

Supporting Information

Transfer hydrogenation of ketones by ceria-supported Ni catalyst

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Experimental

General

The GC (Shimadzu GC-14B) and GCMS (Shimadzu GCMS-QP5000) analyses were carried out with a Rtx-65 capillary column (Shimadzu) using nitrogen or helium as the carrier gas. Commercially available organic and inorganic compounds were used without further purification.

Catalyst preparation

CeO₂ (JRC-CEO-2), TiO₂ (JRC-TIO-4) and SiO₂-Al₂O₃ (JRC-SAL-2, Al₂O₃ = 13.75 wt%, 560 m² g⁻¹) were supplied from Catalysis Society of Japan. γ -Al₂O₃ (with surface area of 124 m² g⁻¹) was prepared by calcination of γ -AlOOH (Catapal B Alumina purchased from Sasol) at 900 °C for 3 h. ZrO₂ (60 m² g⁻¹) was prepared by hydrolysis of zirconium oxynitrate 2-hydrate in distilled water by gradually adding an aqueous NH₄OH solution (1.0 mol dm⁻³), filtration of precipitate, washing with distilled water three times, drying at 100°C, and calcining at 500°C. SiO₂ (Q-10, 300 m² g⁻¹) was supplied from Fuji Silysia Chemical Ltd.

Supported Ni catalysts were prepared by an impregnation method. A mixture of support and an aqueous solution of Ni nitrates were evaporated at 60°C, followed by drying at 90°C for 12 h, calcination in air at 350°C for 4 h, and reduction in H₂ at 500°C for 30 min. These catalysts were used for reaction without being exposed to air.

M/CeO₂ (M = Cu, Co, Ru and Pd) catalysts, with metal loading of 5 wt% were prepared by impregnation method using aqueous solution of metal nitrates (for Cu and Co), RuCl₃, or aqueous HNO₃ solution of Pd(NO₃)₂. These catalyst precursors were dried at 90°C for 12 h, followed by calcination in air at 350°C for 4 h, and reduction in H₂ at 500°C for 30 min. These catalysts were used reaction without being exposed to air.

Typical procedures of catalytic reactions

NiO/CeO₂ (1-3 mol% of Ni with respect to ketone) inside the glass tube was reduced in a flow of H₂ (55 mL min⁻¹) at 500°C for 0.5 h. After cooling it to room temperature in a flow of H₂, the mixture of 2-propanol (1.5 mL) and ketone (1.0 mmol) was injected through a rubber. Then, the

reactor was purged by N₂ and set in a reaction vessel equipped with a condenser. The resulting mixture was stirred and heated at 85°C (reflux condition). Conversion and yields of products were determined by GC-FID using *n*-dodecane as an internal standard. The products were identified by GC-MS equipped with the same column as GC and by comparison with commercially pure products.

Characterization

Ni K-edge XAFS measurements were performed in a transmission mode at the BL01B1 in the SPring-8. The storage ring was operated at 8 GeV. A Si(111) single crystal was used to obtain a monochromatic X-ray beam. Pre-reduced samples were sealed in cells made of polyethylene under N₂ atmosphere and XAFS spectra were taken at room temperature. The analysis of EXAFS was performed using the REX version 2.5 program (RIGAKU). The Fourier transformation of the *k*³-weighted EXAFS oscillation from *k* space to *r* space was performed over the range 30-140 nm⁻¹ to obtain a radial distribution function. The inversely Fourier filtered data were analyzed with a usual curve fitting method in the *k* range of 30-140 nm⁻¹. The parameters for the Ni-O and Ni-Ni shells have been provided by the FEFF6.

CO₂-TPD measurements were carried out using BELCAT-A (BEL Japan, Inc.). Prior to each experiment, catalyst (0.1 g) was heated in a flow of He (20 mL min⁻¹) at 500°C for 10 min, followed by cooling to ca. 40°C under He flow. Then, the catalyst was exposed to a flow of CO₂ (20 mL min⁻¹) for 10 min. After purged in He for 30 min, the catalyst was heated linearly at 10°C min⁻¹ until 900°C in a flow of He, and outlet gases (CO₂, *m/e*=44) were analyzed by the mass spectrometer (BEL Mass, BEL Japan, Inc.).

In situ IR spectra were recorded on a JASCO FT/IR-6100 equipped with a quartz IR cell connected to a conventional flow reaction system. The sample was pressed into a 50 mg of self-supporting wafer and mounted into the quartz IR cell with CaF₂ windows. Spectra were measured accumulating 20 scans at a resolution of 4 cm⁻¹. A reference spectrum of the catalyst wafer in He taken at measurement temperature was subtracted from each spectrum. Prior to each experiment the catalyst disk was heated in 10% O₂/He flow (100 cm³ min⁻¹) at 550°C for 0.5 h, followed by cooling to the desired temperature and purging for 0.5 h in He.

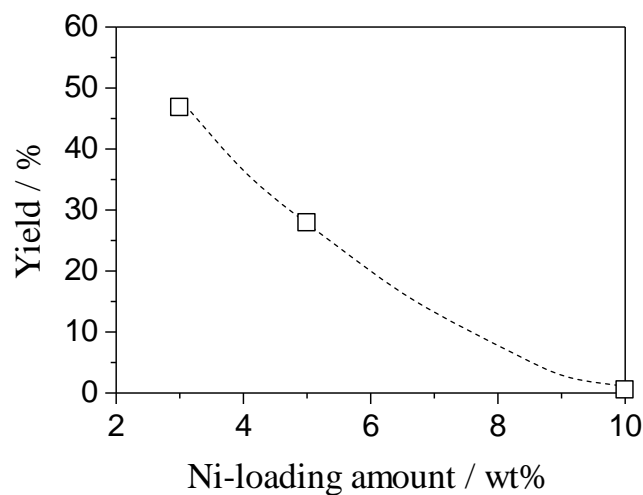


Fig. S1 Effect of Ni loading on the yield of 2-octanol for transfer hydrogenation of 2-octanone by Ni/CeO₂ catalysts (1 mol%) at 80°C for 3 h.

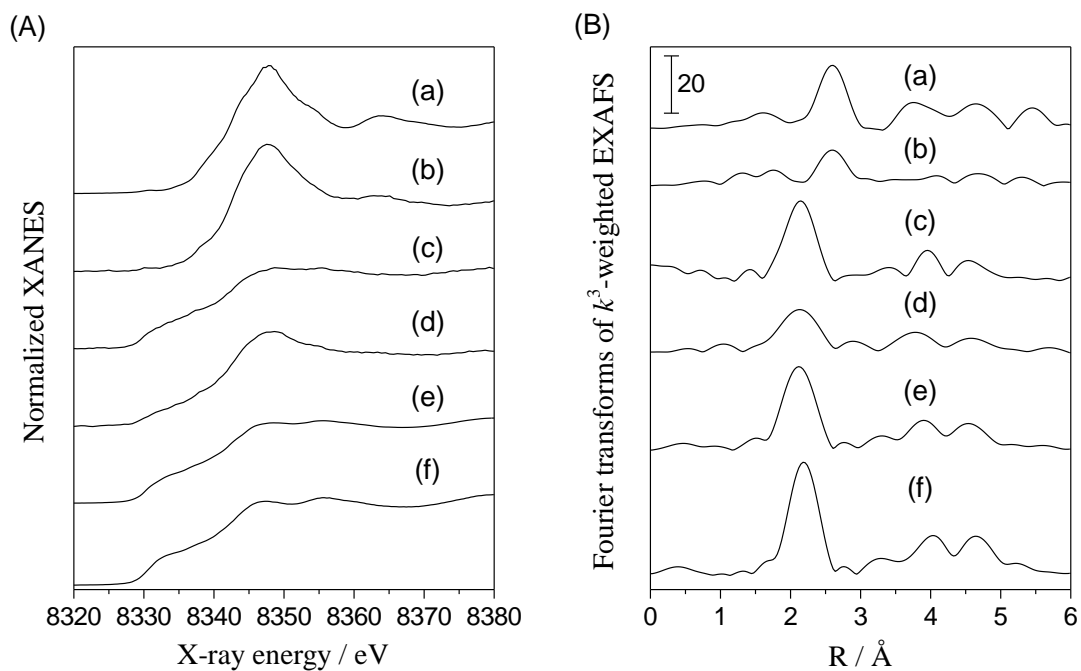


Fig. S2 (A) Ni K-edge XANES spectra and (B) the Fourier transforms of EXAFS spectra of Ni(5 or 10 wt%)/CeO₂ and reference compounds: (a) NiO, (b) NiO(5%)/CeO₂, (c) Ni(5%)/CeO₂, (d) Ni(5%)/CeO₂-air, (e) Ni(10%)/CeO₂ and (f) Ni foil.

Table S1 Curve-fitting analysis of Ni K-edge EXAFS of Ni(5 or 10 wt%)/CeO₂ samples

Sample	Shell	N ^a	R / Å ^b	σ / Å ^c	R _f / % ^d
NiO(5%)/CeO ₂	O	7.5	2.06	0.118	2.47
	Ni	6.0	2.95	0.073	
Ni(5%)/CeO ₂	Ni	7.5	2.47	0.065	0.57
Ni(5%)/CeO ₂ -air	O	2.7	2.08	0.094	0.30
	Ni	7.1	2.49	0.090	
Ni(10%)/CeO ₂	Ni	8.9	2.47	0.072	0.51
NiO ^e	O	6	2.02	-	-
	Ni	12	2.94	-	-
Ni foil ^e	Ni	12	2.49	-	-

^a Coordination number. ^b Bond distance. ^c Debye-Waller factor. ^d Residual factor. ^e Crystallographic data of Ni oxide and Ni metal.

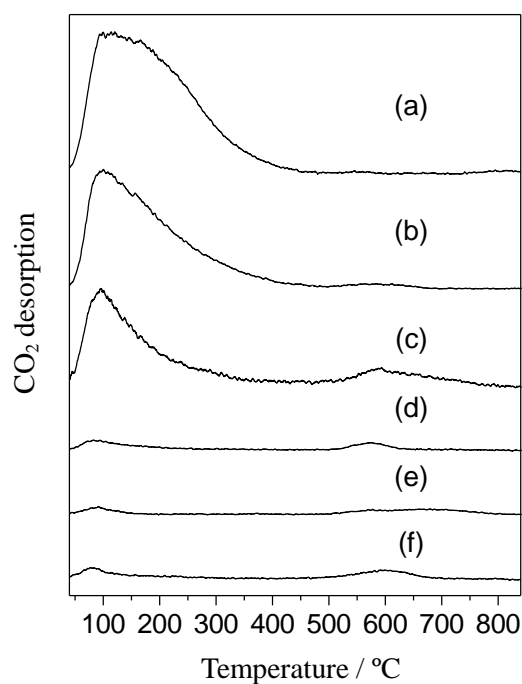


Fig. S3 CO₂-TPD profiles of the supported Ni catalysts: (a) CeO₂, (b) ZrO₂, (c) Al₂O₃, (d) TiO₂, (e) SiO₂-Al₂O₃ and (f) SiO₂.

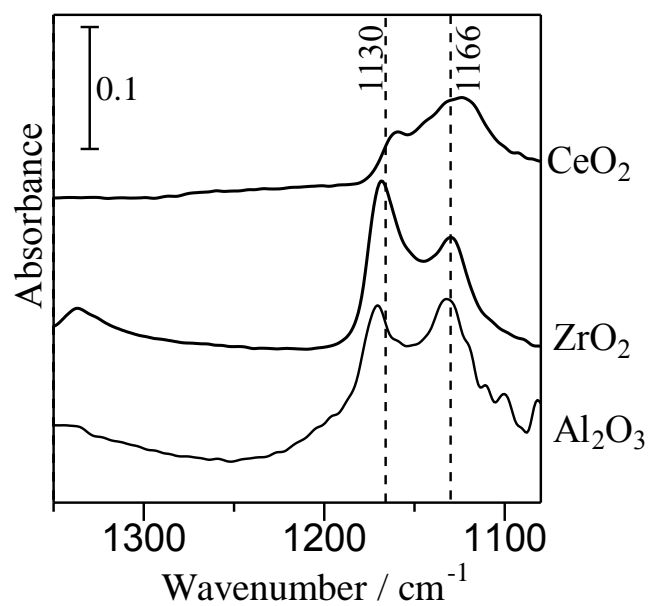


Fig. S4 IR spectra of adsorbed species on metal oxides. The samples were exposed to 2-propanol (0.5 mmol g⁻¹-catal.), followed by purging with He for 10 min.