Electronic Supplementary Information for

Hydrodeoxygenation of potential platform chemicals derived from

biomass to fuels and chemicals

Keiichi Tomishige,* Mizuho Yabushita, Ji Cao, Yoshinao Nakagawa

Department of Applied Chemistry, School of Engineering, Tohoku University, 6-6-07 Aoba, Aramaki, Aoba-ku, Sendai, Miyagi 980-8579, Japan

*Corresponding author: tomi@erec.che.tohoku.ac.jp (K.T.)

S1. Model reactions of single-hydrodeoxygenation of alkyl glycosides: hydrodeoxygenation of 1,2-cyclohexanediol

As a related substrate to alkyl glycosides, the reported results of the hydrodeoxygenation of 1,2cyclohexanediols are introduced here and summarized in Table S1. Figure S1 shows the time course of the hydrodeoxygenation of *trans*-1,2-cyclohexanediol in alkane (n-heptane) solvent using Ir-ReO_x/SiO₂ catalyst. The initial selectivity of *cis*-1,2-cyclohexanediol was rather high, suggesting that the isomerization of trans-1,2-cyclohexanediol proceeded readily. This behavior is different from that observed in the hydrodeoxygenation of alkyl glycosides, where their stereochemistry is maintained,^{S1,S2} although the epimerization of alkyl glycosides does not proceed easily because the substituents with the 6-membered ring are present. The maximum yield of cyclohexanol as a singlehydrodeoxygenation product was 74% in the *n*-heptane solvents. The reaction time profile in Figure S1 indicates that the consecutive hydrodeoxygenation of cyclohexanol was suppressed until the concentration of 1,2-cyclohexanediols became rather low. This behavior can be explained by the difference between the adsorption strength of 1,2-cyclohexanediols and cyclohexanol on the Ir-ReO_x/SiO₂ catalyst. During the reaction in the *n*-heptane solvent, the adsorption of 1,2cyclohexanediols on the Ir-ReO_x/SiO₂ catalyst is clearly stronger than that of cyclohexanol. The negative reaction order (-0.25) with respect to the concentration of *trans*-1,2-cyclohexanediol in the hydrodeoxygenation was obtained and can be explained by the strong adsorption of trans-1,2cyclohexanediol on the active site.^{S3} Unfortunately, the application of this system to alkyl glycosides is not easy because of the poor solubility of alkyl glycosides in alkane solvents.

Substrate (amount [g])	Catalyst (amount [g])	Temp. [K]	H ₂ pressure [MPa]	Solvent	Reactio n time [h]	Conv. [%]	Main Product (yield [%])	Ref.
ОН	Ir-ReO _x /SiO ₂		_	<i>n</i> -Heptane	16	88	\bigcirc	он
(0.5)	(0.10)	393	7	Water	20	77	\bigcirc	<u>он</u> S3 Юн
(0.1) (0.1)	Pt-AlO _x /WO ₃	453	3	Water	16	57	(26) (30) ОН	6.4
(0.1) OH	(0.10)	453	3	Water	16	14	(4) (9) ОН	54
(0.5) OH (0.5)	Ru-MnO _x /C (0.05)	433	1.5	Water	2	18 ^{<i>a</i>}	Он (15) (1)	S5
ОН (0.5)	Ru/ZrO ₂ - La(OH) ₃ (0.10)	493	4	Water	4	63 ^{<i>a</i>}	Он (61) (2)	S6
ОН (0.2)	Ni/H-ZSM-5 (0.04)	523	3	None	2	70	Сорон (10) (38) (20) (10) (38)	он S7

Table S1. Single-hydrodeoxygenation of 1,2-cyclohexanediols over heterogeneous catalysts

^a Trans-cis isomerization was excluded for calculation.



Figure S1. Time course of hydrodeoxygenation of *trans*-1,2-cyclohexanediol over $\text{Ir-ReO}_x/\text{SiO}_2$ in *n*-heptane. Reaction conditions: $\text{Ir-ReO}_x/\text{SiO}_2$ (Ir 4 wt%, Re/Ir = 2) 100 mg, *trans*-1,2-cyclohexanediol 0.5 g, *n*-heptane 10 mL, H₂ 6.8 MPa, 393 K. Reprinted from ref. S3 with permission from the Elsevier, copyright 2013.

In addition to the Ir-ReO_x/SiO₂ catalyst, heterogeneous catalysts based on Ru,^{S5,S6} Pt,^{S4} and Ni^{S7} were developed for hydrodeoxygenation of 1,2-cyclohexanediols (Table S1), and water solvent, which is not suitable to be applied to the hydrodeoxygenation of alkyl glycosides, was used in most cases. In the case of the single-hydrodeoxygenation of trans-1,2-cyclohexanediol over Ru-MnO_x/C catalyst, although the trans-cis isomerization was excluded for calculation, the catalyst showed up to 83% selectivity to cyclohexanol. Ru/ZrO₂-La(OH)₃ catalyst also showed excellent performance (97% selectivity to cyclohexanol at 67% conversion level) on the partial hydrodeoxygenation of 1,2cyclohexanediol. However, the component of the substrate, 1,2-cyclohexanediol, was not clarified in the literature, we suppose that their conversion was also calculated by excluding the trans-cis isomerization. The mechanism of mono-hydrodeoxygenation of 1,2-cyclohexanediols over these catalysts can be supposed to be a direct hydrogenolysis of C-O bond on the metal surface. However, such a metal-catalyzed mechanism is not selective. An indirect mechanism composed of acid-catalyzed dehydration and metal-catalyzed hydrogenation can be also involved when strong acid such as H-ZSM-5 is present; however, in the acid-catalyzed dehydration, the pinacol rearrangement to cyclopentylmethyl structure also occurs to decrease the selectivity to the products with retention of the ring structure (cyclohexanol in this case).^{S7,S8} Strong acids are not beneficial in the hydrodeoxygenation of cyclic polyols.

Another example of the hydrodeoxygenation of vicinal OH groups in a cyclic diol to a monoalcohol is that of 1,4-anhydroerythritol (1,4-AHERY) to 3-hydroxytetrahydrofuran catalyzed by WO_x-Pd/ZrO₂ or WO_x-Pd/C catalysts, and the yield of 3-hydroxytetrahydrofuran was around 70%,^{S9} which is mentioned in the section of 1,4-AHERY (see the main text). High reactivity was not observed in the conversion of cyclohexanediols to cyclohexanol; unfortunately, these catalysts are not promising in the synthesis of monodeoxysugars. The development of catalysts for the selective singledeoxygenation of alkyl glycosides with hydrogen reductant is thus needed. However, inorganic catalysts have difficulty in causing the regioselective transformation at specific hydroxy groups of alkyl glycosides without protecting other hydroxy groups compared to enzymes, since such reactions always suffer from low selectivity and activity and thus require precise recognition and manipulation of specific hydroxy groups.^{S10,S11}

S2. Energy profiles for hydrogenolysis of glycerol and erythritol

There are two important mechanisms of indirect hydrogenolysis of glycerol: dehydration + hydrogenation and dehydrogenation + dehydration + hydrogenation that can proceed on wide range of catalysts. The energy profiles of the two reaction routes are shown in Figure S2.

In the dehydration + hydrogenation mechanism (Figure S2A), glycerol (G) is first dehydrated to 2,3-propenediol (i2) or 1,3-propenediol (i1), which are then converted to acetol (i4) and 3-hydroxypropanal (i3), respectively, by keto-enol tautomerization. The hydrogenation of acetol (i4) and 3-hydroxypropanal (i3) gives 1,2-propanediol (12P) and 1,3-propanediol (13P), respectively. In the

case of 3-hydroxypropanal (i3), its dehydration to acrolein (i5) proceeds easily because of the acidic nature of C–H at the α -position of carbonyl group (2-position), and the subsequent hydrogenation of acrolein gives 1-propanol (1P). Therefore, the dehydration of glycerol to 2,3-propenediol (i2) and 1,3propenediol (i1) followed by their hydrogenation gives 1,2-propanediol and 1,3-propanediol + 1propanol, respectively. On the basis of the energy profile, 2,3-propenediol (i2) is more easily formed, and thus, 1,2-propanediol is the main product in the dehydration + hydrogenation mechanism. However, the energy difference between 2,3-propenediol (i2) and 1,3-propenediol (i1) is small, which enables the formation of 1,3-propanediol and 1-propanol to some extent. In the dehydrogenation + dehydration + hydrogenation mechanism (Figure S2B), glycerol (G) can be first dehydrogenated to glyceraldehyde (i6) or dihydroxyacetone (i7). Glyceraldehyde (i6) is easily dehydrated to 2hydroxyacrolein (i8) because of the presence of acidic C–H at the α -position of carbonyl group and the C–OH neighboring the α -C–H (*i.e.*, β -C–OH). The tautomerization and hydrogenation of 2hydroxyacrolein (i8) gives 1,2-propanediol (12PD). On the other hand, dihydroxyacetone (i7) is not easily dehydrated because there is no β -C–OH of carbonyl group. The dehydrogenation + dehydration + hydrogenation route gives 1,2-propanediol in very high selectivity. Both of these two indirect mechanisms give 1,2-propanediol as the main product from glycerol.



Figure S2. Energy profiles for indirect glycerol hydrogenolysis to 1,2-propanediol in the route of dehydration + hydrogenation (A) and dehydrogenation + dehydration + hydrogenation (B). The G2MP2 level theory, for the conditions of gas phase, 298 K, and 1 atm; calculated with the Gaussian 16 program package.

Similar analysis of the energy profiles in the erythritol hydrogenolysis by the two indirect different routes (dehydration + hydrogenation, dehydrogenation + dehydration + hydrogenation) is conducted as shown in Figure S3. The reaction routes are more complex than those in glycerol hydrogenolysis. Of the two routes, the dehydrogenation + dehydration + hydrogenation route (Figure S3B) is less complex, in a similar manner to the case of glycerol hydrogenolysis. There are two dehydrogenation products of erythritol (E): erythrose (dehydrogenation at the terminal position; i20 (chain form) and i20' (cyclic form) and erythrulose (dehydrogenation at the internal position; i21). The dehydration product of erythrose at the α -C–H and β -C–OH positions of the carbonyl group is 2,4dihydroxycrotonaldehyde (i22). Further dehydration after the tautomerization of 2,4dihydroxycrotonaldehyde gives 3-buten-1,2-dione (i26). The hydrogenation of these intermediates produces 1,2,4-butanetriol (124BT) and 1,2-butanediol (12BD). The dehydration product of erythrulose (i21) at the α -C–H and β -C–OH positions of the carbonyl group is 1,3-dihydroxy-3-buten-2-one (i24). 1,3-Dihydroxy-3-buten-2-one (i24) and its tautomerization product (i25) do not have pairs of α -C–H and β -C–OH positions of a carbonyl group, and therefore, further dehydration does not occur. The hydrogenation of 1,3-dihydroxy-3-buten-2-one (i24) produces 1,2,3-butanetriol (123BT). After all, the dehydrogenation at a terminal and an internal position gives 1,2,4-butanetriol + 1,2-butanediol and 1,2,3-butanetriol, respectively. Although erythrulose (precursor of 1,2,3-butanetriol; i21) is energetically more stable, steric effect of metal-catalyzed dehydrogenation is generally large, which favors the formation of erythrose (dehydrogenation product at the terminal position, i20; precursor of 1,2,4-butanetriol and 1,2-butanediol). The ratio of 1,2,4-butanetriol + 1,2-butanediol to 1,2,3butanetriol depends on the catalyst. The dehydration + hydrogenation route (Figure S3A) is very complex. The energy levels of the initial dehydration products of erythritol (i10-12) are similar, and therefore, both 1,2,3-butanetriol and 1,2,4-butanetriol are produced. Further dehydration of intermediates also enables the formation of 1,4-butanediol, 1,2-butanediol, and 2,3-butanediol. An important point of the dehydration of erythritol is the possibility in the formation of the cyclic product, namely 1,4-AHERY. 1,4-AHERY is more stable than the other primary dehydration products (i10-12) of erythritol. In fact, 1,4-AHERY can be synthesized from erythritol with a strong Brønsted acid almost quantitatively, as mentioned above. The C-O hydrogenolysis of erythritol by dehydration + hydrogenation routes is unselective by formation of various products or even does not proceed by the formation of 1,4-AHERY.



Figure S3. Energy profiles for indirect erythritol hydrogenolysis in the route of dehydration + hydrogenation (A) and dehydrogenation + dehydration + hydrogenation (B). The G2MP2 level theory, for the conditions of gas phase, 298 K, and 1 atm; calculated with the Gaussian 16 program package.

S3. Hydrogenolysis of glycerol to 1,3-propanediol

Table S2 lists the selected results in the glycerol hydrogenolysis to 1,3-propanediol. The systems with high 1,3-propanediol yield or high formation rate of 1,3-propanediol are selected. Pt-WO_x catalysts tend to exhibit high yield of 1,3-propanediol, and Ir-ReO_x catalysts tend to show high formation rate of 1,3-propanediol even at lower reaction temperature than the case of Pt-WO_x catalysts. This tendency indicates that Ir-ReO_x catalysts has an advantage in terms of the catalytic activity, which enables the lower reaction temperature, and Pt-WO_x catalysts have an advantage from the viewpoint of high yield of target products and selectivity.

Catalyst	(W or Re)/NM	Temp. [K]	Conv. [%]	Sel. to 1,3-PrD	Yield of 1,3-PrD	Rate $[g_{1,3-PrD} g_{NM^{-1}} h^{-1}]$		Ref.
	molar			[%]	[%]	Initial	Average at	
	ratio						maximum yield	
Ir-ReO _x /SiO ₂ , Ir 4 wt%	1	393	81	46	38	18	5.7	S12
Ir-ReO _x /SiO ₂ , Ir 20 wt%	0.34	393	69	47	32	22	7.4	S13
Ir-ReO _x /TiO ₂	0.25	393	69	52	36	52	17	S14
Pt-W/AlOOH	4.7	453	100	66	66	n.r.	2.3	S15
Pt/W-SBA-15	0.14	423	87	71	62	n.r.	1.7	S16
$Pt-WO_x/t-ZrO_2$	4.1	413	78	63	49	n.r.	5.1	S17
Pt-WO _x /SiO ₂	0.25	413	100	57	57	6.5	2.5	S18
Pt-WO _x / <i>t</i> -Ta ₂ O ₅	0.79	433	87	46	40	n.r.	19	S19
Pt/W-silicafoam	0.28	423	100	63	63	n.r.	2.2	S20

Table S2. Selected systems of glycerol hydrogenolysis to 1,3-propanediol

NM: noble metal (Ir or Pt); PrD: propanediol; n.r.: not reported.

Supplementary references

- S1 M. Tamura, N. Yuasa, J. Cao, Y. Nakagawa and K. Tomishige, *Angew. Chem. Int. Ed.*, 2018, 57, 8058–8062.
- S2 J. Cao, M. Tamura, Y. Nakagawa and K. Tomishige, ACS Catal., 2019, 9, 3725–3729.
- S3 Y. Nakagawa, K. Mori, K. Chen, Y. Amada, M. Tamura and K. Tomishige, *Appl. Catal. A: Gen.*, 2013, 468, 418–425.
- S4 K. Kaneda and H. Matsuda, Jpn. Pat., 2014185112A, 2013.
- S5 M. Ishikawa, M. Tamura, Y. Nakagawa and K. Tomishige, *Appl. Catal. B: Environ.*, 2016, **182**, 193–203.
- S6 G.-Y. Xu, J.-H. Guo, Y.-C. Qu, Y. Zhang, Y. Fu and Q.-X. Guo, *Green Chem.*, 2016, 18, 5510–5517.
- S7 W. Song, Y. Liu, E. Baráth, C. Zhao and J. A. Lercher, *Green Chem.*, 2015, 17, 1204–1218.
- S8 J. S. Yoon, J.-W. Choi, D. J. Suh, K. Lee, H. Lee and J.-M. Ha, *ChemCatChem*, 2015, 7, 2669–2674.
- S9 Y. Amada, N. Ota, M. Tamura, Y. Nakagawa and K. Tomishige, *ChemSusChem*, 2014, 7, 2185–2192.
- S10 W. R. Gunther, Y. Wang, Y. Ji, V. K. Michaelis, S. T. Hunt, R. G. Griffin and Y. Román-Leshkov, *Nat. Commun.*, 2012, 3, 1109.
- S11 X. Li, J. Wu and W. Tang, J. Am. Chem. Soc., 2022, 144, 3727–3736.
- S12 Y. Nakagawa, Y. Shinmi, S. Koso and K. Tomishige, J. Catal., 2010, 272, 191–194.
- S13 L. Liu, S. Kawakami, Y. Nakagawa, M. Tamura and K. Tomishige, Appl. Catal. B: Environ., 2019, 256, 117775.
- S14 L. Liu, T. Asano, Y. Nakagawa, M. Tamura, K. Okumura and K. Tomishige, ACS Catal., 2019, 9, 10913-

10930.

- S15 R. Arundhathi, T. Mizugaki, T. Mitsudome, K. Jitsukawa and K. Kaneda, ChemSusChem, 2013, 6, 1345–1347.
- S16 Y. Fan, S. Cheng, H. Wang, D. Ye, S. Xie, Y. Pei, H. Hu, W. Hua, Z. H. Li, M. Qiao and B. Zong, *Green Chem.*, 2017, **19**, 2174–2183.
- S17 Y. Fan, S. Cheng, H. Wang, J. Tian, S. Xie, Y. Pei, M. Qiao and B. Zong, *Appl. Catal. B: Environ.*, 2017, 217, 331–341.
- S18 L. Liu, T. Asano, Y. Nakagawa, M. Tamura and K. Tomishige, Green Chem., 2020, 22, 2375–2380.
- S19 B. Zhao, Y. Liang, L. Liu, Q. He and J. Dong, Green Chem., 2020, 22, 8254–8259.
- S20 S. Cheng, Y. Fan, X. Zhang, Y. Zeng, S. Xie, Y. Pei, G. Zeng, M. Qiao and B. Zong, *Appl. Catal. B: Environ.*, 2021, 297, 120428.