

Supplementary Information

Hydrogenative Ring-Rearrangement of Biomass Derived 5-(Hydroxymethyl)furfural to 3-(Hydroxymethyl)cyclopentanol Using Combination Catalyst Systems of Pt/SiO₂ and Lanthanoid Oxides

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Table S1. Composition of diastereomers of 3-(hydroxymethyl)cyclopentanol (HCPO) for Table 1.

Entry	Catalyst	(1R,3R) or (1S,3S)	(1R, 3S) or (1S, 3R)
1	Pt/SiO ₂ +Nd ₂ O ₃	31	57
2	Pt/SiO ₂ +La ₂ O ₃	28	54
3	Pt/SiO ₂ +CeO ₂	26	48
4	Pt/SiO ₂ +Dy ₂ O ₃	20	36
5	Pt/SiO ₂ +Yb ₂ O ₃	27	52
6	Pt/SiO ₂ +Ta ₂ O ₅	0	4
7	Pt/SiO ₂ +Al ₂ O ₃	15	36
8	Pt/SiO ₂	3	6
9	Pt/SiO ₂ +TiO ₂	14	29
10	Pt/SiO ₂ +ZrO ₂	4	8
11	Pt/SiO ₂ +Nb ₂ O ₅	12	27
12	Pt/SiO ₂ +SAH	10	21
13	Pt/SiO ₂ +HT	6	14
14	Pt/SiO ₂ +MgO	2	5
15	Pt/La ₂ O ₃	0	0
16	Pt/SiO ₂ +H ₃ PO ₄ ^d	0	1

Table S2. Composition of diastereomers of 3-(hydroxymethyl)cyclopentanol (HCPO) for Table 2.

Entry	Catalyst	(1R,3R) or (1S,3S)	(1R, 3S) or (1S, 3R)
1	Pt/SiO ₂	10	26
2	Pt/SiO ₂ +Ta ₂ O ₅	5	11
3	Pt/SiO ₂ +Al ₂ O ₃	18	34
4	Pt/SiO ₂ +Nb ₂ O ₅	23	42
5	Pt/SiO ₂ +SAH	13	27
6	Pt/SiO ₂ +MgO	5	13

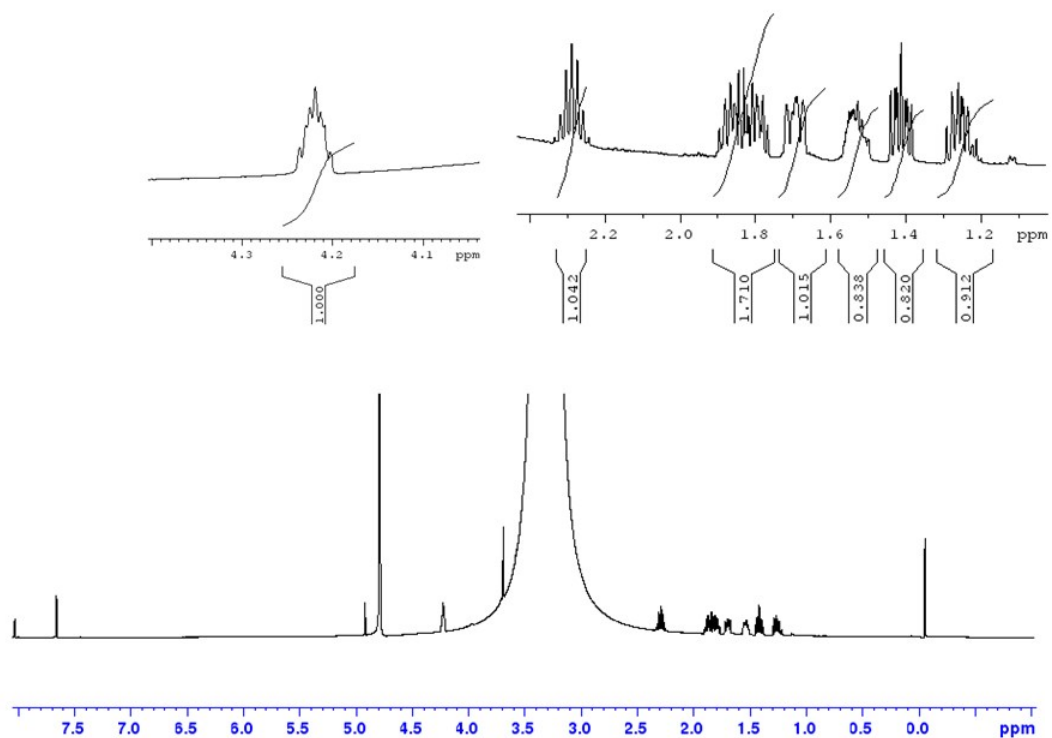
(1R,3R) or (1S,3S)-3-(hydroxymethyl)cyclopentanol

^1H NMR ($\text{CD}_3\text{OD}/\text{CDCl}_3$ 2:1, 500MHz)

δ in ppm: 4.23 (m, 1H), 2.26 (m, 1H), 1.83 (m, 2H), 1.69 (m, 1H), 1.53 (m, 1H), 1.41 (m, 1H), 1.26 (m, 1H).

GC-MS: $m/z = 116$ $[\text{M}]^+$

^1H NMR chart of (1R,3R) or (1S,3S)-3-(hydroxymethyl)cyclopentanol



(1R,3S) or (1S,3R)-3-(hydroxymethyl)cyclopentanol

^1H NMR (CD_3OD , 500MHz)

δ in ppm: 4.29 (m, 1H), 3.61 (m, 1H), 2.71 (br, 2H), 2.29 (m, 1H), 2.02 (m, 1H), 1.80 (m, 2H), 1.68 (m, 3H), 1.50 (m, 1H).

GC-MS: $m/z = 116$ $[\text{M}]^+$

^1H NMR chart of (1R,3S) or (1S,3R)-3-(hydroxymethyl)cyclopentanol

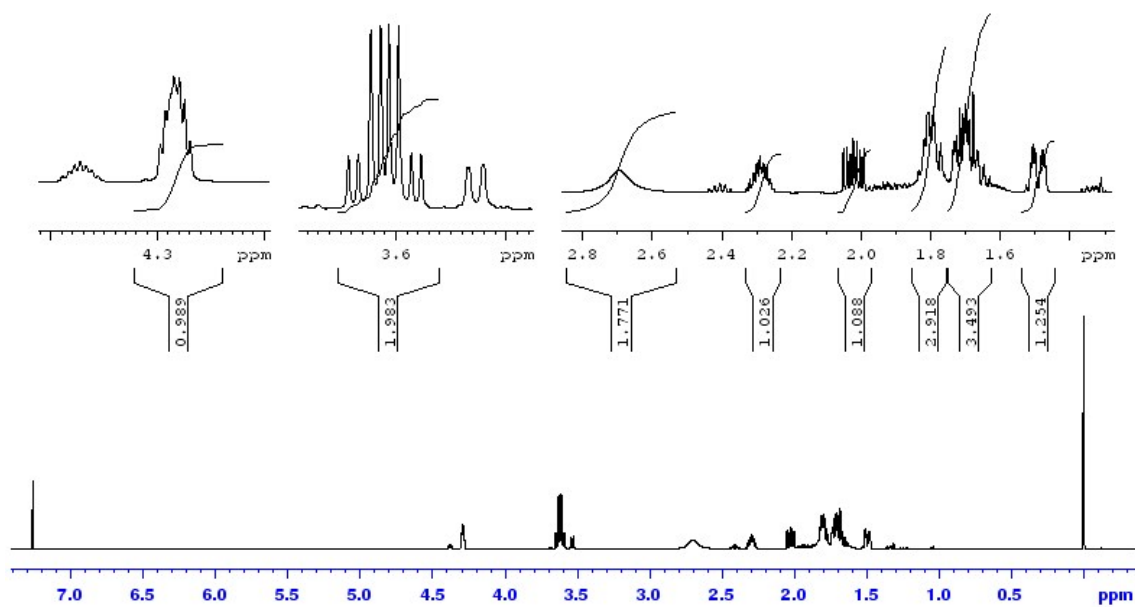


Table S3. Peak wavenumber of FT-IR band due to ν_{8a} mode of pyridine adsorbed on MOx.

Metal oxide	Wavenumber (cm ⁻¹)
MgO	1588
La ₂ O ₃	1592
Nd ₂ O ₃	1597
CeO ₂	1598
Dy ₂ O ₃	1602
HT	1602
Yb ₂ O ₃	1603
ZrO ₂	1604
TiO ₂	1604
Nb ₂ O ₅	1604
Ta ₂ O ₅	1607
Al ₂ O ₃	1614
SAH	1619

The HMF hydrogenation was conducted using Pt/SiO₂ + 50 mg of Nd₂O₃ (five times amount of the catalyst in Table 1). As presented in Table 4 (entry 1), 90% yield of HCPO was obtained under the same reaction conditions as Table 1. In other words, the amount of Nd₂O₃ did not affect the yield of the ring-rearranged product. The result suggests that the Lewis acid amount of Nd₂O₃ has little effect on the ring-rearrangement.

The ring-rearrangement of BHF to HHCPEN was conducted using Nd₂O₃ as shown in Table S4 (entry 2 and 3). The ring-rearrangement reaction was improved by Nd₂O₃ in comparison with the reaction without solid catalysts, although the yield of HHCPEN was low. The low yield of HHCPEN might be due to the undesired degradation of BHF, because BHF is relatively easily polymerized.

Table S4. Product yields for HMF hydrogenation on 10 mg Pt/SiO₂ + 50 mg Nd₂O₃ (entry 1), and those for BHF hydrogenation on 10 mg Nd₂O₃ (entry 2) and without catalyst (entry 3).

Entry	Catalyst	Product yield (%) ^b							
		HCPO ^b	HCPN	HHCPEN	BHF	BHTHF	HHD	HDN	1,2,6-HT
1	10 mg Pt/SiO ₂ + 50 mg Nd ₂ O ₃	90	0	0	0	0	0	0	0
2	10 mg Nd ₂ O ₃	0	0	35	0	0	0	0	0
3	-	0	0	28	0	0	0	0	0

^a Reaction conditions: 0.067 M HMF or BHF aq. 3 mL; H₂ 3 MPa, 140°C, 30 h. ^b Reaction conditions: 0.067 M BHF aq. 3 mL; H₂ 3 MPa, 140°C, 6 h.