

Supplementary Information

Highly Atom-Efficient and Chemoselective Reduction of Ketones in the Presence of Aldehydes Using Heterogeneous Catalysts

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Experimental

1) General

All organic reagents were purified before use. Na-mont (Kunipia-F) was obtained from Kunimine Industry Co., Ltd. Inductively coupled plasma measurements were performed on a SII Nano Technology SPS7800. ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a JNM-GSX270 spectrometer. GC-FID and GC-MS were carried out on a Shimadzu GC-17A: InertCap Capillary Column ($30\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$) and a GCMSQP-5050A, respectively. Ru K-edge X-ray absorption spectra were recorded at room temperature under air or H_2 atmosphere using a fluorescence-yield collection technique at the beam line 01B1 station attached to a Si (311) monochromator at SPring-8, Japan Atomic Energy Research Institute (JASRI), Harima, Japan. Data analysis was performed using the REX 2000 program, ver. 2.0.4 (Rigaku). Fourier transformation (FT) of the k^3 -weighted extended X-ray absorption fine structure (EXAFS) data was performed to obtain the radial structural function. Transmission electron microscopy (TEM) observations were carried out using a FEI Tecnai U2 20ST analytical electron microscope operating at 200 kV. Continuous flow reactor (mass flow controller, column oven, and stainless steel column) was purchased from YMC Co., Ltd.

2) Catalyst Preparation

Synthesis of Ti-mont^{1S}

Na-mont (Kunipia-F, 2.1 g) was soaked in 100 mL of an aqueous solution of TiCl₄ (33 mM) and stirred at 50 °C for 12 h in air. The resulting slurry was filtered, washed with deionized water and dried at 110 °C, yielding Ti-mont as a light gray powder (Ti content: 0.68 mmol/g).

Synthesis of Ru_{nano}HAP

Hydroxyapatite (HAP, 2.0 g)^{2S} was stirred in 150 mL of an aqueous solution of RuCl₃ (13.4 mM) at room temperature for 24 h. The resulting solid was filtered, washed with deionized water and dried at 110 °C to afford RuHAP as a black powder (Ru content: 1.0 mmol/g). The obtained RuHAP was treated under H₂ flow for 1 h at 100 °C, yielding Ru nanoparticles on HAP (Ru_{nano}HAP) as a brown powder.

3) Characterization of Ru_{nano}HAP

• XAFS analysis

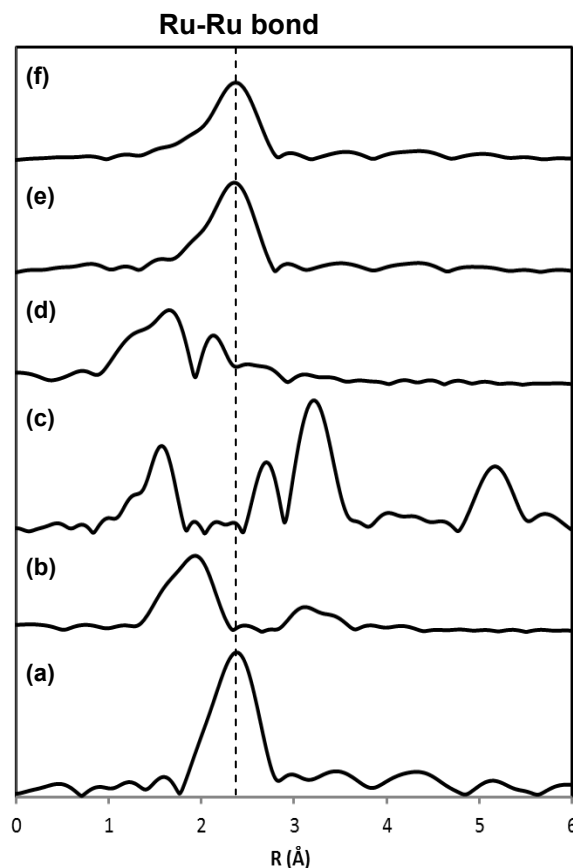


Figure S1 Fourier transformation of k^3 -weighted Ru K-edge EXAFS of the Ru catalysts. (a) Ru foil, (b) RuCl₃, (c) RuO₂, (d) RuHAP, (e) Ru_{nano}HAP, (f) Ru_{nano}HAP after hydrogenation.

Table S1 Curve fitting analysis of RuHAPs.

Sample	Shell	C.N. ^a	R ^b (Å)	$\Delta\sigma^c$ (Å)
RuHAP	Ru-O(1)	4.1	1.97	0.0067
	Ru-O(2)	2.1	2.28	0.0008
	Ru-O(3)	1.7	2.62	-0.0054
	Ru-Cl	1.2	2.32	0.0010
Ru _{nano} HAP	Ru-Ru	7.2	2.76	0.0076
Ru _{nano} HAP after hydrogenation	Ru-Ru	8.0	2.77	0.010

^a Coordination number. ^b Interatomic distance. ^c Difference between Debye-Waller factor

• TEM

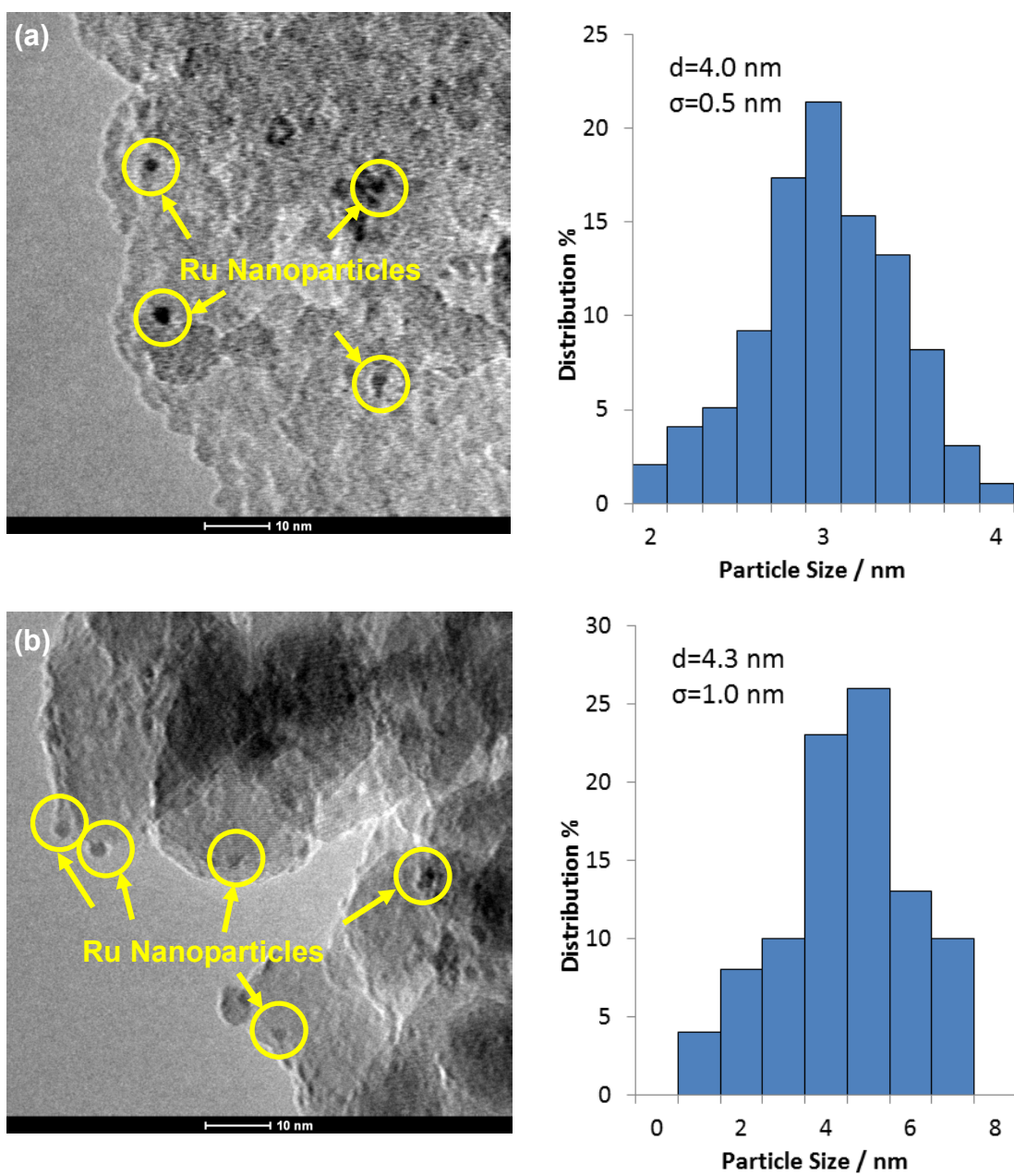


Figure S2 TEM images of Ru_{nano}HAP (a) before and (b) after hydrogenation.

4) Typical reaction procedure

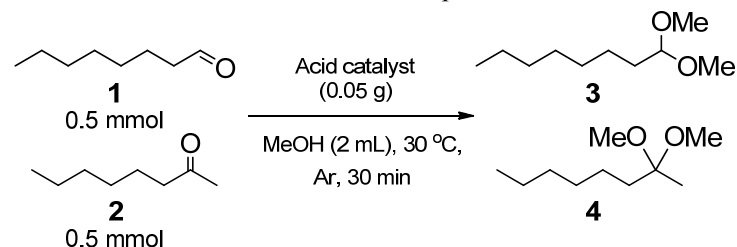
Ti-mont (0.05 g: acid 0.09 mmol) and Ru_{nano}HAP (0.05 g: Ru 0.05 mmol) were placed in a reaction vessel connected to a gas bag and heated at 150 °C under Ar flow for 1 h to remove the adsorbed water. After the reaction vessel was cooled, MeOH (2 mL) and substrate (0.5 mmol) were added and the heterogeneous mixture was stirred for 30 min. Next, hydrogen gas was introduced to the vessel. Hydrogenation was conducted at 40 °C and periodically monitored by GC until the ketone was completely converted. After complete consumption of the ketones, hydrogen was purged by Ar, 4 mL of water was added and resulting aqueous solution was stirred vigorously for 30 min at 80 °C. The yields of the products were determined using naphthalene as an internal standard.

5) Large-scale reaction of 8-oxononanal using continuous flow reactor

A stainless steel column (inner diameter: 5 mm, length: 50 mm) was filled with Ti-mont (0.05 g: column-I) or Ru_{nano}HAP (0.1 g: column-II) with SiO₂ (WAKO-GEL C-400HG: 45 µm, 0.2 g). A solution of 8-oxononanal in MeOH (15.6 g: 100 mmol in 500 mL) was passed through the column-I (0.2 mL/min) at 30 °C. Next, the reaction mixture was further introduced to column-II kept at 40 °C with hydrogen gas (2.0 mL/min). Finally, the reaction solution was mixed with water (0.4 ml/min) and fed into the column-I heated at 80 °C. After the reaction was completed, NaCl was added to the reaction mixture, and the solution was extracted three times with CH₂Cl₂. The combined organic layer was dried with MgSO₄ and evaporated to afford 8-hydroxynonanal as a colorless oil (14.7 g, 94%).

6) Catalyst test

Table S2 Acetalization of octanal in the presence of 2-octanone



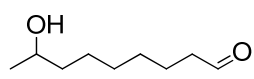
Entry	Catalyst	Yield ^a (%)	
		3	4
1	Ti-mont	>99	20
2	Fe-mont	85	15
3	mont K-10	38	1
4	H-USY	20	2
5	H-ZSM-5	4	<1
6	H-beta	2	<1
7	Nafion-H NR50	5	<1
8	Na-mont	0	0

^a Determined by GC using an internal standard technique.

7) Product identification

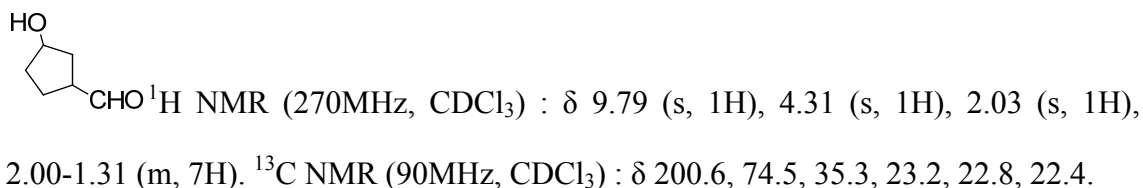
The products were characterized by GC, GC-MS, and NMR. Retention times (GC) and chemical shifts (¹H and ¹³C NMR) of the products (Table 2, Entries 1-6) were in agreement with those of authentic samples (commercially available).

8-hydroxynonanal: CAS registry No. [85926-51-8].

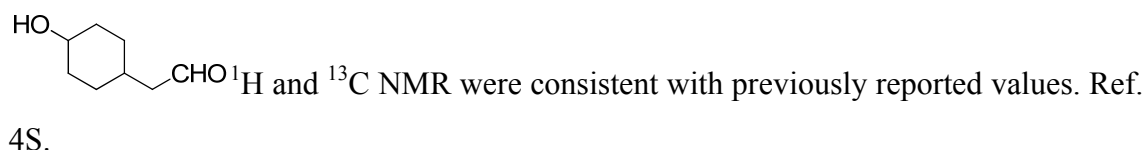
 ¹H and ¹³C NMR were consistent with previously reported values.

Ref. 3S.

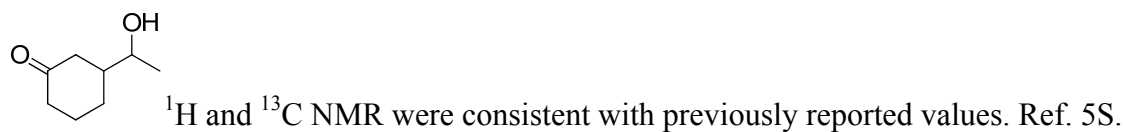
3-hydroxycyclopentanecarboxaldehyde: CAS registry No. [69492-90-6].



2-(4-hydroxycyclohexyl)-acetaldehyde: CAS registry No. [1357255-94-7].



3-(1-hydroxyethyl)-cyclohexanone: CAS registry No. [55941-64-5].



References

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- 2S S. Sugiyama, T. Minami, H. Hayashi, M. Tanaka, N. Shigemoto and J. B. Moffat, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 293.
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