

Electronic Supplementary Information (ESI)

Hydrogenolysis of isosorbide to diols and triols over a heterogeneous SiO₂-supported Rh catalyst

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Experimental section

1. Catalyst preparation

Generally, the 4 wt% M/SiO₂ catalysts (M=Ru, Rh, Ir, Pt, Pd) were prepared by impregnation method as follows: metal precursor solutions (Ir(NO₃)₄ HNO₃ solution, Furuya Metals Co., Ltd., 8.68 wt%; Rh(III) nitrate solution, Sigma-Aldrich, 8 wt%, Ruthenium(III) nitrosyl nitrate solution, Sigma-Aldrich, 1.5 wt%; Tetraammineplatinum(II) nitrate solution, Sigma-Aldrich, 50.6 wt% and Palladium(II) nitrate solution, Sigma-Aldrich, 4.62 wt%) were first loaded on the SiO₂ (Fuji Silysia Chemical Ltd., G-6, 535 m²/g). After evaporating the solvent, the catalysts were dried at 383 K for 12 h, followed by the calcination process in air at 773 K for 3 h. The standard loading amount of noble metal (M) was 4 wt %. Similarly, Rh loaded on other metal oxide supports including ZrO₂ (Daiichi Kigenso Kagaku Kogyo), Al₂O₃ (Sumitomo Chemical), CeO₂ (Daiichi Kigenso Kagaku Kogyo), MgO (Ube Industries) catalysts were also prepared by the same method.

2. Catalytic reactions

The activity tests were carried out in a stainless-steel autoclave (190 mL) equipped with a glass inner vessel. Typically, isosorbide, catalysts and water were added into the autoclave with a magnetic stirrer. After being sealed, the air inside the reactor was purged with H₂ (1 MPa) three times and

increased to 5.5 MPa at ambient temperature for the reaction. The autoclave was then heated to 453 K (defined as 0 h of reaction time) with H₂ pressure reaching 8 MPa (at 453 K) at a stirring rate of 500 rpm, and the temperature was monitored using a thermocouple inserted in the autoclave. Isosorbide was completely dissolved in water under reaction conditions. After an appropriate reaction time, the reactor was cooled down and the gases were collected in a gas bag, followed by the analysis using a gas chromatograph (Shimadzu, GC-2014) equipped with an FID detector and a DB-1 capillary column (Agilent, length = 30 m, i.d. = 0.25 mm, film thickness = 0.25 μm) by using dichloromethane as internal standard. In the case of methane and ethane, an external method was applied. After filtration of the reaction mixture, the liquid solution underwent silylation by adding certain amount of TMSI (Thermo Scientific), followed by reacting at 323-333 K for 30 min. The mixture was separated by centrifugation at 6000 rpm for 5 min and then analyzed by GC-FID under the same condition as gas products with mesitylene as internal standard. The qualitative analysis of the liquid sample was carried out by using a gas chromatograph-mass spectrometry (Shimadzu, GCMS-QP2020) equipped with an FID detector and a DB-1 capillary column (Agilent, length = 30 m, i.d. = 0.25 mm, film thickness = 0.25 μm). The conversion, yield and selectivity were calculated by the following equations: Conversion (%) = $\{1 - (\text{sum of C-based mol of residual substrate}) / (\text{C-based mol of substrate input})\} \times 100$; Yield (%) = $\{(\text{C-based mol of product}) / (\text{C-based mol of substrate input})\} \times 100$; Selectivity (%) = $\{(\text{C-based mol of product}) / (\text{sum of C-based mol of products})\} \times 100$. The carbon balance of experiments was within the experimental error ($\pm 10\%$).

3. Characterization of catalysts

X-ray diffraction (XRD) patterns were recorded by a diffractometer (Rigaku MiniFlex-600) with Cu K α ($\lambda = 0.154$ nm, 45 kV, 40 mA) radiation. Transmission electron microscopy (TEM) images of the samples were recorded on a JEM-2100F electron microscope operated at 200 kV. Temperature-programmed reduction with hydrogen (H₂-TPR) was measured with a Microtrac-BEL equipped with a thermal conductivity detector (TCD). The sample amount was about 100 mg. The sample was heated

under 5% H₂/Ar with 30 mL/min flow rate from 173 K to 1073 K at a heating rate of 10 K/min.

4. Reusability test

The solid catalyst in the collected mixture was separated by filtration and washed with H₂O (3 g) 3 times to remove organic compounds on the surface of the catalyst. The washed catalyst was dried at 383 K in air overnight and then used for the next run under the same reaction condition as the first run. Several batches were carried out in parallel, and the catalyst collected from the parallel reactions was used to compensate for the catalyst loss in the procedure of reuse.

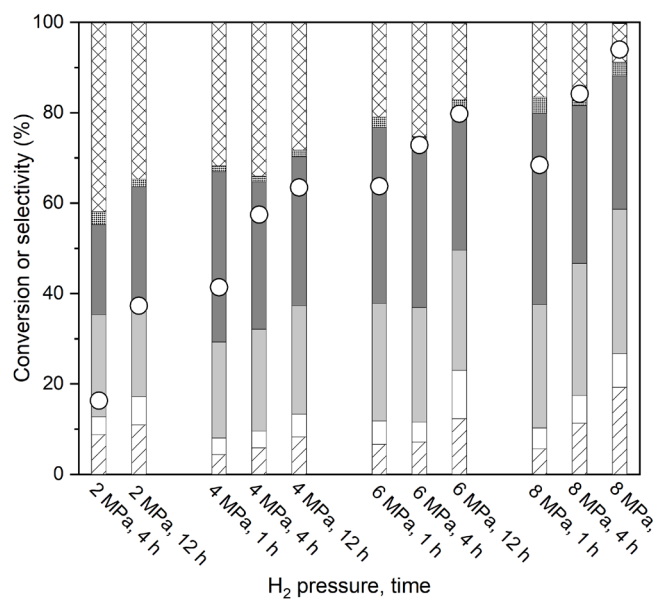


Fig. S1 The dependence of H₂ pressure (at 453 K) on isosorbide hydrogenolysis (○: conversion, bars: selectivities (stripe: alkanes, white: mono-ols, gray: diols, dark gray: triols, gray grid: tetraols, across stripe: isomers of isosorbide, black: others). Reaction conditions: 4 g isosorbide, 2 g H₂O, 0.6 g Rh/SiO₂, 453 K.

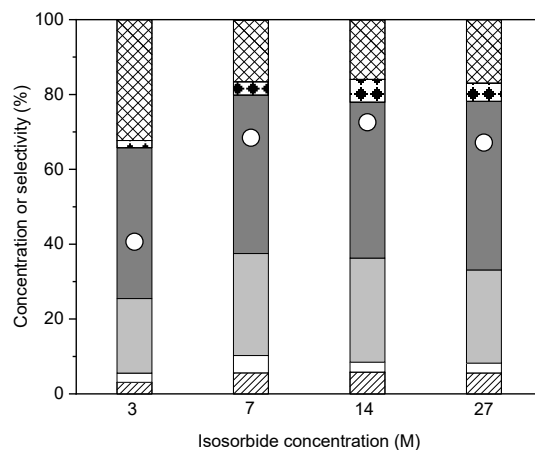


Fig. S2 The effect of isosorbide concentration on its hydrogenolysis over Rh/SiO₂ catalyst (○: conversion, bars: selectivities (stripe: alkanes, white: mono-ols, gray: diols, dark gray: triols, gray gride: tetraols, across stripe: isomers of isosorbide, black: others). Reaction conditions: 4 g isosorbide, 1-10 g H₂O, 0.6 g Rh/SiO₂, 453 K, 8 MPa H₂ (at 453 K), 1 h.

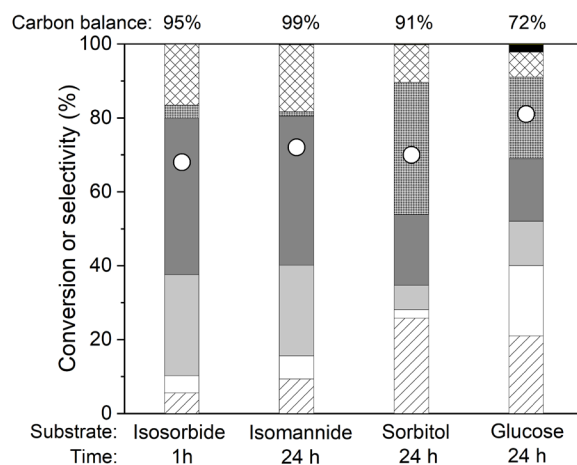


Fig. S3 The hydrogenolysis of C6 sugars over Rh/SiO₂ catalyst (○: conversion, bars: selectivities (stripe: alkanes, white: mono-ols, gray: diols, dark gray: triols, gray gride: tetraols, across stripe: isomers of isosorbide, black: others)). Reaction condition: 28 mmol substrate, 2 g H₂O, 0.6 g Rh/SiO₂, 8 MPa H₂ (at 453 K), 453 K.

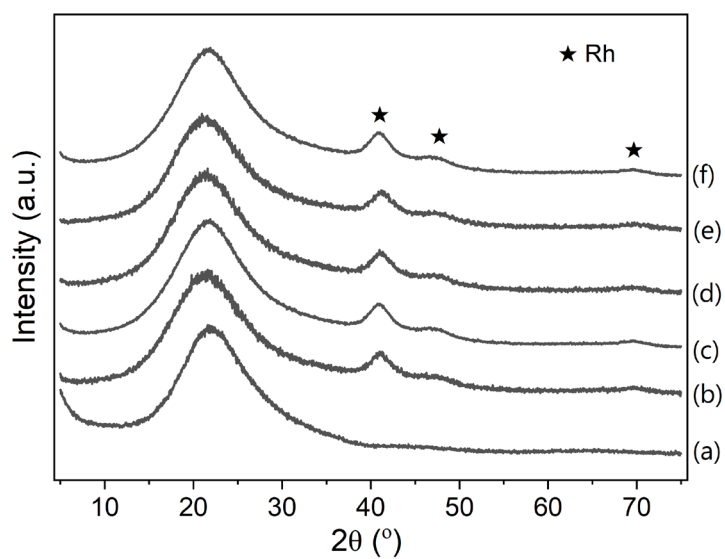


Fig. S4 XRD patterns of reused Rh/SiO₂ catalysts. (a) SiO₂, (b) Rh/SiO₂ at 0 h, (c) Rh/SiO₂ after 1 run, (d) Rh/SiO₂ after 2 runs (e) Rh/SiO₂ after 3 runs (f) Rh/SiO₂ after 4 runs. Reaction conditions: 4 g isosorbide, 2 g H₂O, 0.6 g Rh/SiO₂, 8 MPa H₂ (at 453 K), 453 K, 4h.

Table S1 The dependence of H₂ pressure (at 453 K) on isosorbide hydrogenolysis.

Entry	H ₂ (MPa)	t (h)	Conv. (%)	Yield (selectivity) (%)							
				Tetraols	Triols	Diols	Triols +diols	Alkanes	Mono-ols	Isomers	Others
1	2	4	16	0.3 (2.8)	1.9 (22)	2.2 (23)	4.1 (45)	0.8 (8.9)	0.4 (4.0)	4.0 (42)	<0.1 (2.3)
2		12	37	0.5 (1.6)	8.3 (28)	6.3 (20)	15 (48)	3.4 (11)	2.0 (6.2)	11 (35)	<0.1 (0.2)
3	4	1	41	0.5 (1.2)	15 (38)	8.4 (21)	23 (59)	1.7 (4.4)	1.4 (3.6)	13(32)	<0.1 (0.1)
4		4	57	0.6 (1.2)	16 (33)	11 (23)	27 (56)	2.9(5.8)	1.8 (3.7)	17 (34)	<0.1 (0.1)
5	6	12	63	0.8 (1.4)	18 (33)	13 (24)	31 (57)	4.5 (8.3)	2.7 (5.0)	15 (28)	0.1 (0.1)
6		1	64	1.3 (2.3)	23 (39)	16 (26)	39 (65)	3.9 (6.6)	3.1 (5.2)	12 (21)	0.1 (0.1)
7	8	4	73	1.4 (2.1)	23 (36)	17 (25)	40 (61)	4.7 (7.1)	2.9 (4.4)	17 (25)	0.1 (0.1)
8		12	80	1.5 (1.9)	24 (31)	20 (27)	45 (60)	9.3 (12)	8.1 (11)	13 (17)	0.2 (0.2)
9	8	1	68	2.3 (3.6)	27 (42)	17 (27)	44 (69)	3.5 (5.6)	2.9 (4.6)	10 (17)	0.1 (0.1)
10		4	84	2.8 (3.5)	28 (35)	23 (29)	51 (64)	9.0 (11)	4.9 (6.2)	12 (15)	0.1 (0.2)
11		8	96	4.1 (4.5)	29 (32)	29 (33)	58 (65)	14 (16)	8.0 (8.7)	5.6 (6.2)	0.2 (0.2)

Reaction conditions: 4 g isosorbide, 2 g H₂O, 0.6 g Rh/SiO₂, 453 K.

Table S2 The effect of reaction temperature on hydrogenolysis of isosorbide over Rh/SiO₂ catalyst.

Entry	T (K)	t (h)	Conv. (%)	Yield (selectivity) (%)								Carbon balance (%)
				Tetraols	Triols	Diols	Triols + diols	Alkanes	Mono-ols	Isomers	Others	
1	433	1	48	2.0 (4.4)	24 (52)	11 (24)	35 (76)	1.1 (2.3)	1.2 (4.0)	7.0 (15)	<0.1 (0.1)	99
2		4	74	3.9 (5.7)	29 (43)	17 (25)	46 (68)	4.1 (6.0)	4.4 (6.2)	9.5 (14)	0.1 (0.1)	93
3	453	1	68	2.3 (3.6)	27 (42)	17 (27)	44 (69)	3.5 (5.6)	2.9 (3.6)	10 (17)	0.1 (0.1)	94
4		4	84	2.8 (3.5)	28 (35)	23 (29)	51 (64)	9.0 (11)	4.9 (3.7)	12 (15)	0.1 (0.2)	94
5	473	1	74	1.7 (2.3)	24 (34)	20 (27)	44 (61)	6.2 (6.6)	4.0 (8.7)	16 (22)	0.1 (0.2)	97
6		4	90	2.4 (2.8)	22 (28)	24 (26)	46 (54)	16 (19)	9.9 (12)	11 (13)	0.2 (0.2)	94

Reaction conditions: 4 g isosorbide, 2 g H₂O, 0.6 g Rh/SiO₂, 8 MPa H₂ (at 453 K).

Table S3 The effect of isosorbide concentration on its hydrogenolysis over Rh/SiO₂ catalyst.

Entry	Concentration (mM)	Conv. (%)	Yield (selectivity) (%)							
			Tetraols	Triols	Diols	Triols +diols	Alkanes	Mono-ols	Isomers	Others
1	3	41	0.7 (1.9)	15 (40)	7.3 (20)	22 (60)	1.1 (3.1)	0.9 (2.5)	12 (32)	<0.1 (<0.1)
2	7	68	2.3 (3.6)	27 (42)	17 (27)	44 (69)	3.5 (5.6)	2.9 (4.6)	10 (16)	0.1 (0.1)
3	14	73	4.2 (6.1)	29 (42)	19 (28)	48 (70)	4.0 (5.8)	1.8 (2.6)	11 (16)	<0.1 (0.1)
4	27	67	3.4 (4.9)	31 (45)	17 (25)	48 (70)	3.9 (5.6)	1.8 (2.6)	12 (17)	<0.1 (<0.1)

Reaction conditions: 4 g isosorbide, 1-10 g H₂O, 0.6 g Rh/SiO₂, 8 MPa H₂ (at 453 K), 453 K, 1 h.

Table S4 The reusability of Rh/SiO₂ catalyst for hydrogenolysis of isosorbide.

	Particle size (nm) ^a	Conv. (%)	Yield (%)							Carbon balance (%)
			Tetraols	Triols	Diols	Alkanes	Mono-ols	Isomers	Others	
Fresh	3.9	84	2.8	28	23	9.0	4.9	12	0.1	94
Run 1	3.9	88	3.3	25	21	13	8.2	12	0.1	95
Run 2	3.7	81	3.8	26	20	7.7	5.8	14	0.1	96
Run 3	3.9	78	3.1	27	20	5.6	2.8	16	0.1	95

Reaction conditions: 4 g isosorbide, 2 g H₂O, 0.6 g Rh/SiO₂, 8 MPa H₂ (at 453 K), 453 K, 4 h.

^a Measured by XRD analysis in Fig. S4.

Table S5 The evolution of the products along with reaction time.

Entry	<i>t</i> (h)	Conv. (%)	Yield (selectivity) (%)							Carbon balance (%)	
			Tetraols	Triols	Diols	Triols +diols	Alkanes	Mono-ols	Isomers		Others
1	0	26	0.2 (1.0)	7.2 (29)	5.7 (22)	13 (51)	1.0 (4.0)	0.8 (3.2)	10 (41)	<0.1 (0.2)	99
2	1	68	2.3 (3.6)	27 (42)	17 (27)	44 (70)	3.5 (5.6)	2.9 (4.6)	10 (17)	0.1 (0.1)	95
3	4	84	2.8 (3.5)	28 (35)	23 (29)	51 (64)	9.0 (11)	4.9 (6.2)	12 (15)	0.1 (0.2)	96
4	6	90	3.1 (3.8)	27 (33)	25 (31)	52 (64)	12 (15)	5.0 (6.1)	9.5 (12)	0.2 (0.2)	92
5	8	96	4.1 (4.5)	29 (32)	30 (33)	59 (65)	14 (16)	8.0 (8.7)	5.6 (6.2)	0.2 (0.2)	96

Reaction conditions: 4 g isosorbide, 2 g H₂O, 0.6 g Rh/SiO₂, 8 MPa H₂ (at 453 K), 453 K.