig. S4 Cellulose conversions and product yields for the hydrogenolysis of cellulose over Ru/AC catalyst in combination with different amounts of tungsten acid. Reaction conditions: 0.5 g catalyst, 5 g cellulose, 100 mL water, reaction temperature 493 K, 65 bar of hydrogen pressure (measured at reaction temperature), 1000 rpm, 3 hours reaction time, \*: experiment only with 0.5 g of Ru/AC, \*: experiment only with 0.5 g of tungsten acid.

**Table S1.** Carbon efficiency coefficients (CEL) for experiments with ball-milled cellulose.

#	Time of ball-milling [min]	Reaction Time [h]	CEL [%]
1	0	1	76.4
2	0	2	81.5
3	0	3	76.7
4	4	1	79.5
5	4	2	76.4
6	4	3	74.2
7	15	1	68.5
8	15	2	66.3
9	15	3	64.9
10	30	3	59.5
11	120	3	56.7
12	720	3	18.5
13	4 mix-milling	3	89.9