

## Supporting Information

### **Ru/TiO<sub>2</sub> catalysts for selective formation of ring hydrogenation or ring-opening products from biomass-derived 5-hydroxymethylfurfural**

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**Table S1.** Catalytic activity tests of Ru/TiO<sub>2</sub> in water at different reaction temperatures

Temp. [°C]	HMF Conversion [%]	Product Yield [%]					
		BHMF	BHMTHF	HHD	1,2,5-HT	HCPO	Others
80	81	59	1	17	0	0	4
120	100	2	5	83	5	4	1
160	100	0	3	0	66	6	25

Reaction conditions: 0.15 g catalyst, 1 g HMF, 70 bar H<sub>2</sub>, 150 min, 30 mL water, 650 rpm

**Table S2.** Influence of water on catalytic activity for a test duration of 60 min

Water:Dioxane ratio	HMF Conversion [%]	Product Yield [%]			
		BHMF	BHMTHF	HHD	Others
0:1	46	44	1	0	1
1:1	68	39	5	11	13
1:0	83	5	0	61	17

Reaction conditions: 0.15 g catalyst, 1 g HMF, 70 bar H<sub>2</sub>, 120 °C, 60 min, 30 mL solvent, 650 rpm

**Table S3.** Influence of the solvent in the Ru leaching

Water:Dioxane ratio	Ru leaching	
	Ppb *	% **
0:1	204.0	0.0041
1:1	150.2	0.003
1:0	5.62	0.0001

Reaction conditions: 0.15 g catalyst, 1 g HMF, 120 °C, 70 bar H<sub>2</sub>, 150 min, 30 mL solvent, 650 rpm

\* Ru concentration in the reaction media after test as determined by ICP analysis

\*\* wt. fraction of the Ru content in the fresh catalyst

**Table S4.** Recyclability tests of Ru/TiO<sub>2</sub> in water with different pretreatment methods

Cycle	Pretreatment	HMF	HHD
		Conversion [%]	Selectivity [%]
First	Fresh catalyst	100	90
Second	Catalyst reused without washing	70	94
Second	Catalyst reused after washing with water	84	83
Second	Catalyst reused after washing with dioxane	95	91

Reaction Conditions: 0.15 g catalyst (without reduction), 1 g HMF, 70 bar H<sub>2</sub>, 120 °C, 140 min, 30 mL water, 650 rpm

**Reusability tests.** For the reusability tests, the catalysts were recovered by centrifugation after each run, washed twice with dioxane, and dried at 120 °C for 2 h prior to reuse. Pretreatment conditions were optimized based on the results shown in Table S4. The catalysts reused without any pretreatment or washed only with water exhibited reduced activity (70% and 84% of the initial performance, respectively). In contrast, dioxane-washed samples retained both activity and selectivity comparable to those of the first run, and this procedure was therefore adopted as the standard pretreatment method.

**Table S5.** Adsorption energy of BHMF on a Ru(0001) surface ( $\Delta E_{\text{ads}}$ ), activation energy ( $\Delta E_{\text{act}}$ ) and reaction energy ( $\Delta E_{\text{r}}$ ) of the C-O bond scission to open the furanic cycle of BHMF, in function of the nature of the electrostatic environment. Geometries are optimized in absence of any solvent (vacuum). Dioxane and water solvent environment are modelled using a continuum model using VASPsol with the corresponding relative dielectric constant (2.2 and 78). In the case of water, we used also the following parameters: LAMBDA\_D\_K = 3, C\_MOLAR=1, R\_ION=4.

	Vacuum	Dioxane	Water
$\Delta E_{\text{ads}}$ (eV)	-2.36	-2.44	-2.50
$\Delta E_{\text{act}}$ (eV)	0.58	0.59	0.61
$\Delta E_{\text{r}}$ (eV)	-0.98	-0.97	-0.89

**Table S6.** Key Ru-C bond distance in the optimized transition states and intermediates involved in Scheme 2. The numbering of carbon atoms follows IUPAC nomenclature

	Ru – C Bond Distance in Å					
	Ru - C2	Ru - C3	Ru - C4	Ru1 - C5	if C5 on bridge site	if C5 on hollow site
					Ru2 - C5	Ru3 - C5
<b>TS*1</b>	2.22	2.20	2.27	1.92	-	-
<b>TS*2</b>	2.38	2.21	2.26	2.19	2.24	-

<b>TS*3</b>	2.37	2.18	2.23	2.06	2.38	-
<b>TS*4</b>	2.21	2.30	2.19	2.83	2.96	-
<b>TS*5</b>	2.28	2.29	2.27	2.90	-	-
<b>TS*6</b>	2.33	2.32	2.26	1.96	-	-
<b>BHMF</b>	2.14	2.21	2.24	2.10	-	-
<b>Int-C</b>	2.28	2.19	2.26	2.07	2.16	-
<b>Int-D</b>	2.24	2.27	2.21	2.29	2.81	-
<b>Int-E</b>	2.16	2.33	2.17	2.06	2.28	2.43
<b>Int-F-a</b>	2.17	2.28	2.20	2.58	2.62	2.71
<b>Int-F-b</b>	2.28	2.38	2.20	2.45	2.73	2.82
<b>Int-G</b>	2.16	2.31	2.22	2.63	2.65	-
<b>HHD</b>	2.20	3.23	3.30	3.13	-	-

**Table S7.** Key Ru-O bond distance in the optimized transition states and intermediates involved in Scheme 2. The numbering of carbon atoms originates from the numbering of the carbon atoms to which they are bonded.

	Ru – O Bond Distance in Å				
	Ru - O1	Ru - O2	Ru - O5	Ru - O6	Ru - O in free OH
<b>TS*1</b>	2.28	2.18	-	2.35	-
<b>TS*2</b>	2.31	2.09	-	2.29	2.15
<b>TS*3</b>	2.41	2.11	-	-	2.03
<b>TS*4</b>	2.40	2.26	2.07	-	2.10
<b>TS*5</b>	2.29	2.09	2.95	-	2.08
<b>TS*6</b>	2.27	2.07			2.01
<b>BHMF</b>	2.26	2.47	2.47	2.38	-
<b>Int-C</b>	2.37	2.10	-	2.21	-
<b>Int-D</b>	2.29	3.07	2.12	2.29	-
<b>Int-E</b>	2.27	2.17	-	-	-
<b>Int-F-a</b>	2.25	2.35	2.12	-	-
<b>Int-F-b</b>	2.29	2.10	2.28	-	-
<b>Int-G</b>	2.29	2.18	2.19	-	-
<b>HHD</b>	2.20	2.06	2.14	-	-

**Table S8.** Influence of stirring speed on the catalytic activity in pure dioxane

rpm	HMF Conversion [%]	Product Yield [%]		
		BHMF	BHMTHF	Others
350	41	39	1	1
650	46	44	1	1
1000	51	49	1	1

Reaction conditions: 0.15g catalyst, 1g HMF, 70 bar H<sub>2</sub>, 120 °C,

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60 min., 30 mL dioxane

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**Table S9.** Influence of stirring speed on the catalytic activity in pure water

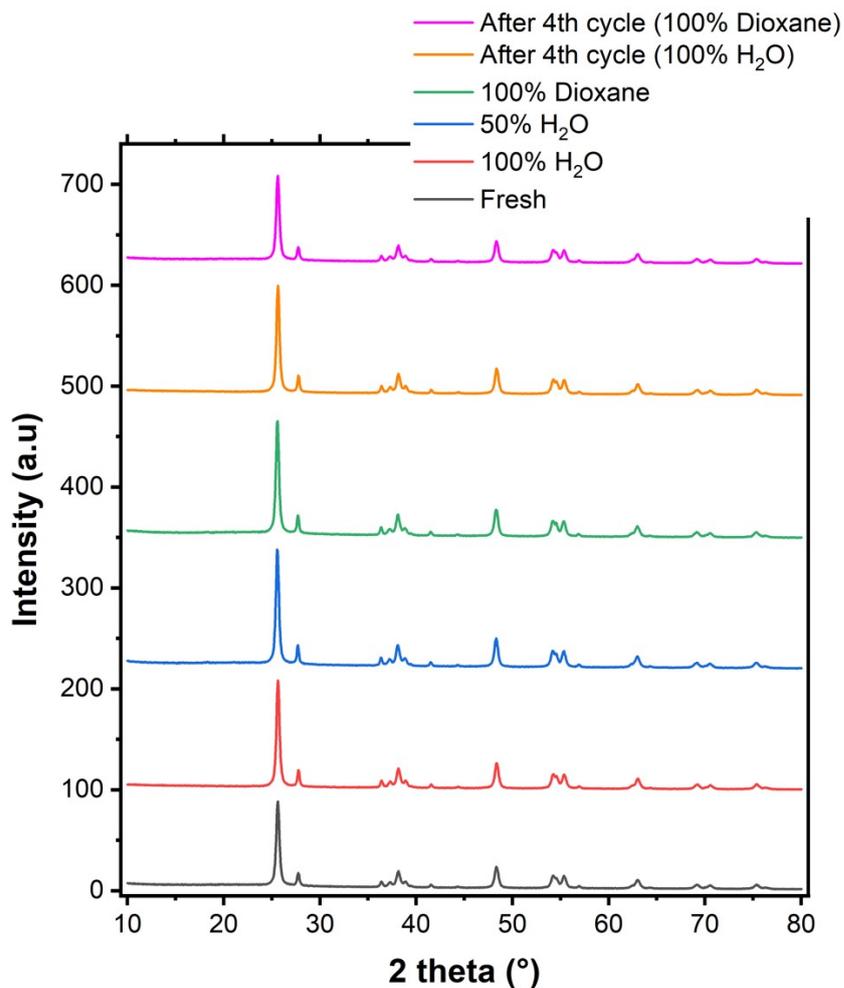
rpm	HMF Conversion [%]	Product Yield [%]		
		BHMF	HHD	Others
350	59	4	51	4
650	83	5	61	17
1000	71	3	59	9

Reaction conditions: 0.15g catalyst, 1g HMF, 70 bar H<sub>2</sub>, 120 °C, 60 min., 30 mL water

**Table S10.** Catalytic tests using HHD as the substrate

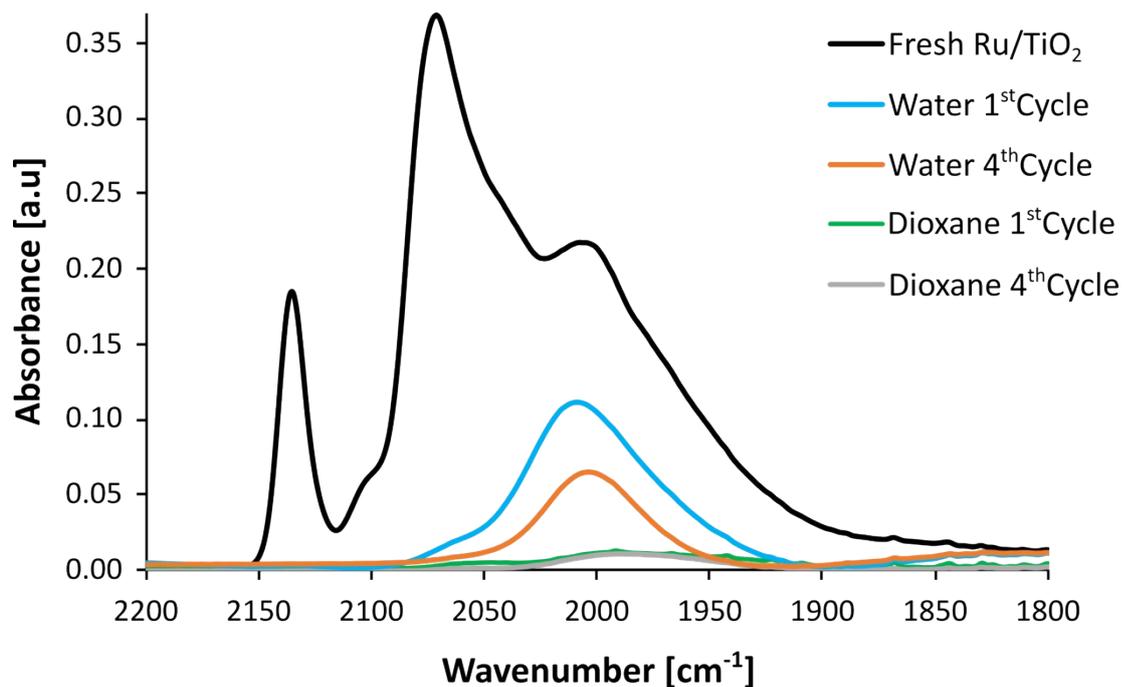
Water:Dioxane ratio	HHD Conversion [%]	Product Yield [%]	
		1,2,5-HT	Others
0:1	100	91	9
1:1	97	46	51
1:0	45	5	40

Reaction conditions: 0.03g catalyst, 0.2g HHD, 70 bar H<sub>2</sub>, 120 °C, 60 min., 30mL solvent, 650rpm



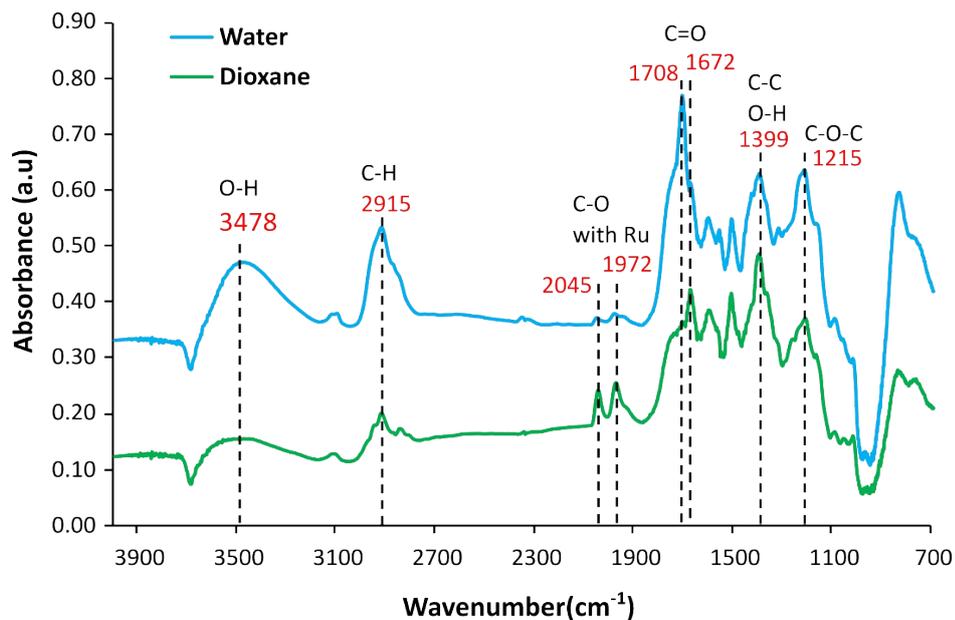
**Figure S1.** XRD patterns of the fresh Ru/TiO<sub>2</sub> catalyst and of spent catalysts after reaction in pure dioxane, 50% water/dioxane, and pure water, as well as the four-times-cycled catalysts tested in pure dioxane and pure water.

The anatase/rutile composition remains constant at about 88% anatase and 12% rutile, with a mean anatase crystallite size of  $26 \pm 1$  nm, as well as the BET specific surface area (about  $56 \pm 3$  m<sup>2</sup>/g), irrespective of solvent composition and number of reaction cycles.

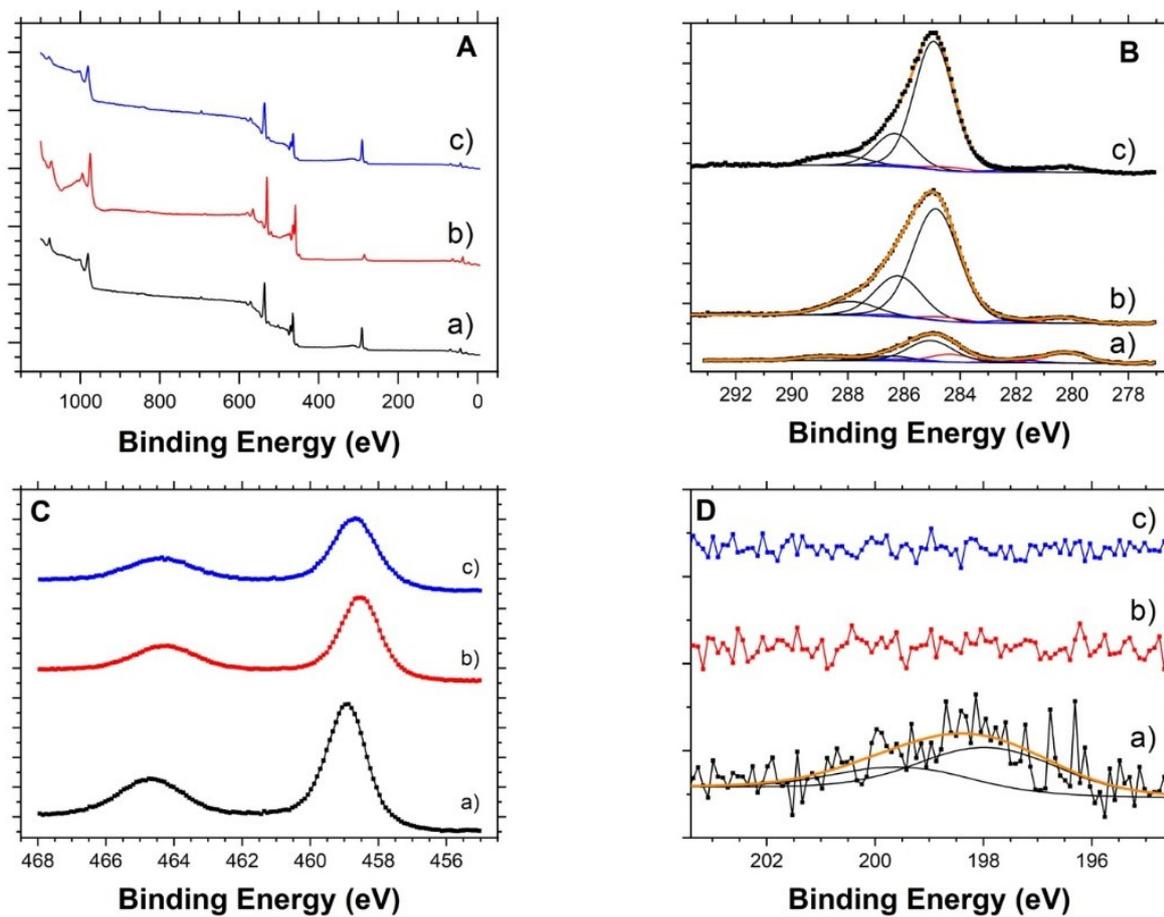


**Figure S2.** CO-adsorbed FTIR spectra of the spent Ru/TiO<sub>2</sub> catalysts after 1<sup>st</sup> and 4<sup>th</sup> test cycles in pure water and in pure dioxane.

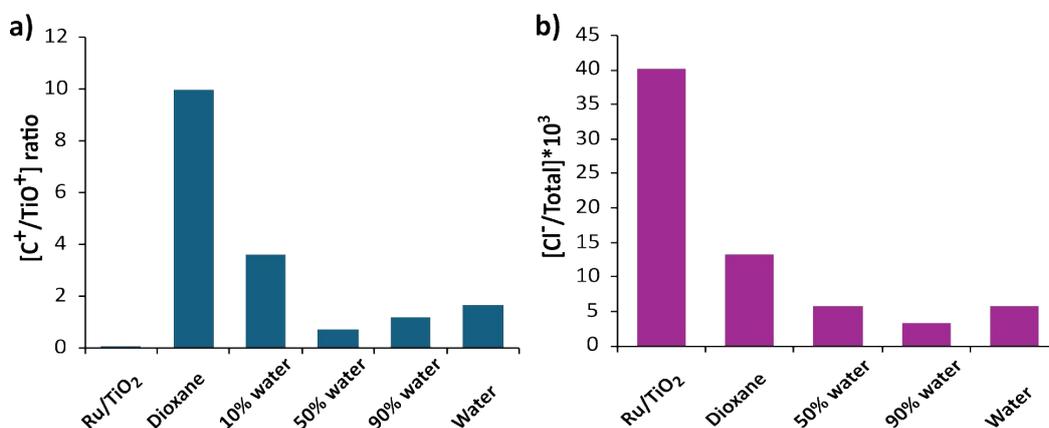
A similar trend was observed for the four-times-cycled Ru/TiO<sub>2</sub> catalysts after extended cycling in pure water and pure dioxane compared with the spent catalysts after the first reaction cycle. In pure dioxane, the near-complete suppression of CO bands indicates extensive coverage of Ru sites. By contrast, the four-times-cycled catalyst cycled in pure water retained bands corresponding to both multi-coordinated and linear CO adsorption (albeit at lower intensity), confirming that water helps preserve the availability of metallic Ru surface sites.



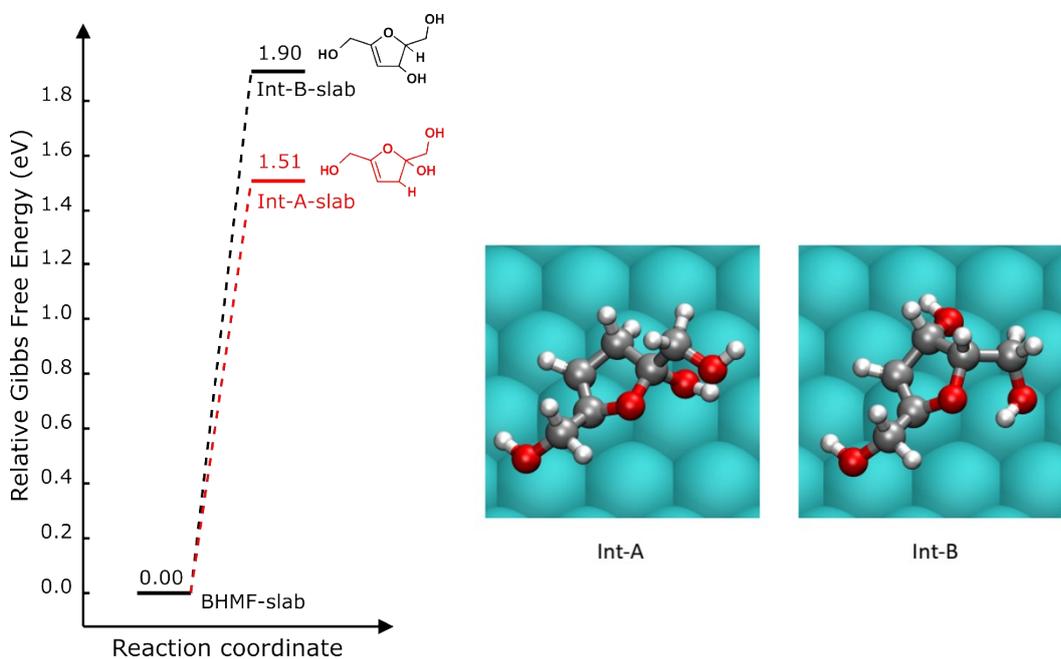
**Figure S3.** FTIR spectra of Ru/TiO<sub>2</sub> catalyst spent in pure water and dioxane.



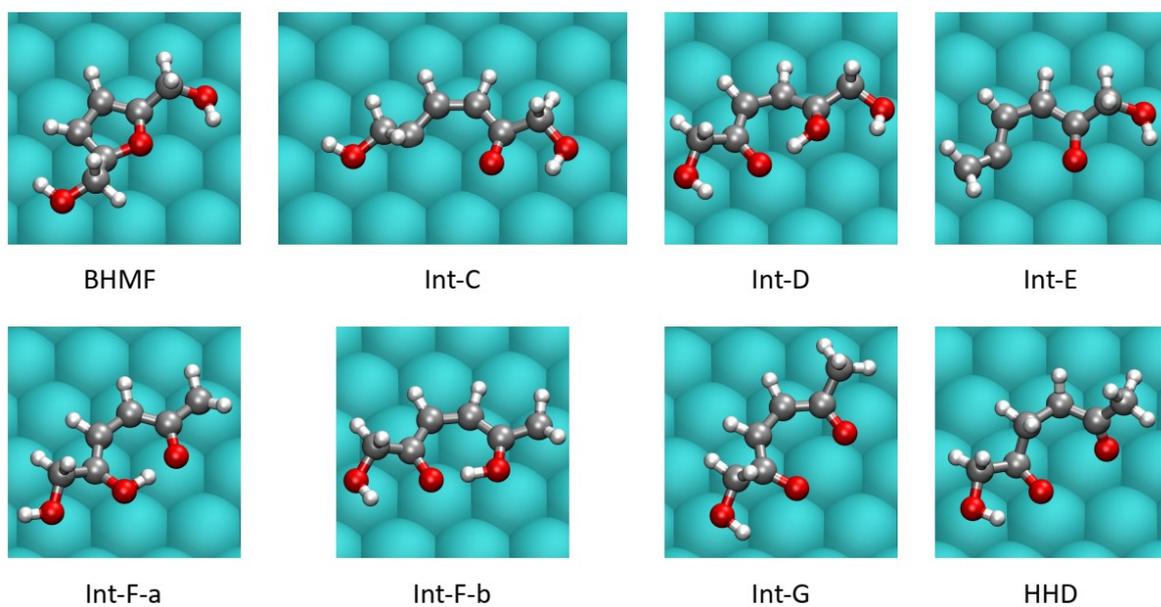
**Figure S4.** XPS profile recorded for (a) the fresh Ru/TiO<sub>2</sub> catalyst, and the spent catalyst used in pure (b) water and (c) dioxane. A) wide scan survey spectrum, B) Ru 3d - C 1s, C) Ti 2p, and D) Cl 2p core orbitals. In the Ru 3d - C 1s spectra, blue represents Ru<sup>0</sup> (3d), red represents oxidized Ru<sup>δ+</sup> (3d), and black corresponds to the multi-component envelope of adventitious carbon (1s).



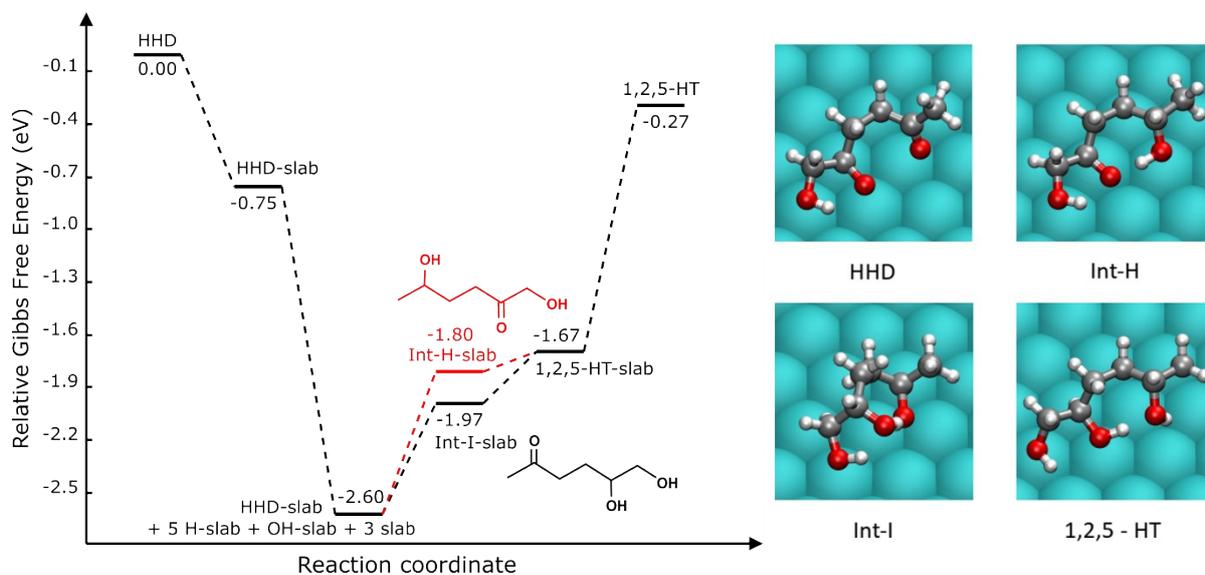
**Figure S5.** Normalized intensities of selected ions obtained from ToF-SIMS spectra of the Ru/TiO<sub>2</sub> catalysts spent in different reaction media a) C<sup>+</sup>/TiO<sup>+</sup> and (b) Cl<sup>-</sup>



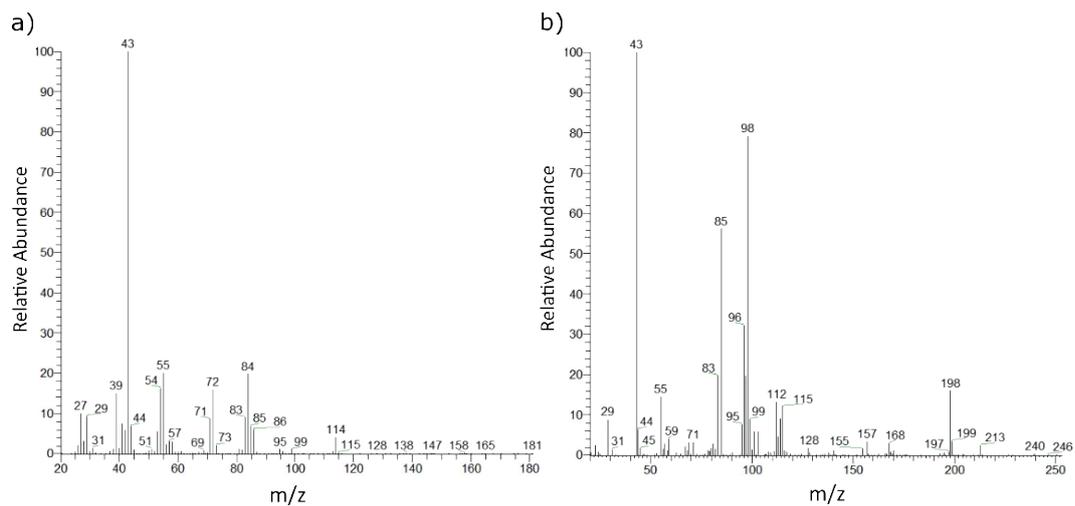
**Figure S6** DFT-derived energy pathway for direct addition of water to BHMF<sup>1</sup> and the top view of the optimized products.



**Figure S7.** Top view of the optimized key intermediates involved in **Scheme 2**.



**Figure S8.** Energy profile diagram for HHD hydrogenation to 1,2,5-HT and the top view of the optimized structures of intermediates and products.



**Figure S9.** MS spectra of possible intermediates a) Int-P and b) Acetals from HHD to 1,2,5-HT synthesis.

## References

1. Ramos, R. *et al.* Selective conversion of 5-hydroxymethylfurfural to diketone derivatives over Beta zeolite-supported Pd catalysts in water. *J. Catal.* **375**, 224–233 (2019).