

## **- Supplementary Information -**

### **Toward an Intensified Process of Biomass-Derived Monomers: The Influence of 5-(Hydroxymethyl)furfural Byproducts on the Gold-Catalyzed Synthesis of 2,5-Furandicarboxylic Acid**

*Weiss Naim<sup>†‡</sup>, Oliver R. Schade<sup>†‡</sup>, Erisa Saraçi<sup>†‡</sup>, Dominik Wüst<sup>§</sup>, Andrea Kruse<sup>§</sup> and Jan-Dierk Grunwaldt<sup>†‡\*</sup>*

<sup>†</sup> Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology, Engesserstraße 18, 76131 Karlsruhe, Germany

<sup>‡</sup> Institute for Catalysis Research and Technology, Karlsruhe Institute of Technology, Herrmann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

<sup>§</sup> Department of Conversion Technologies of Biobased Resources, Institute of Agricultural Engineering, University of Hohenheim, Garbenstraße 9, 70593 Stuttgart, Germany

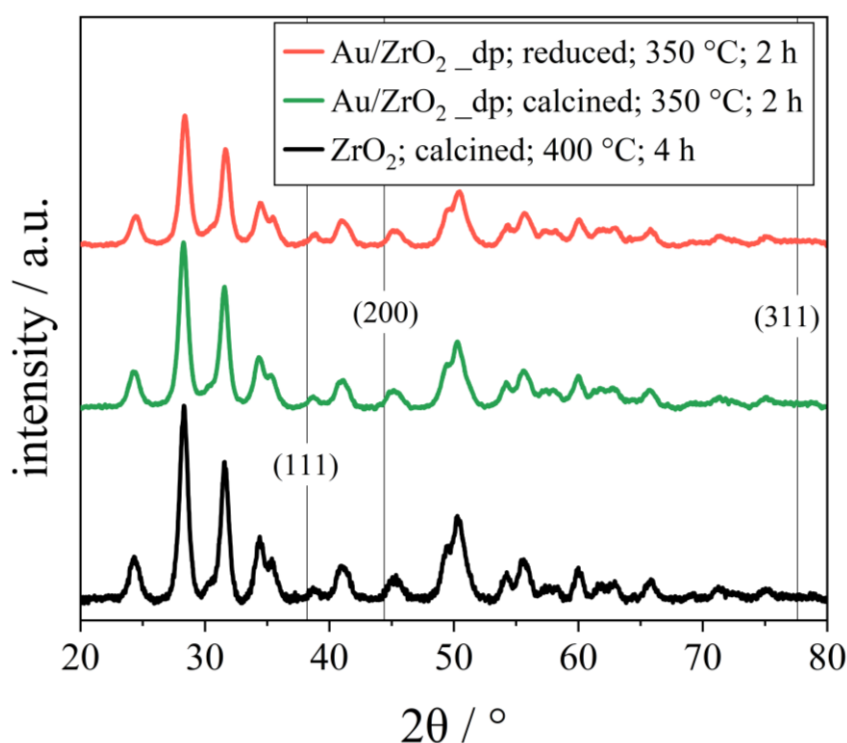
\* [grunwaldt@kit.edu](mailto:grunwaldt@kit.edu)

Total number of pages: 7

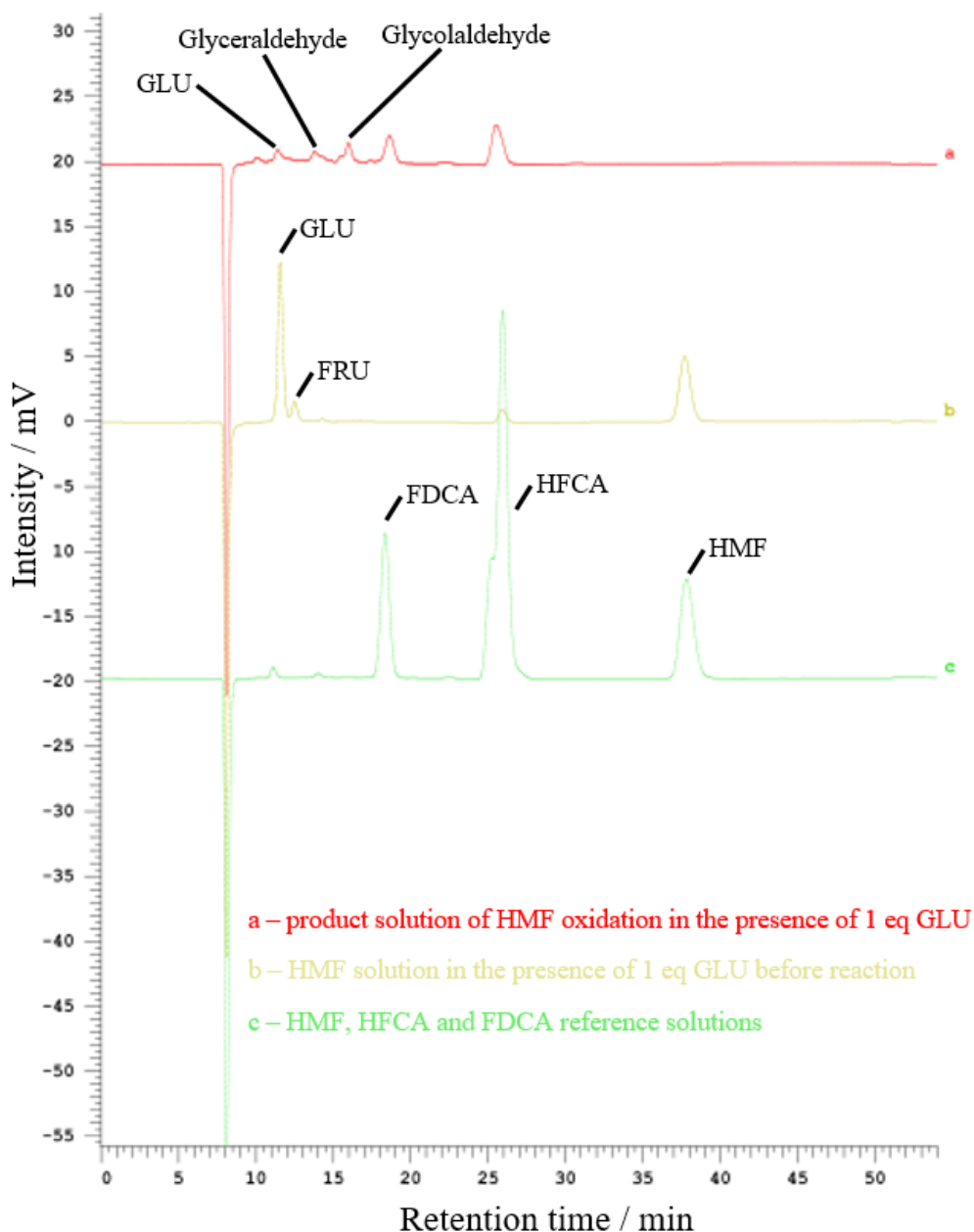
Total number of figures: 6

## Table of contents

<b>Figure S 1.</b> XRD patterns of the used Au/ZrO <sub>2</sub> catalyst.....	S2
<b>Figure S 2.</b> Representative HPLC chromatograms of a reference solution and HMF solution before and after the reaction in the presence of one equivalent of glucose.....	S3
<b>Figure S 3.</b> Normalized IR absorption spectrum of spent Au/ZrO <sub>2</sub> after the reaction in the presence of one equivalent of glucose.....	S4
<b>Figure S 4.</b> <sup>1</sup> H NMR spectrum of the extracted reaction product.....	S4
<b>Figure S 5.</b> <sup>13</sup> C NMR spectrum of the extracted reaction product.....	S5
<b>Figure S 6.</b> Characterization of the spent catalyst at different reaction conditions .....	S6
<b>References</b> .....	S7

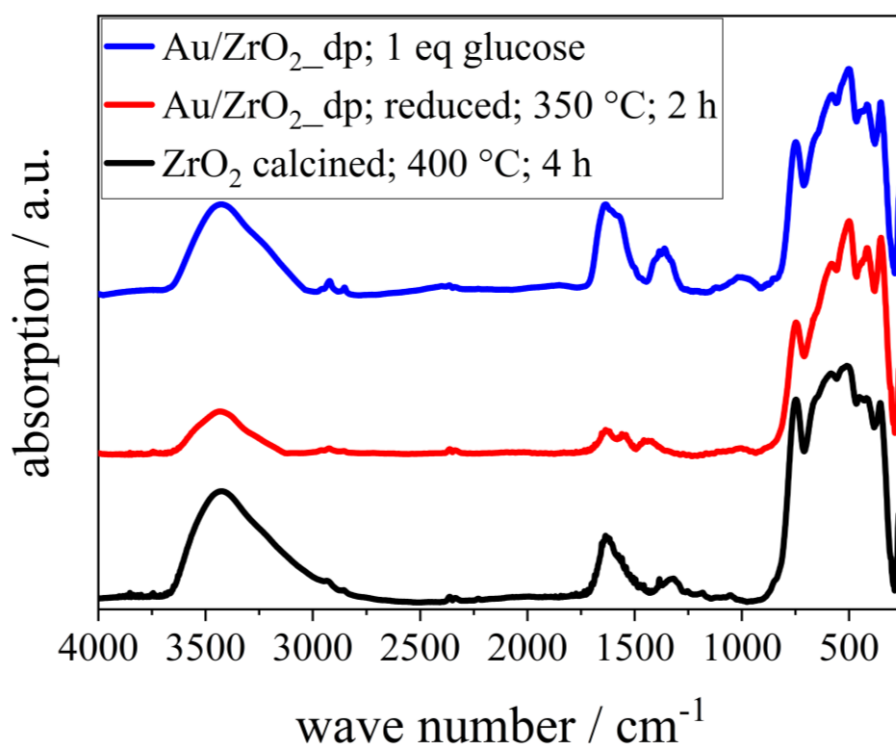


**Figure S 1.** XRD patterns of Au/ZrO<sub>2</sub> catalysts via deposition-precipitation (dp) in reduced, calcined state and of ZrO<sub>2</sub> support.

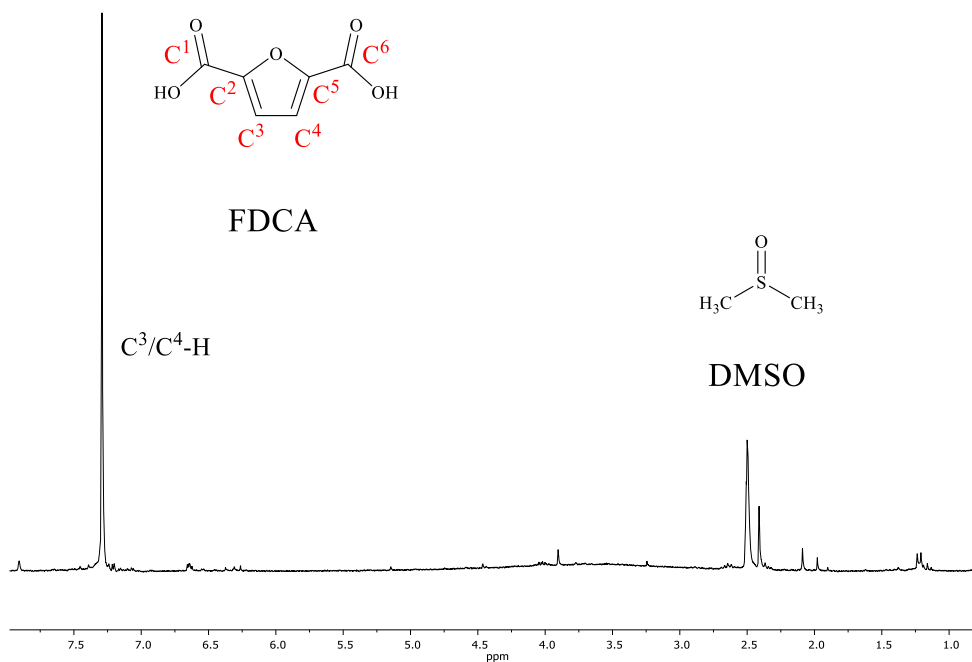


**Figure S 2.** Representative HPLC chromatograms of a reference solution and HMF solution before and after the reaction in the presence of 1 eq. of GLU. Reaction conditions: 100 °C, 4 eq. of NaOH, 10 bar air, 5 h, 98.5 mg of catalyst, 0.1 M HMF in 10 mL.

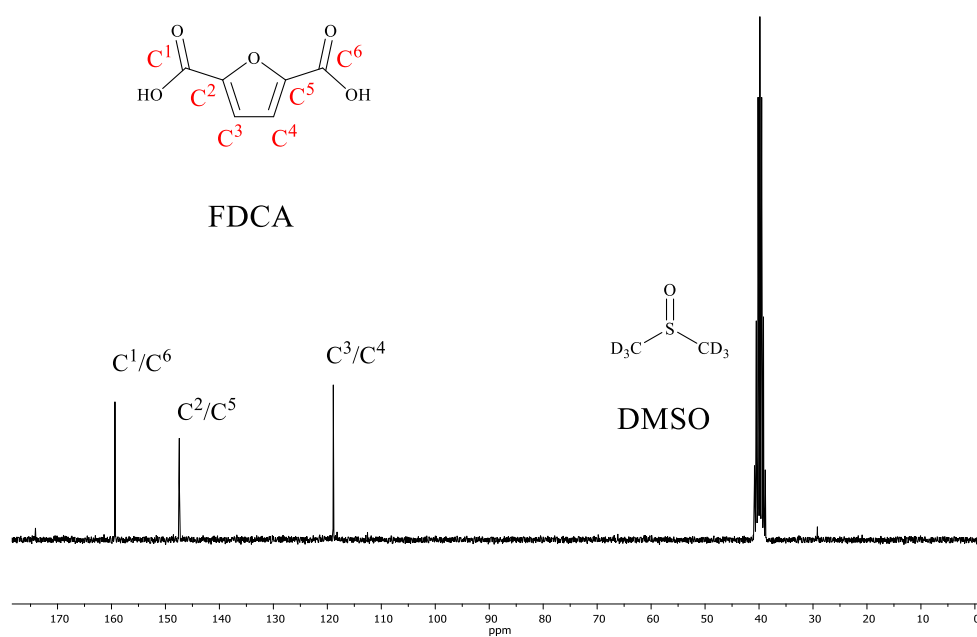
The degradation of GLU under the chosen reaction conditions is mostly unselective and probably gives mostly humins,<sup>1-3</sup> as calibrated degradation products are only observed in low concentrations (Figure S 2).



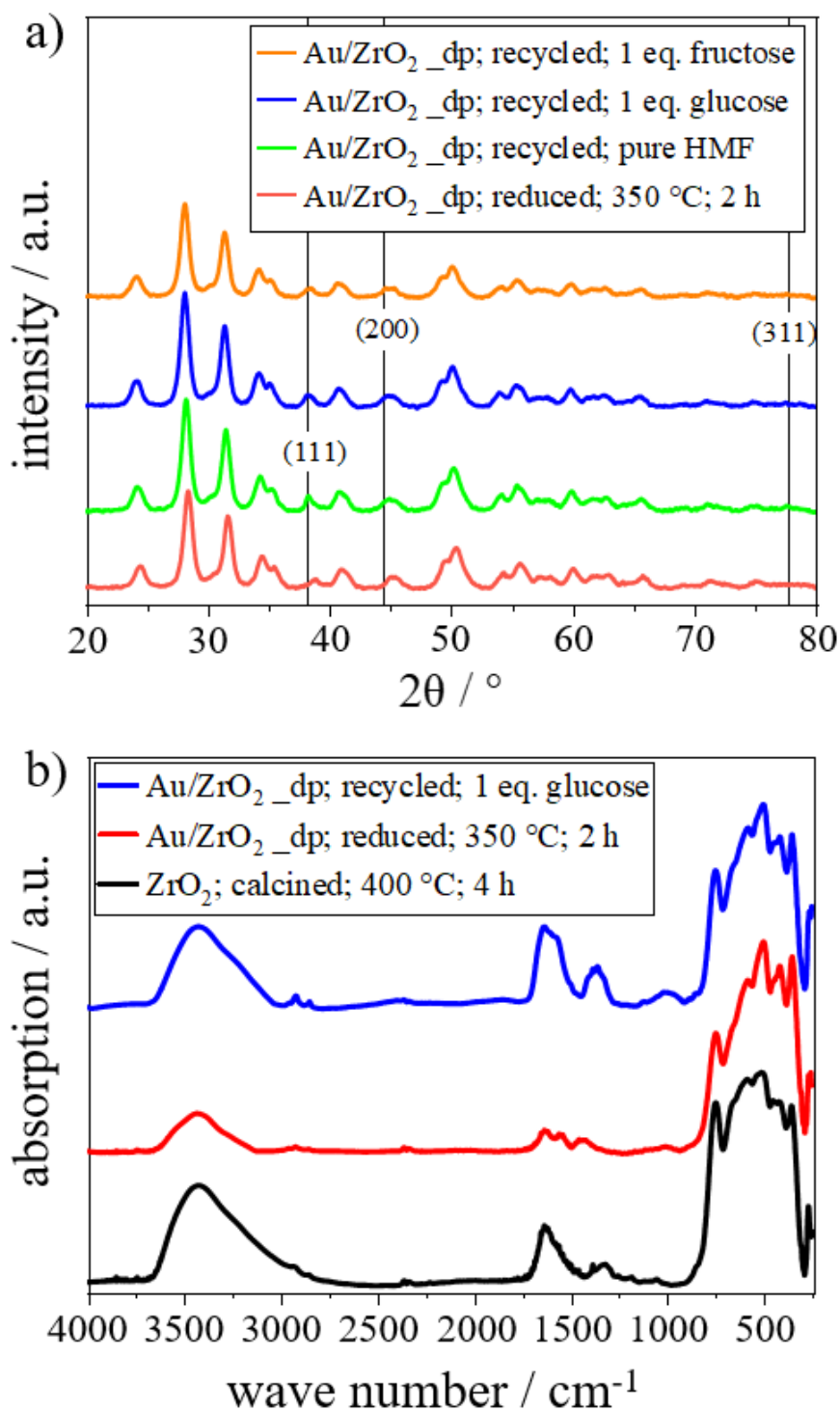
**Figure S 3.** Normalized IR absorption spectra of recovered Au/ZrO<sub>2</sub> after the reaction in the presence of 1 eq. GLU. Spectra of the calcined ZrO<sub>2</sub> support and the fresh catalyst are given for comparison.



**Figure S 4.** <sup>1</sup>H NMR spectrum (250 MHz, DMSO-d<sub>6</sub>, δ = 2.5 ppm, 298 K) of extracted FDCA: 7.3 ppm (s, 2 H, C<sup>3</sup>/C<sup>4</sup>-H).



**Figure S 5.** <sup>13</sup>C NMR spectrum (63 MHz, DMSO-d<sub>6</sub>, δ = 39.8 ppm, 298 K) of extracted FDCA: 118.5 ppm (2 C, C<sup>3</sup>/C<sup>4</sup>), 147.1 ppm (2 C, C<sup>2</sup>/C<sup>5</sup>), 159.0 ppm (2 C, C<sup>1</sup>/C<sup>6</sup>).



**Figure S 6.** Catalyst characterization (a) XRD patterns of recovered Au/ZrO<sub>2</sub> after the third run without by-products, added sugars and in reduced state. (b) Normalized IR spectra of recovered Au/ZrO<sub>2</sub> catalysts after third run in the presence of GLU, in reduced state and calcined ZrO<sub>2</sub> support.

The increased absorbance in the IR spectrum of the spent Au/ZrO<sub>2</sub> catalyst in the presence of GLU at around 1370 cm<sup>-1</sup> may be attributed to the deposition of humins on the catalyst surface.<sup>4</sup>

## References

- (1) Wüst, D.; Correa, C. R.; Jung, D.; Zimmermann, M.; Kruse, A.; Fiori, L. Understanding the influence of biomass particle size and reaction medium on the formation pathways of hydrochar. *Biomass Conver. Biorefin.* **2019**, 1-24. DOI 10.1007/s13399-019-00488-0.
- (2) Kearsley, M. Action of aqueous sodium hydroxide on glucose syrups. *Food Chem.* **1977**, 2, 27-41. DOI 10.1016/0308-8146(77)90005-X.
- (3) Patil, S. K. R.; Hetzel, J.; Lund, C. R. F. Comparison of Structural Features of Humins Formed Catalytically from Glucose, Fructose, and 5-Hydroxymethylfurfuraldehyde. *Energy Fuels* **2012**, 26, 5281-5293. DOI 10.1021/ef3007454.
- (4) Tsilomelekis, G.; Orella, M. J.; Lin, Z.; Cheng, Z.; Zheng, W.; Nikolakis, V.; Vlachos, D. G. Molecular structure, morphology and growth mechanisms and rates of 5-hydroxymethyl furfural (HMF) derived humins. *Green Chem.* **2016**, 18, 1983-1993. DOI 10.1039/C5GC01938A.