Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting information

# Selective Hydrogenation of Amides to Alcohols in Water Solvent over Heterogeneous $CeO_2$-Supported Ru Catalyst

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# 1. Experimental

## 1.1 General

The GC (Shimadzu GC-2014) and GCMS (Shimazu QP5050) analyses were carried out with a CP-Sil5 (Agilent Technologies) using nitrogen as the carrier gas. All the chemicals for organic reactions were analytic reagents from chemical products corporation and were used without further purification.

## 1.2 Catalysts and reagents

$Ru/CeO_2$ catalysts were prepared according to the previous reports [1]. $Ru/CeO_2$ catalysts were prepared by impregnating $CeO_2$ (Daiichi Kigenso Kogyo Co. Ltd., $CeO_2$-HS, calcined at 873 K and 3 h in air, 84 $m^2/g$) with an aqueous solution of $Ru(NO)(NO_3)_{3-x}(OH)_x$ (Ru 1.5 wt%, Sigma-Aldrich). After evaporating the solvent and drying at 383 K for 12 h, the catalyst was heated in $N_2$ (30 ml/min) at 573 K for 1 h. $Ru/MO_x$ ($MO_x$= $\gamma$-$Al_2O_3$, $SiO_2$, $ZrO_2$, $TiO_2$, $SiO_2$-$Al_2O_3$, MgO) catalysts were also prepared by the same method for $Ru/CeO_2$. The information of used supports are as follows: $\gamma$-$Al_2O_3$ (Sumitomo Chemical Co., Ltd. KHO-24, 773 K, 3 h, 82 $m^2/g$), $SiO_2$ (Fuji Silysia Chemical Ltd., G-6, 535 $m^2/g$), $ZrO_2$ (Daiichi Kigenso Kagaku Kogyo Co., Ltd. 118 $m^2/g$) and $TiO_2$ (Nippon Aerosil Co. Ltd., P-25, 48 $m^2/g$), $SiO_2$-$Al_2O_3$ (JRC-SAL-3, 540 $m^2/g$), MgO (Ube Industries, LTD., 500A, 34 $m^2/g$). M'/$CeO_2$ (M'=Rh, Pd, Pt, Ir) catalysts were also prepared by the same method for $Ru/CeO_2$. The information of used noble metal precursors are as follows: $Rh(NO_3)_3$aq (Rh: 9.0 wt%, WAKO Pure Chemical Industries, Ltd.), $Pd(NO_3)_2$aq (Pd: 4.6 wt%, Sigma-Aldrich), $Pt(NO_2)_2(NH_3)_2$aq (Pt: 4.6 wt%, Tanaka Kikinzoku Kogyo K. K.) and $Ir(NO_3)_4$ (Ir: 8.8 wt%, Furuya Metal Co., Ltd.). The loading amount of noble metals (Ru, Rh, Pd, Pt, Ir) was 4 wt%. Carbon-supported noble metal (M'/C, M'=Pt, Pd, Ru, Rh) catalysts were commercially available, and the loading amount of noble metals was 5 wt%: Pt/C (Wako Pure Chemical Industries, Ltd.), Pd/C (Wako Pure Chemical Industries, Ltd.), Ru/C (Wako Pure Chemical Industries, Ltd.) and Rh/C (Wako Pure Chemical Industries, Ltd.). The prepared catalysts were used after the reduction treatment ($H_2$ 30 mL/min, 473 K, 1 h and then 2% $O_2/N_2$ 10 mL/min, r.t., 30 min). Carbon-supported noble metal catalysts were used without the reduction treatment.

### 1.3 A typical procedure for hydrogenation of cyclohexanecarboxamide.

Activity tests were performed in a 190 ml stainless steel autoclave with an inserted glass vessel. A reduced $Ru/CeO_2$ catalyst (typically 0.5 g), water (20 ml) and cyclohexanecarboxamide 0.2 g (1.5 mmol) were put into an autoclave together with a spinner under air. After sealing the reactor, the air content was quickly purged by flushing three times with 1 MPa $H_2$ (99.99%; Nippon Peroxide Co., Ltd.). The autoclave was then heated to 333 K, and the $H_2$ pressure was increased to 8 MPa, and the temperature was monitored by using a thermocouple inserted in the autoclave. During the reaction, the stirring speed was fixed at 500 rpm (magnetic stirring). After the reaction, the gas phase was collected in a gas bag. The catalyst was separated by centrifugation, and the liquid phase in the autoclave was collected and transferred to a vial with 2-propanol (10 ml). The catalyst was washed by mixture of 2-propanol (5 ml) and acetic acid (1 mmol) three times in order to take the adsorbed acid species on the catalyst away, and the washing solvents were also transferred to the vial. Details of the reaction conditions are described in each result. The products in the gas phase and liquid phase were analyzed by GC with Porapak N (GL Science Inc.) and GC with CP-Sil5 (Agilent Technologies, diameter 0.25 mm$\phi$, 50 m), respectively. Conversion of the substrate, and yield and selectivity of the products were determined on carbon basis by GC using 1,4-dioxane (~0.2 ml) as an internal standard. Typical GC chart is shown in Figure S6.

Reusability test was conducted as follows: After the reaction, the used catalyst and the liquid phase were separated by centrifugation, and the collected catalyst was washed with 2-propanol (5 ml) and acetic acid (1 mmol) three times, and then the collected wet catalyst was dried at 353 K for 12 h. The dried catalyst was heated at 573 K under $N_2$ for 1 h, and was reduced at 473 K for 1 h and then used for the next reaction.

Leaching test was conducted as follows: The reaction was carried out under the same conditions as the time-course dependence (Figure 1). After 4 h reaction time (approximately 50% conversion), the autoclave was cooled to room temperature, and then the catalyst was removed from the reaction mixture by filtration under air. After the removal of the catalyst, the filtrate was reacted under the same conditions for 44 h.

### 1.4 Catalyst characterization (XRD, FE-STEM, TPR, ICP-AES, CO-adsorption, XAS)

X-ray diffraction (XRD) patterns were recorded by a diffractometer (MiniFlex600; Rigaku). Cu *K*α ($\lambda$ = 0.154 nm, 45 keV, 40 mA) radiation was used as an X-ray source. Average metal particle size was estimated using the Scherrer‘s equation.

Field Emission-Scanning Transmission electron microscope (FE-STEM) images were taken with HD-2700 (Hitachi High-Technologies Corporation). The samples were dispersed in ethanol and placed on Cu grids under air atmosphere.

Temperature-programmed reduction (TPR) was carried out in a fixed-bed reactor equipped with a thermal conductivity detector and frozen acetone trap using 5% $H_2$ diluted with Ar (30 ml/min). The amount of catalyst was 0.1 g, and the temperature was increased from 223 K to 1073 K at a heating rate of 10 K/min.

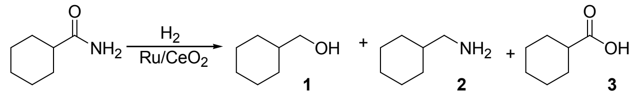
The amount of eluted metals (Ir and Fe) into the reaction solution was analysed by inductively-coupled plasma atomic emission spectroscopy (ICP-AES, Thermo Fisher Scientific iCAP 6500).

The amount of CO chemisorption was measured in a high-vacuum system using a volumetric method. $Ru/CeO_2$ (≈ 0.1 g) in the measurement cell was reduced with $H_2$ at 473 K for 1 h and evacuated at 473 K for 1 h. After cooling, the adsorption amount of CO was measured at room temperature. Gas pressure at adsorption equilibrium was about 1.1 kPa. The dead volume of the apparatus was about 60 $cm^3$.

X-ray absorption spectroscopy (XAS) was conducted at the BL01B1 station at SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI; Proposal No. 2017B1467). The storage ring was operated at 8 GeV, and a Si (111) single crystal was used to obtain a monochromatic X-ray beam. Two ion chambers for $I_0$ and $I$ were filled with 100% Ar and 20% Kr+80% Ar, respectively, for Ru *K*-edge measurement. We used the sample after the reduction and reaction. After the catalyst reduction at 473 K for 1 h under $H_2$, the reduced catalyst powder was transferred to the measurement cell in a glove bag filled with nitrogen. After the reaction, the used catalyst was collected and transferred to the measurement cell in a glove bag filled with nitrogen. The thickness of the cell filled with the powder was adjusted to give an edge jump of 0.2 ~ 1 for Ru *K*-edge. The EXAFS data were collected in a transmission mode. For EXAFS analysis, the oscillation was first extracted from the EXAFS data using a spline smoothing method [2]. Fourier transformation of the $k^3$-weighted EXAFS oscillation from the $k$ space to the $r$ space was performed to obtain a radial distribution function. The inversely Fourier filtered data were analyzed using a usual curve fitting method [3,4]. For curve fitting analysis, the empirical phase shift and amplitude function for the Ru-Ru bond was extracted from the data for Ru powder. Analyses of EXAFS and XANES data were performed using a computer program (REX2000, ver. 2.5.9; Rigaku Corp.).

## 2. Supporting Tables

**Table S1.** Effect of Ru loading amount of Ru/CeO$_2$ catalyst in hydrogenation of cyclohexanecarboxamide



| Entry | Ru loading amount (wt%) | Conv. (%) | Selectivity (%) | | | |
|---|---|---|---|---|---|---|
| | | | **1** | **2** | **3** | Others |
| 1 | 1 | 33 | 94 | 0.4 | 4.1 | 1.6 |
| 2 | 2 | 42 | 96 | <0.1 | 2.2 | 2.0 |
| 3 | 4 | 52 | 97 | 0.2 | 0.8 | 2.0 |
| 4 | 8 | 46 | 98 | 0.4 | 0.7 | 1.3 |
| 5 | 12 | 42 | 98 | 0.4 | 0.7 | 1.1 |

Reaction conditions: Ru/CeO$_2$ 0.17-2.0 g (Ru: 0.20 mmol), cyclohexanecarboxamide 1.5 mmol, water 20 ml, H$_2$ 8 MPa, 333 K, 4 h. Others include cyclohexane, methylcyclohexane and methane.

**Table S2.** Curve fitting results of Ru *K*-edge EXAFS of Ru/CeO$_2$[a]

| Catalyst | State | Shells | CN[b] | $R$ / $10^{-1}$ nm[c] | $\sigma$ / $10^{-1}$ nm[d] | $\Delta E_0$ / eV[e] | $R_f$/ %[f] |
|---|---|---|---|---|---|---|---|
| Ru/CeO$_2$ | Reduction | Ru-Ru | 4.1 | 2.58 | 0.092 | 1.2 | 2.2 |
| Ru/CeO$_2$ | Reaction[g] | Ru-Ru | 5.3 | 2.60 | 0.099 | -1.1 | 1.9 |
| Ru powder | - | Ru-Ru | 12 | 2.65 | - | - | - |

[a] FT range 30-120 nm$^{-1}$, Fourier filtering range: 0.1688-0.2884 nm.

[b] Coordination number.

[c] Bond distance.

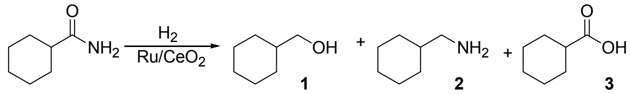
[d] Debye–Waller factor.

[e] Difference in the origin of photoelectron energy between the reference and the sample.

[f] Residual factor.

[g] Reaction conditions: Ru/CeO$_2$ 0.5 g (Ru: 4 wt%, 0.20 mmol), cyclohexanecarboxamide 1.5 mmol, water 20 ml, H$_2$ 8 MPa, 333 K, 48 h.

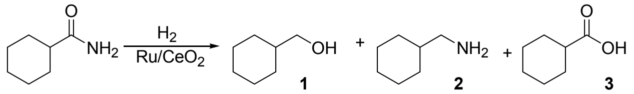
**Table S3.** Effect of reaction temperature in hydrogenation of cyclohexanecarboxamide over Ru/CeO$_2$ catalyst



| Entry | *T* (K) | Conv. (%) | Selectivity (%) | | | |
|---|---|---|---|---|---|---|
| | | | **1** | **2** | **3** | Others |
| 1 | 313 | 20 | 97 | <0.1 | 1.5 | 1.3 |
| 2 | 323 | 32 | 98 | <0.1 | 0.9 | 1.7 |
| 3 | 333 | 52 | 97 | 0.2 | 0.8 | 2.0 |
| 4 | 353 | 70 | 87 | <0.1 | 11 | 2.1 |
| 5 | 373 | 74 | 77 | <0.1 | 19 | 4.4 |
| 6 | 393 | 84 | 66 | <0.1 | 22 | 12 |
| 7 | 413 | 91 | 54 | <0.1 | 23 | 24 |

Reaction conditions: Ru/CeO$_2$ 0.5 g (Ru: 4 wt%), cyclohexanecarboxamide 1.5 mmol, water 20 ml, H$_2$ 8 MPa, 4 h. Others include cyclohexane, methylcyclohexane and methane.

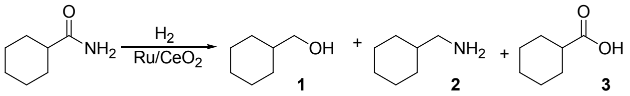
**Table S4.** Effect of solvent in hydrogenation of cyclohexanecarboxamide over Ru/$CeO_2$ catalyst



| Entry | Solvent | Conv. (%) | Selectivity (%) | | | |
|---|---|---|---|---|---|---|
| | | | **1** | **2** | **3** | Others |
| 1 | Water | 52 | 97 | 0.2 | 0.8 | 2.0 |
| 2 | 1,2-Dimethoxyethane | 34 | 92 | <0.1 | 8.5 | <0.1 |
| 3 | THF | 25 | 81 | <0.1 | 16 | 3.6 |
| 4 | 2-Propanol | 20 | 94 | 1.4 | 2.1 | 2.8 |
| 5 | Methanol | 1.5 | >99 | <0.1 | <0.1 | <0.1 |

Reaction conditions: Ru/$CeO_2$ 0.5 g (Ru: 4 wt%), cyclohexanecarboxamide 1.5 mmol, solvent 20 ml, $H_2$ 8 MPa, 333 K, 4 h. Others include cyclohexane, methylcyclohexane and methane.

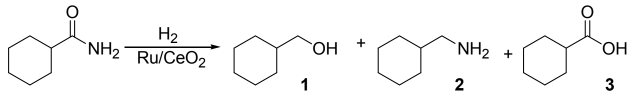
**Table S5.** Effect of substrate concentration in hydrogenation of cyclohexanecarboxamide over $Ru/CeO_2$ catalyst



| Entry | Solvent amount (ml) | Substrate concentration (mmol/ml) | Conv. (%) | Selectivity (%) | | | |
|---|---|---|---|---|---|---|---|
| | | | | **1** | **2** | **3** | Others |
| 1 | 40 | 0.038 | 7.9 | 96 | <0.1 | 3.1 | 1.1 |
| 2 | 30 | 0.050 | 10 | 94 | <0.1 | 4.3 | 1.5 |
| 3 | 20 | 0.075 | 16 | 96 | <0.1 | 2.1 | 1.8 |
| 4 | 10 | 0.149 | 18 | 96 | <0.1 | 2.6 | 2.2 |

Reaction conditions: $Ru/CeO_2$ 0.5 g (Ru: 4 wt%), cyclohexanecarboxamide 1.5 mmol, water 10-40 ml, $H_2$ 8 MPa, 333 K, 15 min. Others include cyclohexane, methylcyclohexane and methane.

**Table S6.** Effect of $H_2$ pressure in hydrogenation of cyclohexanecarboxamide over $Ru/CeO_2$ catalyst



| Entry | $H_2$ pressure (MPa) | Conv. (%) | Selectivity (%) | | | |
|---|---|---|---|---|---|---|
| | | | **1** | **2** | **3** | Others |
| 1 | 1 | 17 | 83 | <0.1 | 13 | 5.0 |
| 2 | 2 | 34 | 92 | <0.1 | 5.4 | 2.6 |
| 3 | 4 | 44 | 95 | <0.1 | 2.2 | 3.1 |
| 4 | 8 | 52 | 97 | 0.2 | 0.8 | 2.3 |

Reaction conditions: $Ru/CeO_2$ 0.5 g (Ru: 4 wt%), cyclohexanecarboxamide 1.5 mmol, water 20 ml, $H_2$ 8 MPa, 333 K, 4 h. Others include cyclohexane, methylcyclohexane and methane.

3. Supporting Figures

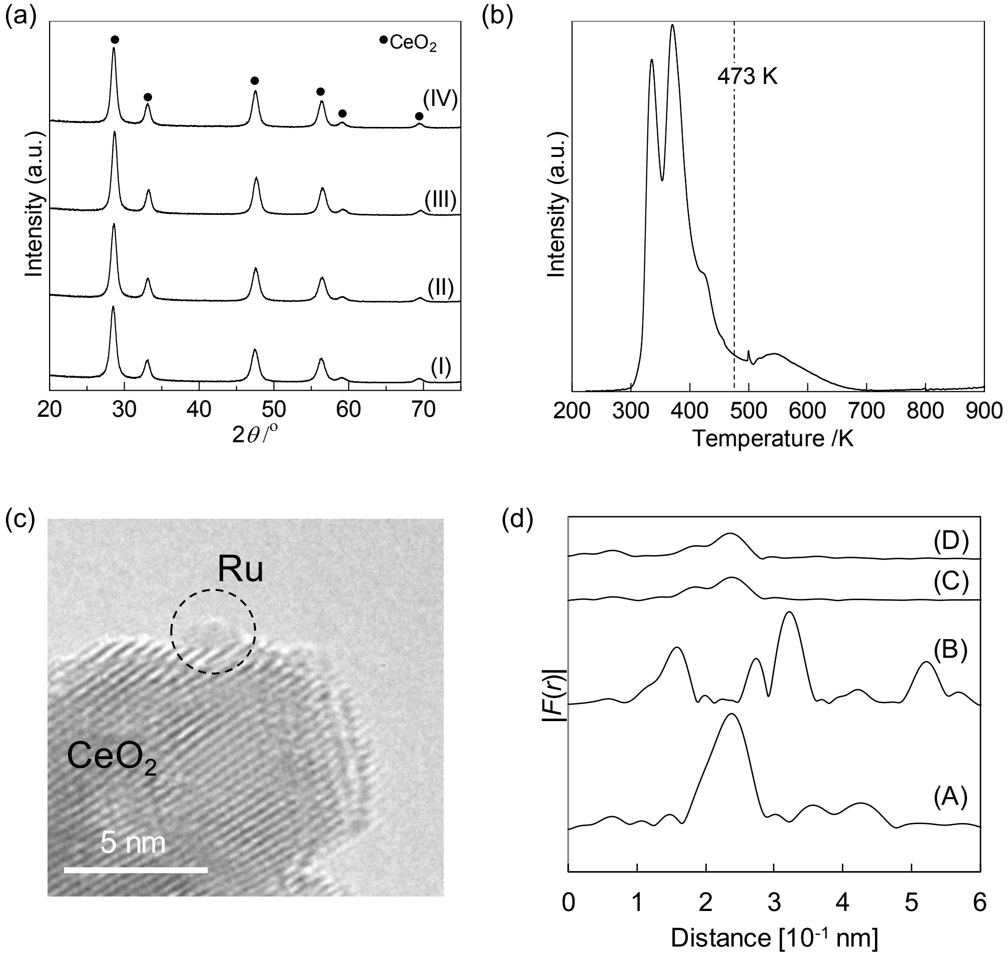


**Figure S1.** Characterization of Ru/CeO$_2$ catalysts. (a) XRD patterns of CeO$_2$ and Ru/CeO$_2$ catalysts ((**I**) CeO$_2$, (**II**) Ru/CeO$_2$ after calcination, (**III**) Ru/CeO$_2$ after reduction, (**IV**) Ru/CeO$_2$ after 24 h reaction), (b) TPR analysis of Ru/CeO$_2$. (c) TEM image of Ru/CeO$_2$ after reduction, (d) Fourier transform of $k^3$-weighted Ru *K*-edge EXAFS analyses ((A) Ru powder, (B) RuO$_2$, (C) Ru/CeO$_2$ after reduction, (D) Ru/CeO$_2$ after 48 h reaction), FT range 30-120 nm$^{-1}$.

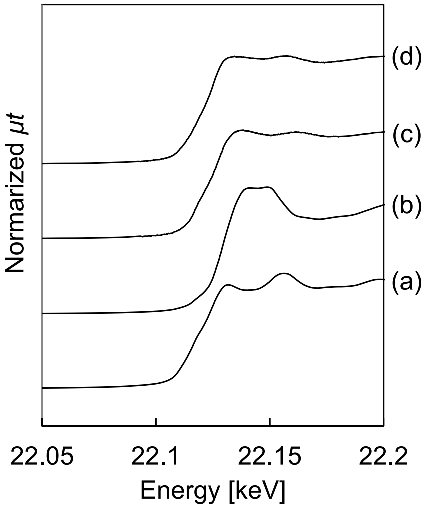


**Figure S2.** Ru *K*-edge XANES spectra for (a) Ru powder, (b) $RuO_2$, (c) $Ru/CeO_2$ after reduction, (d) $Ru/CeO_2$ after reaction.

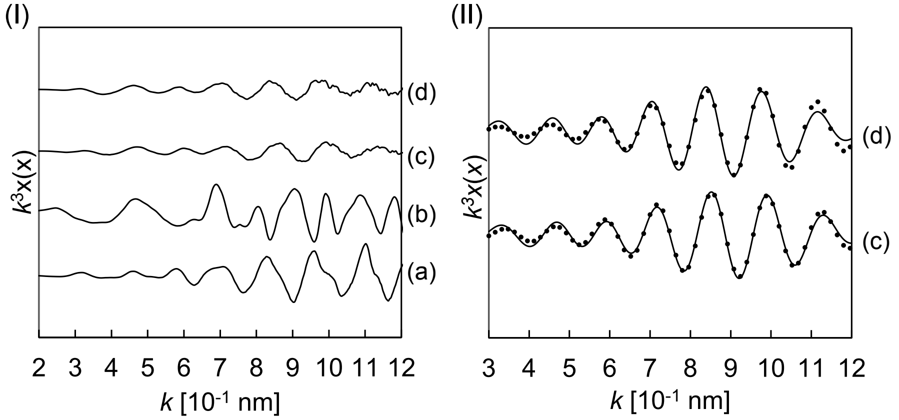


**Figure S3.** Results of Ru *K*-edge EXAFS analyses of Ru samples. (I) $k^3$-Weighted EXAFS oscillations. (II) Fourier filtered EXAFS data (solid line) and calculated data (dotted line), FT range 30-120 nm$^{-1}$, Fourier filtering range: 0.1688-0.2884 nm. (a) Ru powder, (b) $RuO_2$, (c) Ru/$CeO_2$ after reduction, (d) Ru/$CeO_2$ after reaction.

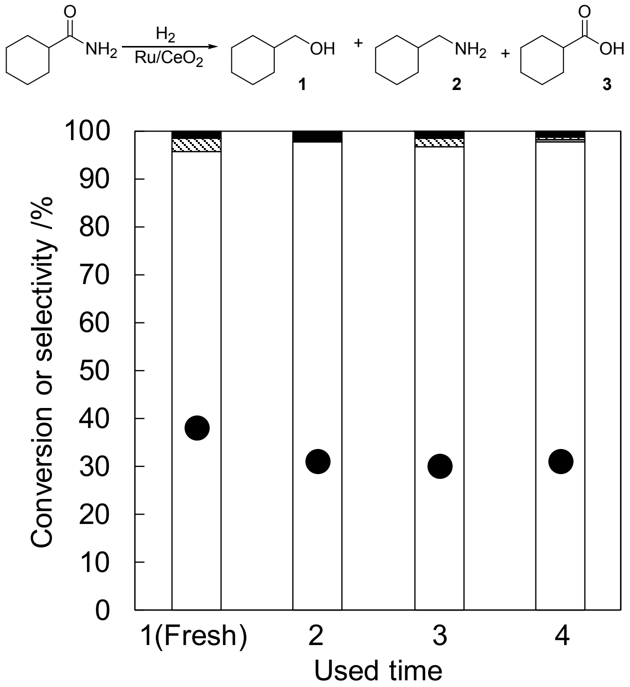


**Figure S4.** Reusability test of hydrogenation of cyclohexanecarboxamide over Ru/$CeO_2$ (●: conversion, white bar: selectivity to **1**, gray bar: selectivity to **2**, stripe bar: selectivity to **3**, black bar: selectivity to others).

Reaction conditions: Ru/$CeO_2$ 0.5 g (Ru: 4 wt%), cyclohexanecarboxamide 1.5 mmol, water 20 ml, $H_2$ 8 MPa, 333 K, 2 h. Others include cyclohexane, methylcyclohexane and methane.

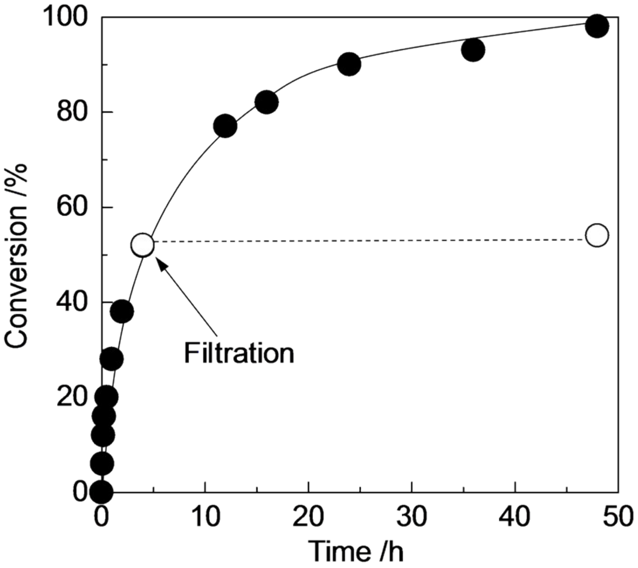
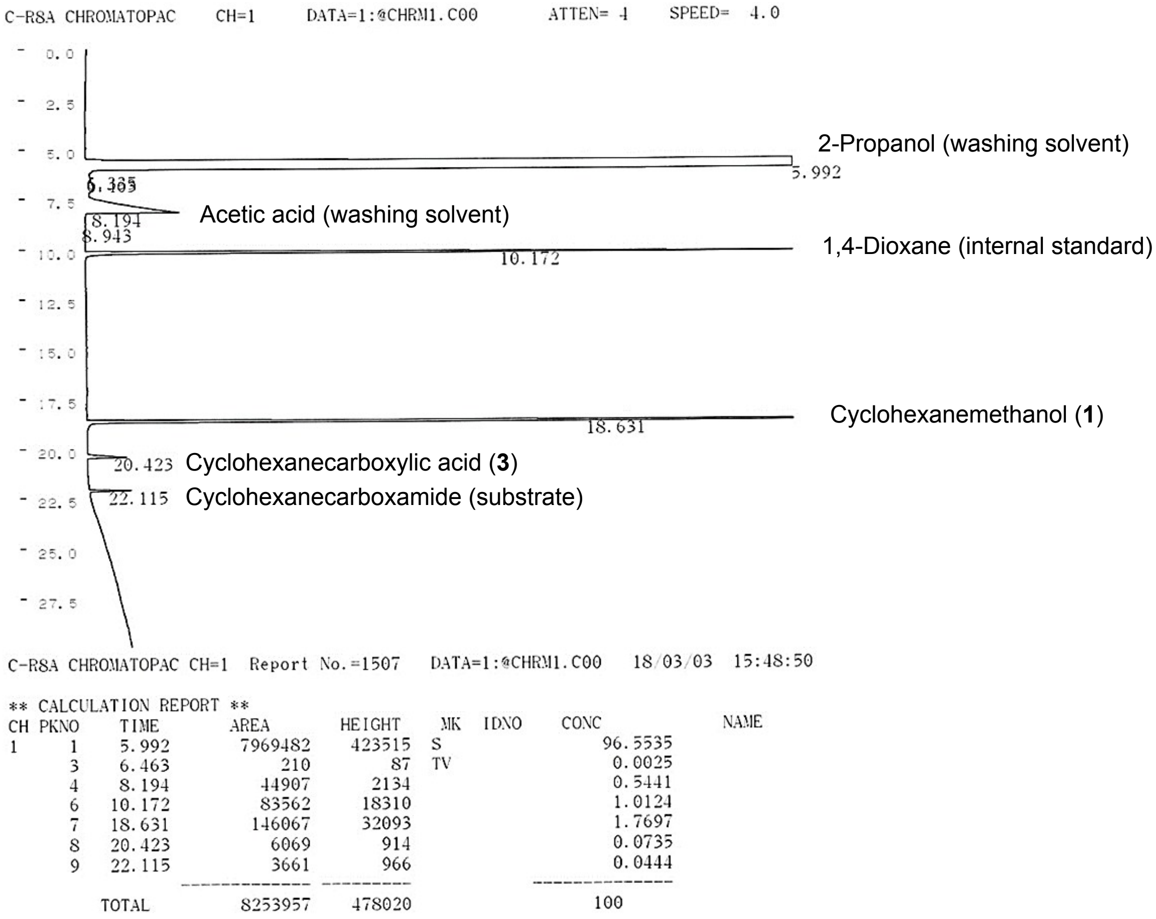


**Figure S5.** Leaching test for hydrogenation of cyclohexanecarboxamide over Ru/CeO$_2$. (●) Without removal of Ru/CeO$_2$. (○) With removal of Ru/CeO$_2$. An arrow indicates removal of Ru/CeO$_2$ at 4 h by filtration.

Reaction conditions: Ru/CeO$_2$ 0.5 g (Ru: 4 wt%), cyclohexanecarboxamide 1.5 mmol, water 20 ml, H$_2$ 8 MPa, 333 K.



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      7    18.631       146067       32093                   1.7697
      8    20.423         6069         914                   0.0735
      9    22.115         3661         966                   0.0444
                  ------------- ----------            ---------------
          TOTAL        8253957      478020                 100
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**Figure S6.** GC chart of hydrogenation of cyclohexanecarboxamide over Ru/$CeO_2$ at 48 h.

Reaction conditions: Ru/$CeO_2$ 0.5 g (Ru: 4 wt%), cyclohexanecarboxamide 1.5 mmol, water 20 ml, $H_2$ 8 MPa, 333 K, 48 h.

## 4. References

[1] (a) S.-i. Oya, D. Kanno, H. Watanabe, M. Tamura, Y. Nakagawa and K. Tomishige, *ChemSusChem* 2015, **8** 2472. (b) Y. Nakagawa, S.-i. Oya, D. Kanno, Y. Nakaji, M. Tamura and K. Tomishige, *ChemSusChem* 2017, **10**, 189.
[2] J. W. Cook Jr and D. E. Sayers, *J. Appl. Phys.*1981, **52**, 5024.
[3] K. Okumura, J. Amano, N. Yasunobu and M. Niwa, *J. Phys. Chem. B* 2000, **104**, 1050.
[4] K. Okumura, S. Matsumoto, N. Nishiaki and M. Niwa, *Appl. Catal. B* 2003, **40**, 151.