

## Electronic Supplementary Information

# Catalytic Hydrogenation of Amino Acids to Amino Alcohols with Complete Retention of Configuration

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## 1. Experimental

### 1.1. General

The HPLC (Shimadzu Prominence) with Crownpak CR(+) (Daicel, Co., Lt., 4.0 $\phi$ , 150 mm) or Nova-Pak C-18 (Waters, Co. Ltd., 3.9 $\phi$ , 150 mm) and GC (Shimadzu GC-2025) analyses were carried out with a CP-Sil-5 capillary column (Agilent Technologies, Inc., diameter 0.25 mm $\phi$ , 50 m) using nitrogen as the carrier gas. All the chemicals for organic reactions were commercially available from chemical products corporation and were used without further purification.

### 1.2 Details of the reagents used in experiments

The details of the reactants are described below: H<sub>2</sub> (99.99%; Nippon Peroxide Co., Ltd.), L-alanine (Wako Pure Chemical Industries, Ltd., >99.0%), glycine (Wako Pure Chemical Industries, Ltd., >99.0%), L-valine (Wako Pure Chemical Industries, Ltd., >99.0%), L-leucine (Wako Pure Chemical Industries, Ltd., >99.0%), L-isoleucine (Wako Pure Chemical Industries, Ltd., >99.0%), L-serine (Tokyo Chemical industry Ltd., >99%),  $\beta$ -alanine (Wako Pure Chemical Industries, Ltd., >97.0%), 4-aminobutanoic acid (Wako Pure Chemical Industries, Ltd., >98.0%), acetic acid (Wako Pure Chemical Industries, Ltd., >99.9%).

In order to determine the retention time and molar sensitivity, commercially available reagents were used; isopropylamine (Wako Pure Chemical Industries, Ltd., >99.0%), L-alaninol (Wako Pure Chemical Industries, Ltd., >98.0%), D-alaninol (Wako Pure Chemical Industries, Ltd., >98.0%), 2-aminoethanol (Wako Pure Chemical Industries, Ltd., >97.0%), serinol (Tokyo Chemical industry Ltd., >98%), 2-amino-1,3-propanediol (Tokyo Chemical industry Ltd., >99%), 4-amino-1-butanol (Tokyo Chemical industry Ltd., >98%), L-valinol (Wako Pure Chemical Industries, Ltd., >95.0%), L-leucinol (Wako Pure Chemical Industries, Ltd., >93.0%), D-leucinol (Wako Pure Chemical Industries, Ltd., >97.0%), L-isoleucinol (Tokyo Chemical industry Ltd., >97%) . The retention time was determined by HPLC. The yields were calculated

by using the molar sensitivity of corresponding diols and high performance liquid chromatogram area.

### 1.2. Catalyst preparation

Active carbon-supported noble metal catalysts, Rh/C, Ru/C, Pd/C and Pt/C, were purchased from Wako Pure Chemical Industries. Carbon supported M-M'O<sub>x</sub> catalysts (M-M'O<sub>x</sub>/C: M = Rh, Ru, Pd and Pt, M'O<sub>x</sub> = MoO<sub>x</sub>, WO<sub>x</sub> and ReO<sub>x</sub>) were prepared by impregnating the above carbon-supported noble metal catalysts with an aqueous solution of NH<sub>4</sub>ReO<sub>4</sub> (Soekawa Chemical Co., Ltd.), (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O (Wako Pure Chemical Industries, Ltd.) and (NH<sub>4</sub>)<sub>10</sub>W<sub>12</sub>O<sub>41</sub>·5H<sub>2</sub>O (Wako Pure Chemical Industries, Ltd.). After evaporating the solvent and drying at 383 K for 12 h, they were calcined in N<sub>2</sub> at 773 K for 3 h. Rh/SiO<sub>2</sub> was prepared by impregnating SiO<sub>2</sub> (Fuji Silysia Chemical Ltd., G-6, BET surface area 535 m<sup>2</sup>/g) with an aqueous solution of RhCl<sub>3</sub>·3H<sub>2</sub>O (Wako Pure Chemical Industries, Ltd.). SiO<sub>2</sub> supported Rh-M'O<sub>x</sub> catalysts (Rh-M'O<sub>x</sub>/SiO<sub>2</sub>: M'O<sub>x</sub> = MoO<sub>x</sub>, WO<sub>x</sub> and ReO<sub>x</sub>) were prepared by impregnating M/SiO<sub>2</sub> after the drying procedure with aqueous solutions of NH<sub>4</sub>ReO<sub>4</sub> (Soekawa Chemical Co., Ltd.), (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O (Wako Pure Chemical Industries, Ltd.) and (NH<sub>4</sub>)<sub>10</sub>W<sub>12</sub>O<sub>41</sub>·5H<sub>2</sub>O (Wako Pure Chemical Industries, Ltd.). After evaporating the solvent and drying at 383 K for 12 h, they were calcined in air at 773 K for 3 h. The loading amount of metals of commercial M/C and M-M'O<sub>x</sub>/C was 5 wt% and that of Rh-M'O<sub>x</sub>/SiO<sub>2</sub> was 4 wt%. The molar ratio of additive to noble metal was 1/8 unless otherwise noted. The catalyst was reduced at 773 K for 3 h in H<sub>2</sub> flow and then passivated in 10% O<sub>2</sub>/N<sub>2</sub> flow before the reaction.

### 1.3. Typical procedure for hydrogenation of L-alanine to L-alaninol.

Activity tests were performed in a 190-ml stainless steel autoclave with an inserted glass vessel. Catalyst (50 mg), H<sub>3</sub>PO<sub>4</sub> (40 mmol) or H<sub>2</sub>SO<sub>4</sub> (22 mmol), water (19.3 g) and L-alanine (0.4 g) was put into an autoclave together with a spinner. After sealing the reactor, the air content was quickly purged by flushing thrice with 1 MPa hydrogen (99.99%; Nippon Peroxide Co., Ltd.). The autoclave was then heated to 353 K, and the temperature was monitored using a thermocouple inserted in the autoclave. After the temperature reached 353 K, the H<sub>2</sub> pressure was increased from 1.0 to 8.0 MPa. During the experiment, the stirring rate was fixed at 500 rpm (magnetic stirring). After 4 h, the gases were collected in a gas bag. The catalyst was separated by filtration. The filtrate was diluted with 180 g HClO<sub>4</sub>aq (0.16 M, pH=1.1) and transferred to a vial. The reaction conditions were changed appropriately in accordance with the purpose. Details of the reaction conditions are described in each result. The products in gas phase were analyzed using GC with CP-Sil-5 capillary column. The products in liquid phase were analyzed by HPLC with Crownpak CR(+) or Nova-Pak C-18 using the eluent of HClO<sub>4</sub>aq (0.16 M, pH=1.1). Products were also identified using standard compounds.

## 2. Table and figure

### Structure of 1-5

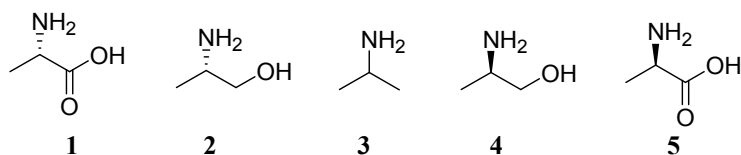


Table S1 The previous reports for hydrogenation of amino acids

Catalyst	Substrate	<i>T</i> /K	<i>P</i> <sub>H<sub>2</sub></sub> /MPa	Yield /%	ee /%	TOF <sup>a</sup> /h <sup>-1</sup>	Ref.
Ru/C	L-Alanine ( <b>1</b> )	373	6.9	91	99.2	6.7	[1]
Ru/Re	L-Alanine ( <b>1</b> )	343	20	80	99.9	2.6	[2]

<sup>a</sup>TOF = L-alanine (mmol) / Total Ru (mmol) /time (h)

Table S2 The effect of the molar ratio of Mo to Rh in Rh-MoO<sub>x</sub>/SiO<sub>2</sub> catalysts on hydrogenation of L-alanine (**1**) to L-alaninol (**2**)

Entry	Mo/Rh	Conv / %	Yield ( <b>2</b> ) / %	Select. / %		
				<b>2</b>	<b>3</b>	Others
1	0	3.7	3.1	84.4	15.6	0.0
2	1/64	28.3	24.2	85.7	14.3	0.0
3	1/32	35.7	30.7	86.2	13.8	0.0
4	1/16	42.9	38.1	89.0	11.0	0.0
5	1/8	46.8	42.2	90.2	11.0	0.0
6	1/4	44.9	41.0	91.3	8.7	0.0
7	1/2	40.3	37.0	91.9	8.1	0.0
8	1	36.6	33.7	92.2	7.8	0.0

Reaction conditions: Rh-MoO<sub>x</sub>/SiO<sub>2</sub> 50 mg, L-alanine 0.4 g, H<sub>3</sub>PO<sub>4</sub>aq(0.29 M) 20 g, H<sub>2</sub> 8 MPa, 353 K, 4 h.

Table S3 Hydrogenation of **1** over Rh-MoO<sub>x</sub>/SiO<sub>2</sub> with various acids

Entry	Additive	Conv / %	Yield ( <b>2</b> ) / %	Select. / %				
				<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	Others <sup>a</sup>
1	H <sub>2</sub> SO <sub>4</sub>	47.4	42.1	88.9	11.1	0.0	0.0	0.0
2	H <sub>3</sub> PO <sub>4</sub>	26.6	23.4	87.8	12.0	0.0	0.2	0.0
3	ZSM-5	4.1	3.8	93.2	5.2	0.0	0.8	0.9
4	SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	3.7	3.4	90.7	7.3	0.0	1.1	0.9
5	None	4.5	4.1	90.9	7.8	0.0	0.6	0.7

Reaction conditions: Rh-MoO<sub>x</sub>/SiO<sub>2</sub> (Mo/Rh=1/8) 100 mg, L-alanine 2.0 g, additive (solid acids 100 mg, H<sub>2</sub>SO<sub>4</sub> 20 mmol, H<sub>3</sub>PO<sub>4</sub> 40 mmol), H<sub>2</sub>O 19.3 g, H<sub>2</sub> 8 MPa, 353 K, 4 h. <sup>a</sup>Others include glycine.

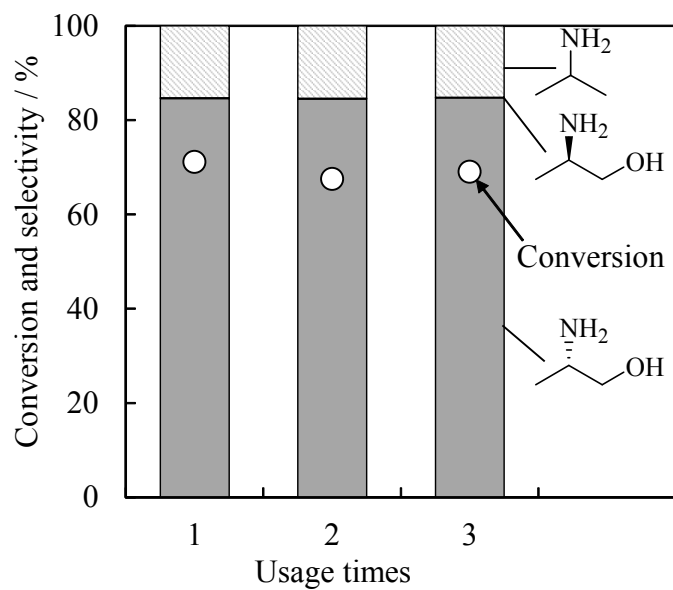
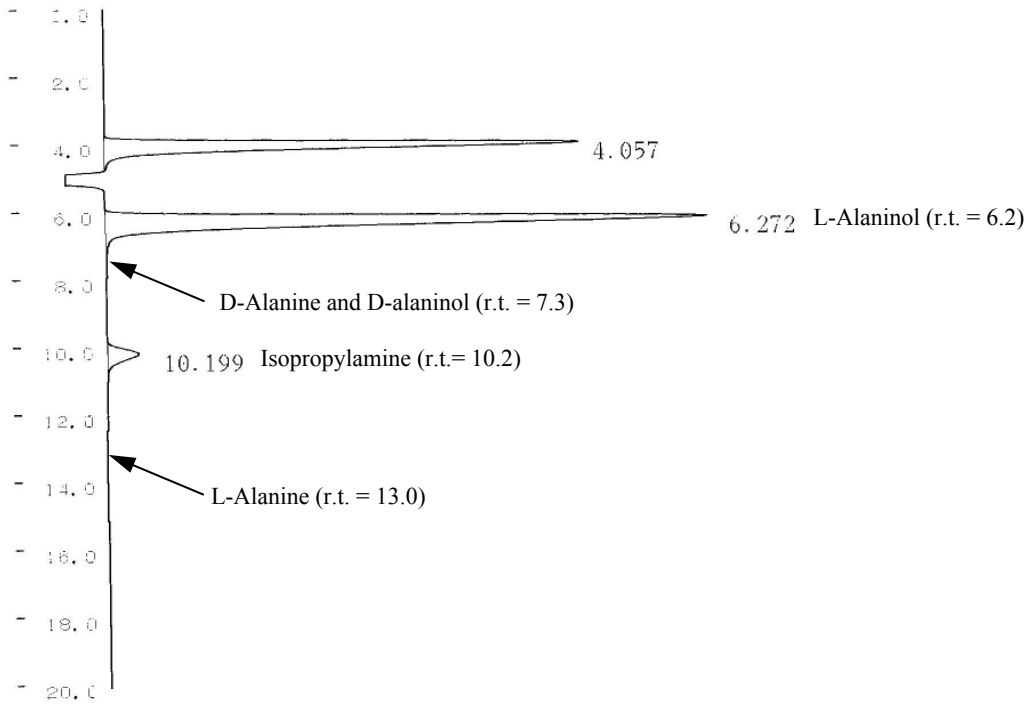


Figure S1 Reusability of Rh-MoO<sub>x</sub>/SiO<sub>2</sub> catalyst.

Reaction conditions: Rh-MoO<sub>x</sub>/SiO<sub>2</sub> (Mo/Rh=1/8) 0.25 g, L-Alanine 2 g (22.5 mmol), H<sub>2</sub>SO<sub>4</sub> 22 mmol, H<sub>2</sub>O 22 g, H<sub>2</sub> 8 MPa, 353 K, 4 h.

# HPLC data

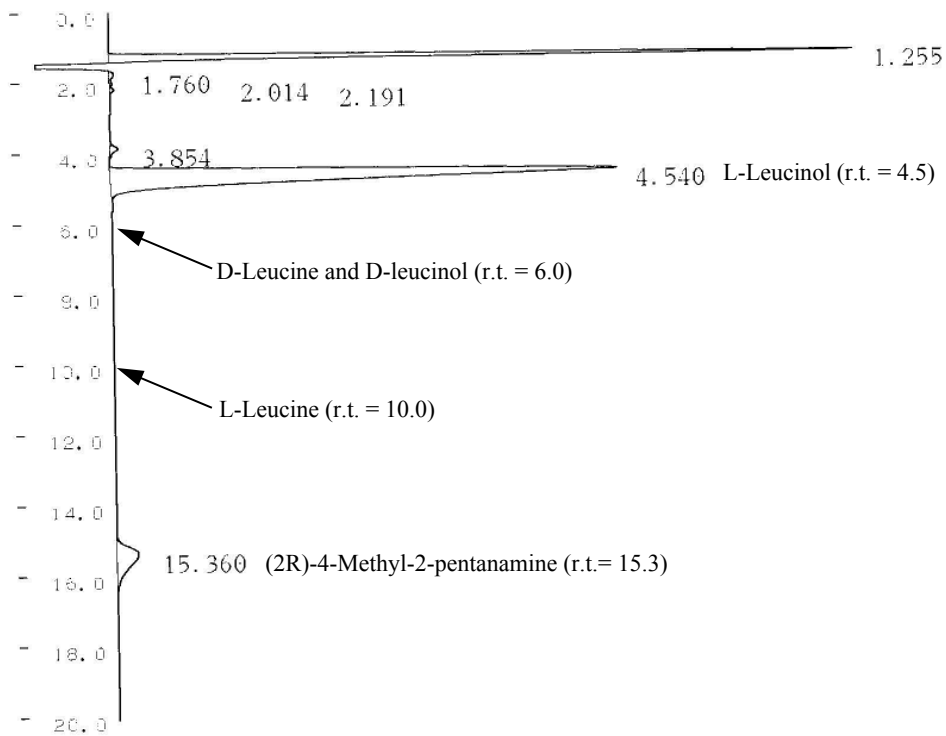
## Hydrogenation of L-alanine



### \*\* CALCULATION REPORT \*\*

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC
2	1	4.057	988674	64309			37.1785
	2	6.272	1568190	81607			58.9709
	3	10.199	102396	4280			3.8506
		TOTAL	2659260	150196			100

Hydrogenation of L-leucine to L-leucinol



\*\* CALCULATION REPORT \*\*

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC
2	1	1.255	295913	48336			29.2414
	2	1.76	3393	299			0.3353
	3	2.014	1380	155	V		0.1364
	4	2.191	2451	298	V		0.2422
	5	3.854	6455	519			0.6379
	6	4.54	646267	32971			63.8625
	7	15.36	56107	1412			5.5443

### **3. References**

1. K. P. Pimparkar, D. J. Miller and J. E. Jackson, *Ind. Eng. Chem. Res.*, 2008, **47**, 7648.
2. S Antos, A. S. Tilling and E. Wolters, *US Patent* 6310254, 2002.