

Supporting Information for

Selective Hydrodeoxygenation of γ -Valerolactone over Silica-supported Rh-based Bimetallic Catalysts

Xin Huang ^{a,b,*}, Shinji Kudo ^{b,*}, U.P.M. Ashik ^b, Hisahiro Einaga ^b, Jun-ichiro Hayashi ^b

^a Key Laboratory of Low-grade Energy Utilization Technologies and Systems of Ministry of Education, School of Energy and Power Engineering, Chongqing University, Chongqing 400044, China

^b Institute for Materials Chemistry and Engineering, Kyushu University, 6-1 Kasuga Koen, Kasuga 816-8580, Japan

* Corresponding author. E-mail: xin_huang@cqu.edu.cn, shinji_kudo@cm.kyushu-u.ac.jp, Tel/Fax: +81 92 583 779

Table of Contents

Page S2: Catalytic performance of silica-supported Rh-based catalysts in water at 160°C (**Table S1**), structural properties of solid acid catalysts (**Table S2**), and reuse of catalysts without recalcination (**Table S3**)

Page S3: XRD patterns of Rh-based bimetallic catalysts (**Figure S1**)

Table S1 Hydrodeoxygenation of GVL over silica-supported Rh-based catalysts in water.

Entry	Catalyst	Conv. (%)	Selectivity (%) ^[a]				
			2-BuOH	2-MTHF	2-PeOH	1,4-PDO	PA
1	Rh/SiO ₂	11	58	9	12	7	14
2	RhMo/SiO ₂ (0.25)	40	14	30	16	40	-
3	RhMo/SiO ₂ (0.5)	38	23	26	13	38	-
4	RhRe/SiO ₂ (0.25)	38	18	25	19	38	-
5	RhRe/SiO ₂ (0.5)	37	23	35	5	37	-

Reaction conditions: 160°C, 6 h, GVL 1 mmol, catalyst 100 mg, H₂O 10 mL, and H₂ 4.5 MPa.^[a] BuOH: butanol, MTHF: methyltetrahydrofuran, PeOH: pentanol, PDO: pentandiol, PA: pentenoic acid.**Table S2** Structural properties of solid acid catalysts used in this study.

Solid acid catalyst	<i>S</i> _{BET} (m ² ·g ⁻¹)	<i>V</i> _{total} (cm ³ ·g ⁻¹)	<i>V</i> _{micro} (cm ³ ·g ⁻¹)	Acid sites (mmol·g ⁻¹)
Amberlyst 70 ^[a]	36	-	-	2.65
S/AC ^[a]	1242	0.558	0.496	0.44
Mordenite ^[a]	501	0.361	0.219	0.717
ZSM-5 ^[a]	419	0.264	0.155	0.325
Yzeolite ^[a]	705	0.356	0.249	N.A.
Beta zeolite ^[a]	508	0.290	0.186	N.A.
Nafion NR50 ^[b]	0.02	-	-	0.900

^[a] ACS Sustainable Chem. Eng., 2019, 7(6), 5892-5899.^[b] Biore sour. Technol. 2015, 191, 300-305.**Table S3** Recyclability of RhMo/SiO₂(0.25) and RhRe/SiO₂(0.5) with and without recalcination.

Catalyst	Recalcination	Temp. (°C)	Conv. (%)	Selectivity (%) ^[a]				
				Butane	Pentane	2-BuOH	2-MTHF	2-PeOH
RhMo/SiO ₂	no	120	49	<1	<1	6	90	4
	yes	120	76	-	<1	3	79	16
RhRe/SiO ₂	no	160	37	<1	<1	5	67	23
	yes	160	100	17	83	-	-	-

Reaction conditions: 6 h, GVL 3 mmol, catalyst 100 mg, heptane 10 mL, and H₂ 4.5 MPa.^[a] BuOH: butanol, MTHF: methyltetrahydrofuran, PeOH: pentanol. PDO: pentandiol.

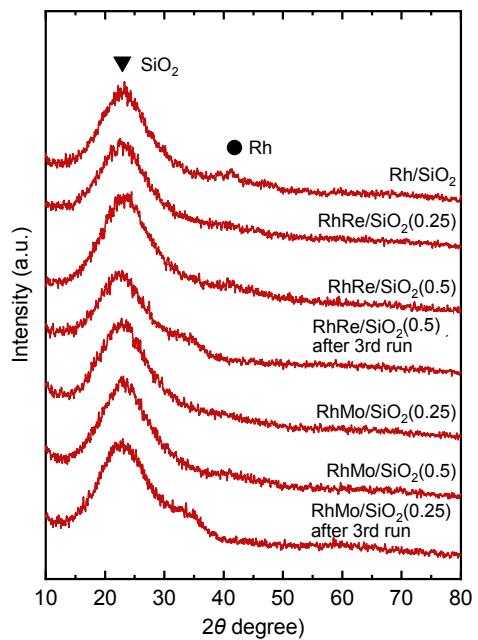


Figure S1. XRD patterns of Rh-based bimetallic catalysts.