

Supplementary Information

Heterogeneous Ru/CeO₂ Catalyst

Effective for Transfer-allylation from Homoallyl Alcohols to Aldehydes

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Materials or Methods. All manipulations were performed under an argon atmosphere using standard Schlenk techniques. Homoallyl alcohols were prepared by the method reported in the literature.^[1] Cerium oxide (CeO₂) was prepared by the treatment of a solution of cerium(III) nitrate hexahydrate (12.6 g, 29 mmol) in 400 cm³ of deionized water with 38 cm³ of 28% aqueous ammonia with stirring for 1 h at room temperature. The resulting precipitates were collected by centrifugation, and then dried at 80 °C overnight. The product was heated in a box furnace at a rate of 10 °C min⁻¹ and maintained at 400 °C for 30 min to afford CeO₂ in an excellent ceramic yield. Magnesium oxide was also prepared by the same method using magnesium nitrate hexahydrate instead of cerium(III) nitrate hexahydrate. Titanium oxide (ST-01), γ -alumina (JRC-ALO-8), and silica (Cabosil) were used as received. Ceria-supported Fe, Cu, Pd, and Rh catalysts were prepared by the impregnation method using iron(III) acetylacetonate, copper(II) acetate monohydrate, palladium(II) acetate, and tetrarhodium dodecacarbonyl, respectively.

Physical and Analytical Measurements. NMR spectra were recorded on a JEOL EX-400 (FT, 400 MHz (¹H), 100 MHz (¹³C)) instrument. Chemical shifts (δ) are referenced to SiMe₄. Nitrogen adsorption/desorption isotherms were obtained with a computer-controlled automatic gas sorption system, Quantachrome NOVA 4200e. Samples were degassed at 573 K for 2 h just before the measurements. The

X-ray powder diffraction analyses (XRD: XD-D1, Shimadzu) were performed using Cu $K\alpha$ radiation and a carbon monochromator. The crystallite size of CeO_2 was calculated from the full width at half maximum (FWHM) of the 111 diffraction peak using Scherrer's equation. X-ray photoelectron spectra (XPS) of the catalysts were acquired using an ULVAC-PHI 5500MT system equipped with a hemispherical energy analyzer using Mg $K\alpha$ radiation (15 kV, 400 W). Samples were mounted on indium foil and then transferred to an XPS analyzer chamber. Binding energies were referenced to the C 1s level of residual graphitic carbon.^[2] Samples were sputtered for 1 min by an Xe^+ ion beam generated at 3.0 kV to remove carbonaceous contaminants. TG-DTA was performed by using a RIGAKU TG8120 system. The sample (*ca.* 8 mg) was heated at the rate of $10\text{ }^\circ\text{C min}^{-1}$ in air flow ($50\text{ cm}^3\text{ min}^{-1}$). Diffuse reflectance IR spectra were recorded using a Nicolet Magna-IR 560 FT-IR spectrometer with DRIFT optical configuration. Temperature-programmed reduction (TPR) was carried out with a flow-type reactor. Hydrogen (1.9 vol.% in argon under atmospheric pressure at $30\text{ cm}^3\text{ min}^{-1}$) was passed through a reaction tube containing 50 mg of the catalyst. The tube was heated with an electric furnace at $2\text{ }^\circ\text{C min}^{-1}$, and the amount of H_2 consumed was monitored with a TC detector of a Shimadzu 4CPT gas chromatograph. Leaching of ruthenium species from the catalysts during the reaction was investigated by the ICP atomic emission spectroscopic analysis by using a Shimadzu ICPS-1000IV analyzer. The products of catalytic runs were analyzed by GC-MS (Shimadzu GC-MS Parvum 2, DB-1 capillary column, i.d. 0.33 mm, length 25 m, at 323–473 K) and gas chromatography (GL Sciences GC353, Inertcap 17 capillary column, i.d. 0.25 mm, length 30 m at 323–473 K).

Characterization of the Ru(2.0 wt%)/ CeO_2 catalyst. The catalyst was characterized by nitrogen gas adsorption, XRD, XPS, and H_2 -TPR. The results are shown below. The Ru(2.0 wt%)/ CeO_2 catalyst shows typical type IV nitrogen adsorption/desorption isotherms (Figure S1), indicating that its pore size distributed in the mesopore region. The $V-t$ plot analysis suggests the absence of micropores. The BET surface area of the Ru/ CeO_2 catalyst was $92\text{ m}^2\text{ g}^{-1}$. Note that Ru catalysts supported on titania (BET surface area $125\text{ m}^2\text{ g}^{-1}$), alumina ($144\text{ m}^2\text{ g}^{-1}$), and magnesia ($42\text{ m}^2\text{ g}^{-1}$) were found to possess pores in the

range of mesopores, while the silica-supported one ($259 \text{ m}^2\text{g}^{-1}$) possessed both mesopores and micropores.

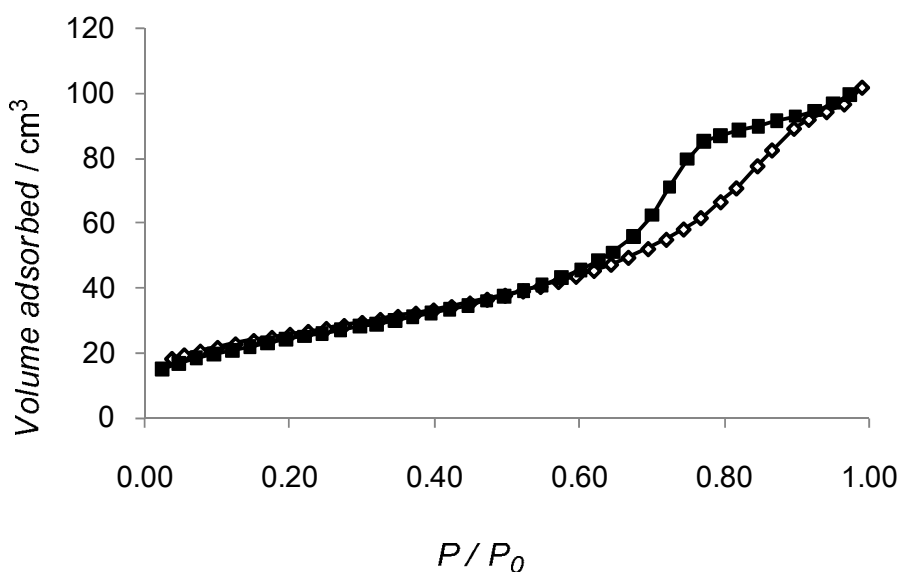


Figure S1. Nitrogen adsorption/desorption isotherms of the Ru(2.0 wt%)/CeO₂ catalyst. Open and filled marks stand for adsorption and desorption data, respectively.

Figure S2 shows the XRD patterns of the Ru/CeO₂ and Ru/TiO₂ catalysts, which only shows broad diffraction peaks due to nanocrystalline cubic cerium oxide and anatase, respectively. The crystalline size of CeO₂ was estimated to be 11 nm by the Scherrer's equation from the (111) peak.

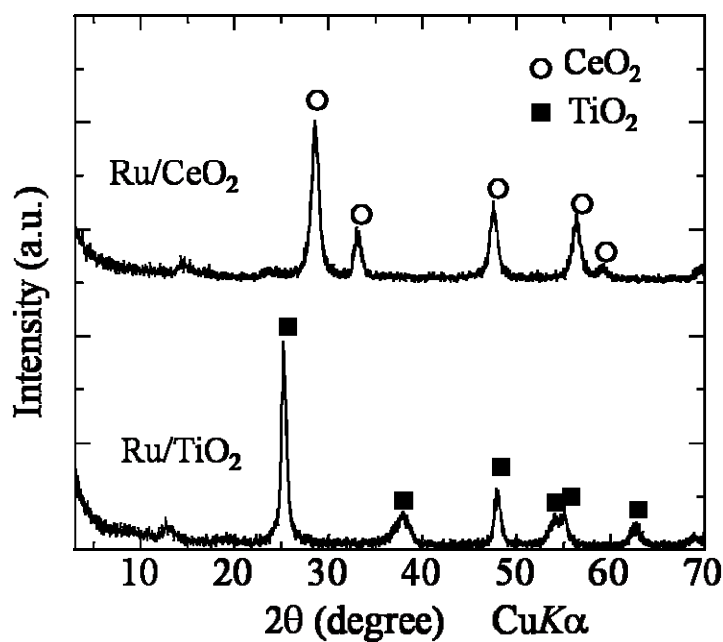


Figure S2. XRD patterns of the Ru(2.0 wt%)/CeO₂ and Ru(2.0 wt%)/TiO₂ catalysts.

The surface states of the catalyst before and after the catalytic run (Entry 3 in Table 1) were analyzed by XPS. Table S1 shows the surface composition and the binding energy of the Ru(2.0 wt%)/CeO₂ catalyst. The atomic ratio of carbon on the surface of the used catalyst was high, more than 18%, probably because of the deposition of carbonaceous materials on the surface during the catalytic run. Note that TG study of the used catalyst revealed that an absolute amount of deposited carbonaceous species was estimated to be small, 6.2 mg, about 2.7 wt% of total amounts of the substrates. A large part of carbonaceous species was removed by calcination at 400 °C for 30 min in air. The surface ratio of Ru was almost unchanged throughout the reaction and the subsequent calcination. Lower Ru 3d_{5/2} binding energy found in the used catalyst suggests the reduction of ruthenium(IV) species during the reaction.

Table S1. XPS analysis of the Ru(2.0 wt%)/CeO₂ catalyst^a

Remarks	C (%)	Ru (%)	Ce (%)	O (%)	Ru3d _{5/2} (eV)
before the reaction	11.87	1.01	30.28	56.84	280.4
after the reaction	18.38	1.08	30.63	49.90	279.2
after the 2nd calcination	11.07	1.08	29.52	58.32	280.6

^a Surface concentrations are shown as atomic %.

Figure S3 shows H₂ TPR profiles of the Ru(2.0 wt%)/CeO₂ and Ru(2.0 wt%)/TiO₂ catalysts. Ruthenium species on ceria was reduced at 72 °C, whereas a bulk ruthenium oxide was reduced at 105 °C. The TPR profile of the Ru(2.0 wt%)/TiO₂ indicated that the amount of Ru species reduced at below 200 °C was significantly smaller than that of the Ru/CeO₂ catalyst. Note that TPR measurements up to 900 °C at higher heating rate (5 °C min⁻¹) with 100 mg of the catalysts revealed that for Ru/TiO₂ a very broad peak appeared at around 200 to 300 °C, indicating that a major part of Ru species on TiO₂ were reduced at higher temperature than Ru species on ceria.

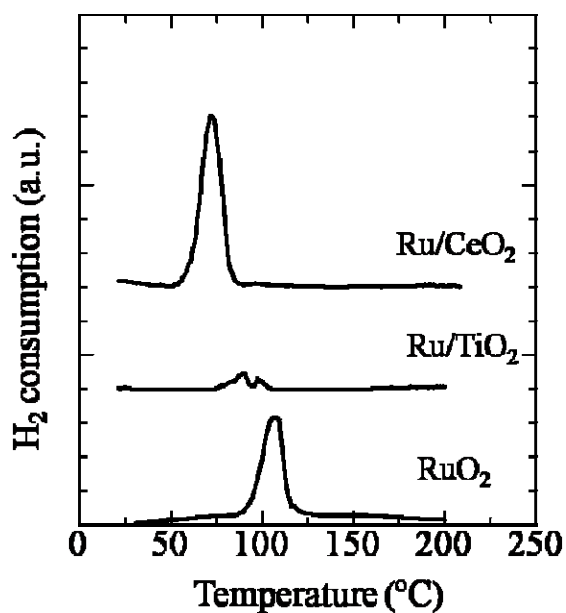


Figure S3. H₂ TPR profiles of the Ru(2.0 wt%)/CeO₂, the Ru(2.0 wt%)/TiO₂, and RuO₂. Heating rate 2 °C min⁻¹.

Figure S4 shows diffuse reflectance IR spectra of the Ru(2.0 wt%)/CeO₂ catalyst, the Ru(2.0 wt%)/TiO₂ catalyst, and CeO₂. An absorption band at 975 cm⁻¹ suggests the formation of Ru=O species on the freshly prepared Ru/CeO₂ catalyst.^[3]

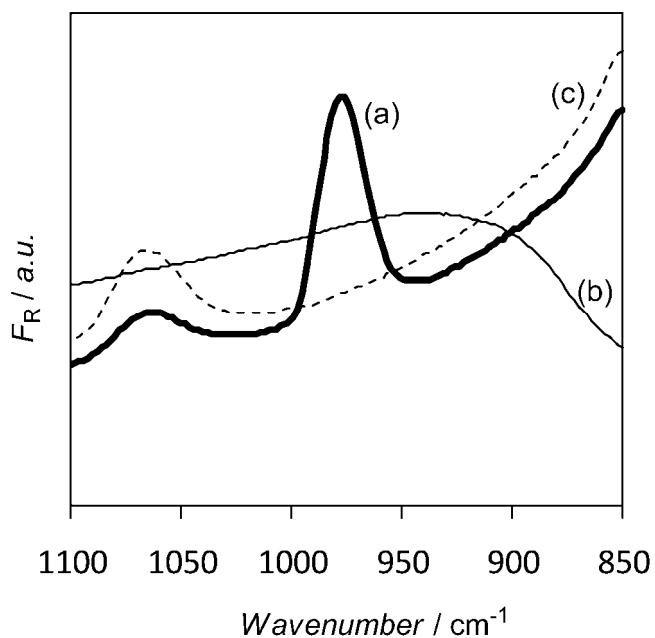
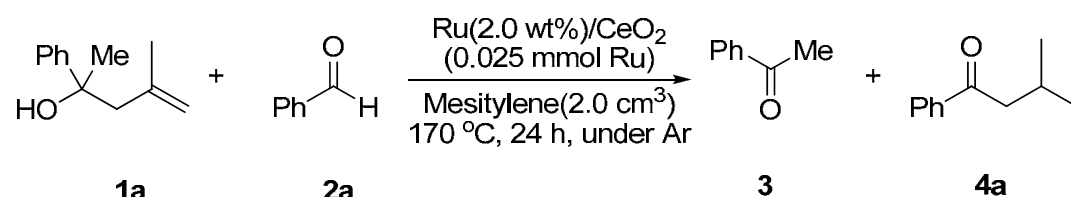


Figure S4. DRIFT spectra of the (a) Ru(2.0 wt%)/CeO₂ catalyst, (b) Ru(2.0 wt%)/TiO₂ catalyst, and (c) CeO₂.

Effect of the amount of the starting materials. The reaction was sensitive to the amount of homoallyl alcohols and aldehydes (see Table S2). The reaction of 0.50 mmol of **2a** with 1.0 mmol of **1a** smoothly proceeded to give the desired ketone **4a** in the best yield. The reaction did not proceed with 1.0 mmol of **2a** (Entries 5, 6). One possible reason of this behaviour might be the predominant adsorption of **2a** onto the catalytically active sites. On the other hand, the reaction of 1.0 mmol of **2a** and 2.0 mmol of **1a** smoothly proceeded in the presence of the Ru(1.0 wt%)/CeO₂ catalyst (0.025 mmol as Ru), to afford **4a** in 65% yield (Entry 7), suggesting the significant effect of the Ru loading level of the catalyst. Further detailed investigation on these behaviors is in progress.

Table S2. Effect of the amount of **1a** and **2a** on the transfer-allylation catalyzed by Ru/CeO₂



Entry	1a (mmol)	2a (mmol)	Yield of 4a (%) ^a
1	0.50	0.50	Trace ^b
2	0.75	0.50	41
3	1.0	0.50	69
4	1.5	0.50	49
5	0.50	1.0	0
6	2.0	1.0	0
7 ^b	2.0	1.0	65

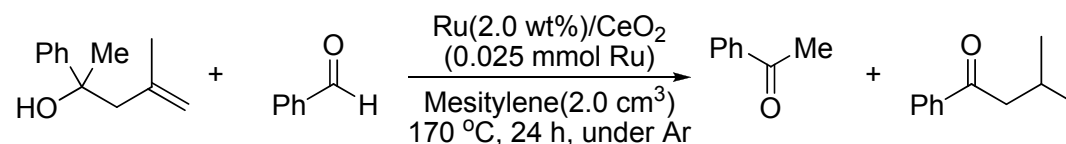
^a Determined by GLC based on **2a**. ^b **5a** was formed in the yield of 10%.

^b With Ru(1.0 wt%)/CeO₂ (0.025 mmol as Ru).

Reuse of the Ru/CeO₂ catalyst. The initial run was performed under the identical conditions shown in Table 1, Entry 3. After separation by the centrifugation, washing three times with diethyl ether (10 cm³) at room temperature, and calcination at 400 °C for 30 min in air, the Ru/CeO₂ catalyst was reused for the reaction under the same conditions as for the initial run. Two series of the experiments were performed

independently, and the results were shown in Table S3. Although the initial yield of **4a** in the series 2 was lower than that of series 1, these results clearly shows that the Ru/CeO₂ catalyst was reusable without a loss of activity. Note that reuse without calcination resulted in a poor yield of **4a** (less than 10% in the 2nd use), probably because of the deposition of a carbonaceous species on the catalyst surface.

Table S3. Activity of the reused Ru/CeO₂ catalyst



Series	Catalyst	Yield of 4a (%) ^a
1	1st use	69
	2nd use	68
2	1st use	61
	2nd use	59
	3rd use	62

^a Determined by GLC based on **2a**.

Hot Filtration tests. A 20 cm³ Schlenk tube was charged with homoallyl alcohol **1a** (1.0 mmol), aldehyde **2a** (0.50 mmol), the Ru(2.0 wt%)/CeO₂ catalyst (0.025 mmol as Ru), and mesitylene (2.0 cm³) together with an internal standard (naphthalene, *ca.* 50 mg) under an argon atmosphere. The mixture was filtered after a certain period of the reaction at 170 °C through a 0.45 μm syringe filter (Millipore Millex LH) to another preheated Schlenk tube. The filtrate was stirred at 170 °C for a prescribed period. The conversion and the yields of the products after the filtration were followed by GC as well as GC-MS.

The hot filtration to remove the bulk of the catalyst after the reaction for 3 h completely suppressed the transfer-allylation reaction, as shown in Figure S5.

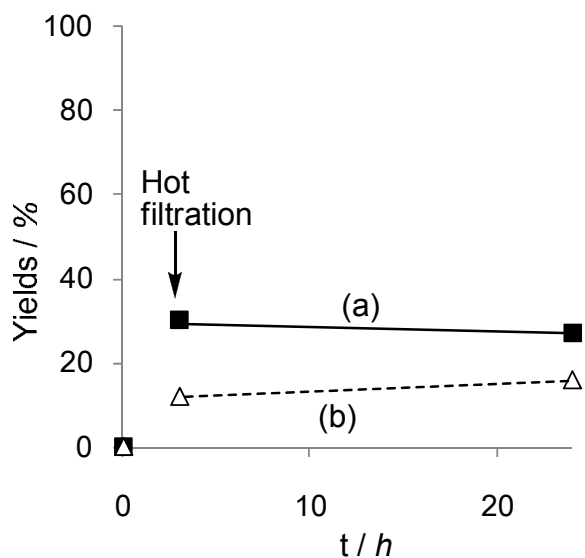


Figure S5. Time-course of the reaction of **1a** with **2a**. The catalyst was removed after the reaction for 3 h. (a) Yield of **4a** (filled squares) and (b) yield of **5a** (open triangles). The other reaction conditions were identical with those shown in Figure 1.

References

- [1] B. J. Wakefield, *Organomagnesium Methods in Organic Synthesis*; Academic Press: London, 1995, chapter 6, p. 111.
- [2] F. Moulder, W. F. Stickle, P. E. Sobol and K. D. Bomben, *Handbook of X-ray Photoelectron Spectroscopy*; Perkin-Elmer Co., Eden Prairie; USA, 1992.
- [3] S. Hosokawa, S. Nogawa, M. Taniguchi, K. Utani, H. Kanai and S. Imamura, *Appl. Catal. A General*, 2005, **288**, 67.