Supplementary information for

Selective hydrogenolysis of polyols and cyclic ethers over bifunctional surface sites on rhodium-rhenium catalysts

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1. Effect of metal-loading ratio on catalytic activity and selectivity

Table S1. Effect of metal-loading ratio on catalytic activity and hydrogenolysis selectivity of 2-(hydroxymethyl)tetrahydropyran **1** to 1,6-hexanediol **2**[a].

Catalyst	Rh:M[b] (mol:mol)	Time (h)	Catalyst: 1 (g:g)	Conversion (%)	Selectivity to 2 (%)	Specific Rate[c] ($\mu molg^{-1}min^{-1}$)
Rh-ReO_x/C	1:0.25	5	1:9	48	82	132
	1:0.5	5	1:9	55	86	153
	1:1	5	1:9	38	92	109
		6	1:9	46	89	99
Rh-MoO_x/C	1:0.05	12	2:7	40	81	16
	1:0.1	12	2:7	55	84	22
	1:0.25	12	2:7	48	85	19
	1:0.5	12	2:7	48	77	20

[a]The nominal loading of Rh was 4 wt% for all catalysts. Reaction conditions: 393 K, 80 bar H_2. Reactant mixtures were 5 wt% **1** in water. [b]M = Re or Mo. [c]Specific rate defined as the moles of **1** reacted per gram of catalyst per minute.

2. Effect of pretreatment conditions on hydrogenolysis activity and extent of Re leaching

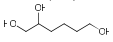
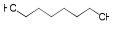
Table S2. Effect of catalyst pretreatment temperature on hydrogenolysis activity of 2-(hydroxymethyl)tetrahydropyran **1** over 4 wt% Rh-ReO_x/C (1:0.5) and extent of rhenium leaching.[a]

H_2 pretreatment temperature (K)	**Conversion (%)**	**Selectivity to 1,6-hexanediol 2 (%)**	**Specific rate[b] ($\mu molg^{-1}min^{-1}$)**	**Re leached (%)**
No pretreatment	27	97	90	2.0
393	25	93	86	1.2
523	16	99	51	< 0.5

[a]Reaction conditions: 393 K, 34 bar H_2, 4 h, mass ratio of catalyst:**1** = 1:9. Reactant mixtures were 5 wt% **1** in water.
[b]Specific rate defined as the moles of **1** reacted per gram of catalyst per minute.

3. Comparison of specific hydrogenolysis rate over 4 wt% Rh-ReO_x/C (1:0.5) and DFT-calculated carbenium ion energies for various cyclic ethers and polyols

Table S3. Comparison of specific hydrogenolysis rates over 4 wt% Rh-ReO_x/C (1:0.5) and DFT-calculated carbenium ion energies for various cyclic ethers and polyols.

Reactant		Specific rate ($\mu molg^{-1}min^{-1}$)	Carbenium Ion Energies (kJ mol^{-1})	Oxocarbenium Ion Energies (kJ mol^{-1})
Structure	**Name**			
Cyclic Ethers with α-OH Groups				
	tetrahydrofurfuryl alcohol **3**	180	-762	-852
	2-(hydroxymethyl)tetrahydro-pyran **1**	90	-756	-845
β-Diols				
	2,4-pentanediol **15**	117	-754/-799	-857
	2,3-butanediol **16**	156	-762	-857
1, 2-Diols and Polyols				
	1,2,4-butanetriol	47	-743	-835
	glycerol **4**	45	-732	-810
	1,2-butanediol **14**	62	-736	-830
	1,2,6-hexanetriol	23	-733	-825
	1,2-hexanediol	40	-734	-832
	1,2-pentanediol **13**	32	-741	-833
Substituted Cyclic Ethers				
	2-methyltetrahydropyran **5**	7	-742	-
	2-methyltetrahydrofuran **7**	7	-743	-
Cyclic Ethers and α,ω-Diols				
	tetrahydropyran **6**	-	-710	-
	tetrahydrofuran **8**	-	-715	-
	1,6-hexanediol **2**	-	-712	-
	1,5-pentanediol **11**	4	-710	-
	1,4-butanediol **12**	8	-707	-

4. Hydrogenolysis rates of 2-(hydroxymethyl)tetrahydro-pyran 1 to 1,6-hexanediol 2 over 4 wt% Rh-ReO_x/C (1:0.5) in a continuous flow reaction system with varying reactant concentrations and P_{H2}

Table S4. Hydrogenolysis rates of 2-(hydroxymethyl)tetrahydropyran **1** to 1,6-hexanediol **2**[a] over 4 wt% Rh-ReOx/C (1:0.5) in a continuous flow reaction system

Concentration of 1 (μmol mL^{-1})	P_{H2} (psi)	Conversion (%)	Selectivity to 2 (%)	Specific rate[b] (μmol$g^{-1}min^{-1}$)
439	520	20	92	32
226	520	31	90	24
94	520	20	85	7
435	760	14	87	21
	520	10	91	15
	340	5	85	10

[a]Reaction conditions: 393 K, water as solvent. The catalyst was pretreated in flowing H_2 (60 cm^3 (STP) min^{-1}) at 523 K for 4 h and cooled to the reaction temperature prior to initiation of liquid feed flow. [b]Specific rate defined as the moles of **1** reacted per gram of catalyst per minute.

5. DFT-calculated metal-catalyzed ring-opening of tetrahydrofurfuryl alcohol 3

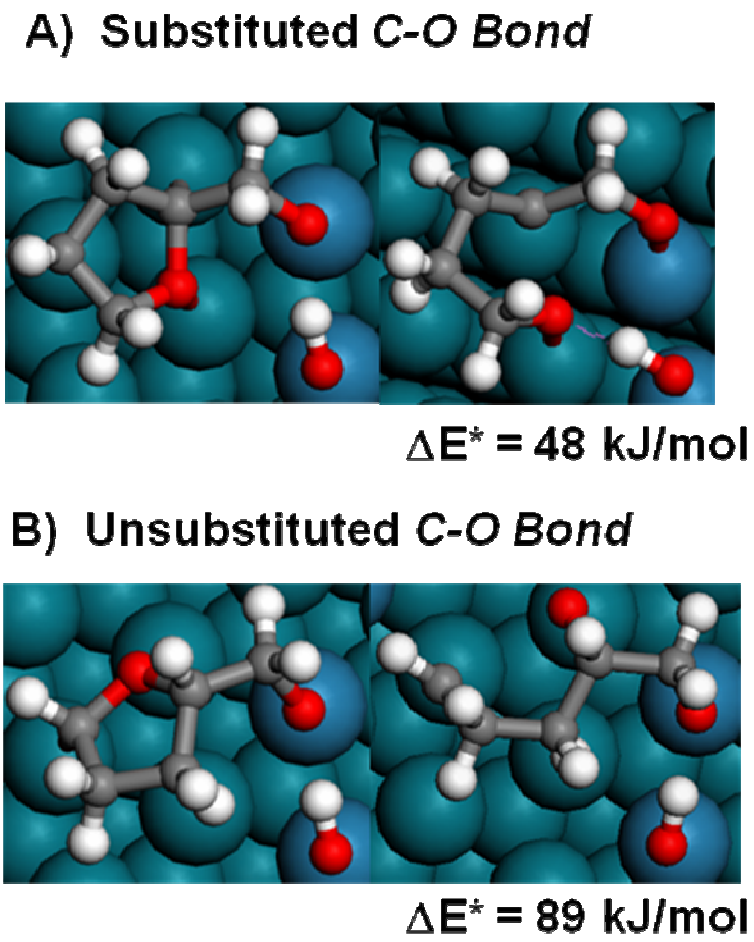


Figure S1. DFT-calculated structures and activation barriers for the metal-catalyzed ring opening of tetrahydrofurfuryl alcohol **3** at the **a)** substituted and **b)** unsubstituted C-O bonds over a model RhReOH alloy surface.

6. DFT-optimized structure for water-stabilized tetrahydrofurfuryl carbenium ion intermediate

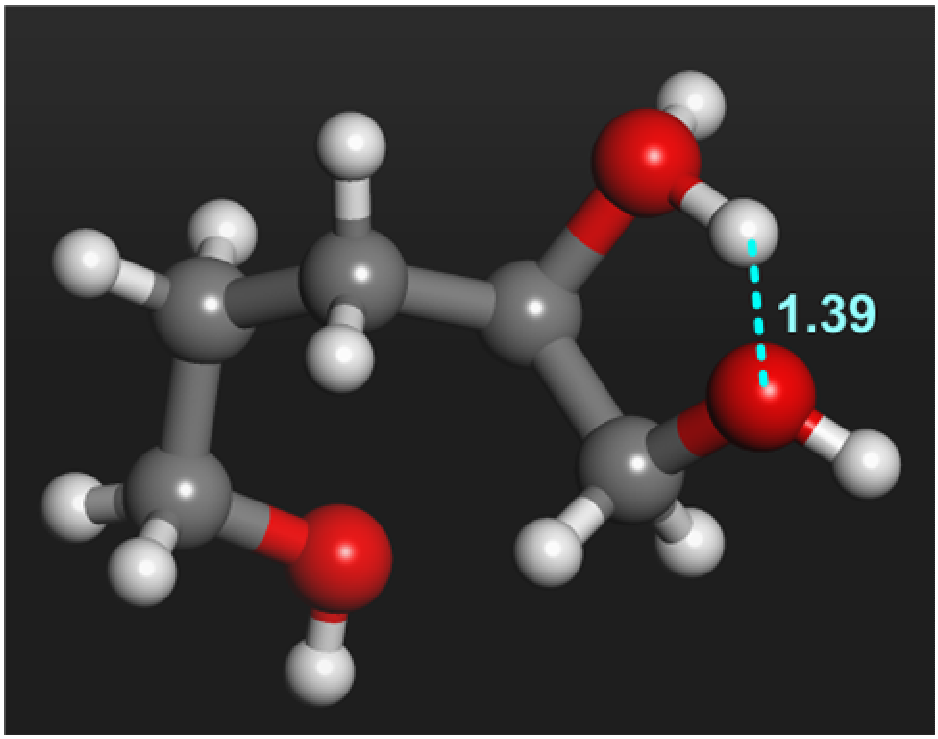


Figure S2. DFT-optimized structure for the water-stabilized tetrahydrofurfuryl carbenium ion intermediate.