Electronic Supplementary Material

Reductive amination of *N*-hexanol to *N*-hexylamine over Ni-Ce/γ-Al_2O_3 catalysts

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1. Catalyst Preparation

Ce-Al. Ce-Al catalysts with 2 wt% cerium loading were manufactured by IWI method with 0.68 g $Ce(NO_3)_3$*$6H_2O$ (RHAWN) solution on 3.84 g γ-Al_2O_3 (Meryer). The impregnated catalyst samples were stored at room temperature for 24 h, followed by drying at 120 °C for 12 h and calcination in air at 500 °C for 4 h.

2. Characterization

The specific surface area and pore volume of the different catalysts was obtained from N_2 physisorption at -196 °C with a Micromeritics Tristar II 3000 Analyzer instrument. The Barrer-Joyner-Halenda (BJH) method was used for measuring the interparticle pore size distributions. The sample were pretreated at 100 °C for 1 h and 300 °C for 3 h. And actual Ni and Ce loadings of the catalysts used in this study were measured with an inductively coupled plasma optical emission spectrometer (ICP-OES, Varian VistaMPX).

X-ray diffraction (XRD) analysis of catalysts was examined. X-ray diffraction patterns were obtained (0.01° per step, 2θ = 20°-90°) on a Rigaku D/MAX 2500 X-ray diffractometer using Cu Kα radiation. The Scherrer equation was used to estimate the average size of the oxide particles from the XRD line broadening. Catalysts were pre-reduced in pure H_2 for 2 h at 550 °C and then passivated at room temperature for 1 hours with 1% O_2-Ar prior to analysis. Then, the samples were transferred into sample tubes quickly under flowing nitrogen. Sample tubes were filled with nitrogen (99.999%).

To obtain high resolution images, we implement transmission electron microscopy (TEM) with the JEM-F200, employing Gatan Digital Micrograph for data acquisition/manipulation. Granular samples for analysis were primarily dispersed in ethanol and sonicated for 0.5 h, and then were placed on the holey carbon/Cu TEM grid.

H_2-temperature programmed reduction (H_2-TPR) was performed to measure the reducibility of the prepared catalysts via Micromeritics AutoChem 2910. 50 mg of the sample were placed in a U-shaped quartz tube, and then heated from room temperature to 780 ºC with a ramp-up of 10 ºC /min in 10 vol. % H_2/Ar mixture (30 mL/min). The consumption of H_2 was also recorded by a TCD.

The surface properties of samples were investigated by Temperature programmed desorption (H_2, CO_2 and NH_3-TPD) with a Micromeritics AutoChem 2910. For each measurement recorded, a 50 mg sample was pretreated at 200 ºC with He followed by exposure to pure detected gas for 1 h. Then the sample was purged with a flow of pure helium to remove physically adsorbed molecules. After that, catalyst samples were heated to the elevated temperature at the helium atmosphere.

X-ray photoelectron spectroscopy (XPS) as well as X-ray Auger electron spectroscopy (XAES) were employed to determine the valence states of surface concentration of Ni^+ catalysts. Note that the XPS results were calibrated by C 1s at 284.8 eV and the surface Ni and Ce species for reduced catalysts were collected. Catalysts were pre-reduced in pure H_2 for 2 h at 550 °C and then passivated at room temperature for 1 hours with 1% O_2-Ar prior to analysis. Then, the samples were transferred into sample tubes quickly under flowing nitrogen. Sample tubes were filled with nitrogen (99.999%). Meanwhile, the surface sputtering of catalysts was carried out before XPS characterization.

The nickel dispersions and specific area on reduced catalyst surface was analyzed by N_2O-H_2 titration on Autochem II 2920 apparatus. The catalyst of approximately 50 mg was weighed and packaged in the U-type tube. After that, the catalyst was reduced for 2 h in pure H_2 flow of 30 ml/min at 550 °C to obtain the metallic nickel, followed by a treatment in pure N_2O to make sure that surface metallic nickel atoms were totally oxidized to NiO. Afterwards, Ar gas was injected into to remove the N_2O gas physically adsorbed on the catalyst surface. Finally, the samples were heated up to 550 °C again and titrated by 10% H_2/Ar (30 ml/min). The reaction of this characterization is stated as follows:

$$NiO + H_2 \xrightarrow{550\ °C} Ni + H_2O \tag{1}$$

$$Ni_{surface} + N_2O \longrightarrow NiO_{surface} + N_2 \tag{2}$$

$$NiO_{surface} + H_2 \xrightarrow{550\ °C} Ni_{surface} + H_2O \tag{3}$$

The dispersion of Ni^0 on catalyst surface was determined by using the amount of consumed hydrogen during the reduction (3). In this work, the dispersion was calculated by using the formulas:

$$Dispersion(\%) = \frac{n_{H_2} \times M_{Ni}}{m_{cat} \times L_{Ni}} \times 100 \quad (4)$$

n_{H_2}, M_{Ni} and m_{cat} represent the hydrogen consumption (3), the relative molecular weight of nickel and the weight of catalyst, respectively. L_{Ni} is the weight content of nickel, which is characterized by ICP-OES.

3. N_2 adsorption–desorption isotherms

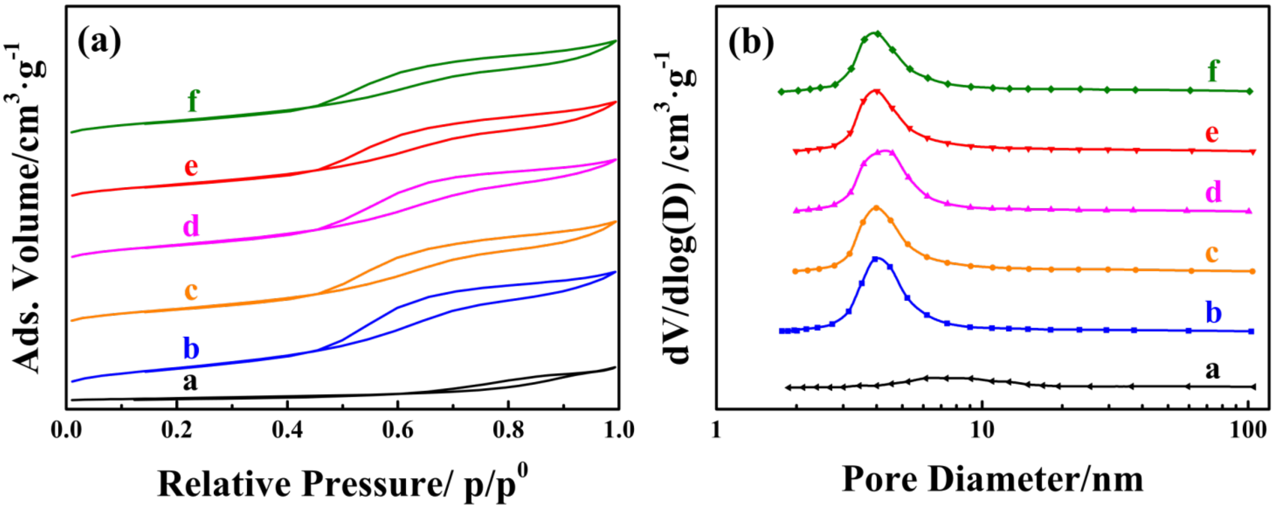

Fig. S1. (a) N_2 adsorption–desorption isotherms and (b) pore-size distribution patterns of catalysts: (a) Ni/CeO_2, (b) Ni-0Ce, (c) Ni-1Ce, (d) Ni-2Ce, (e) Ni-3Ce, (f) Ni-5Ce.

4. TEM images and corresponding EDS mapping

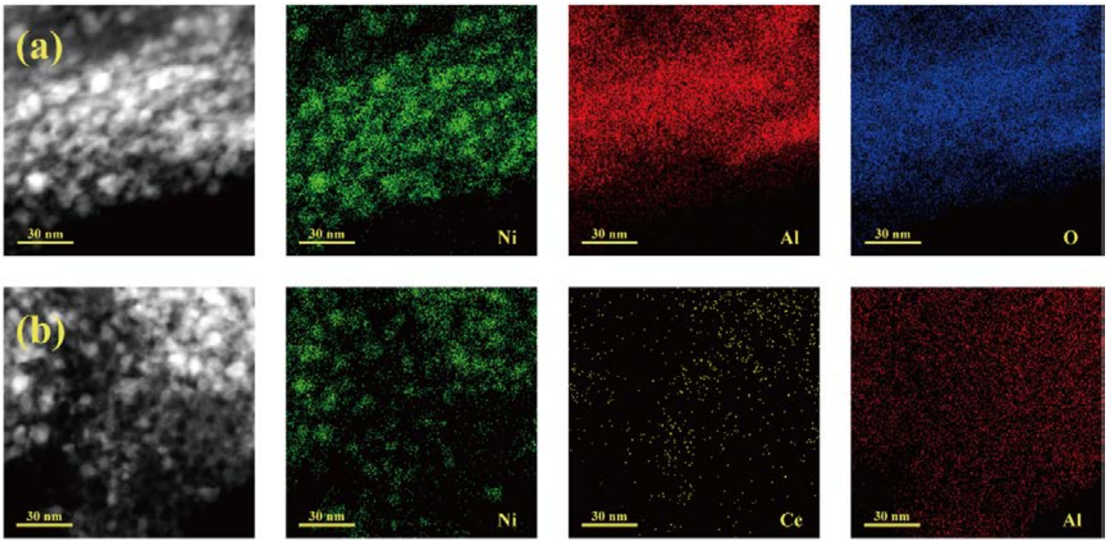

Fig. S2. TEM images and corresponding EDS mapping: (a) Ni-0Ce; (b) Ni-2Ce.

5.NH$_3$-TPD profiles including that of Ni-Al, Ni/CeO2, Ni-Ce-Al, Al and Ce-Al systems

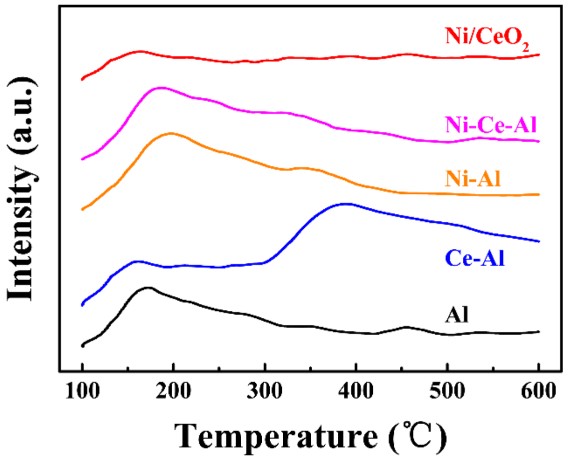

Fig. S3. NH$_3$-TPD profiles of catalysts.

6. The performance of Ni-2Ce at different GHSV

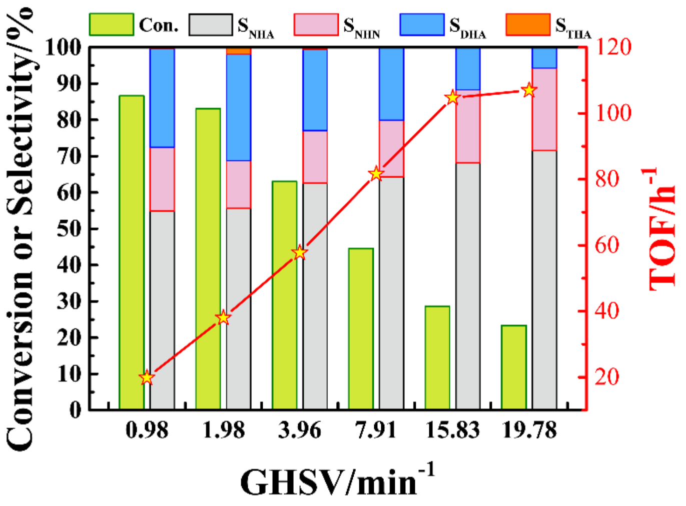

Fig. S4. Ni-2Ce catalytic performance. Reaction conditions: 0.25 g cat., T = 200 °C, P = 0.1 MPa, hexanol/H_2/NH_3= 1:9:11.

7. Reductive amination of NHO with Ni-0Ce catalyst according to experimental variables

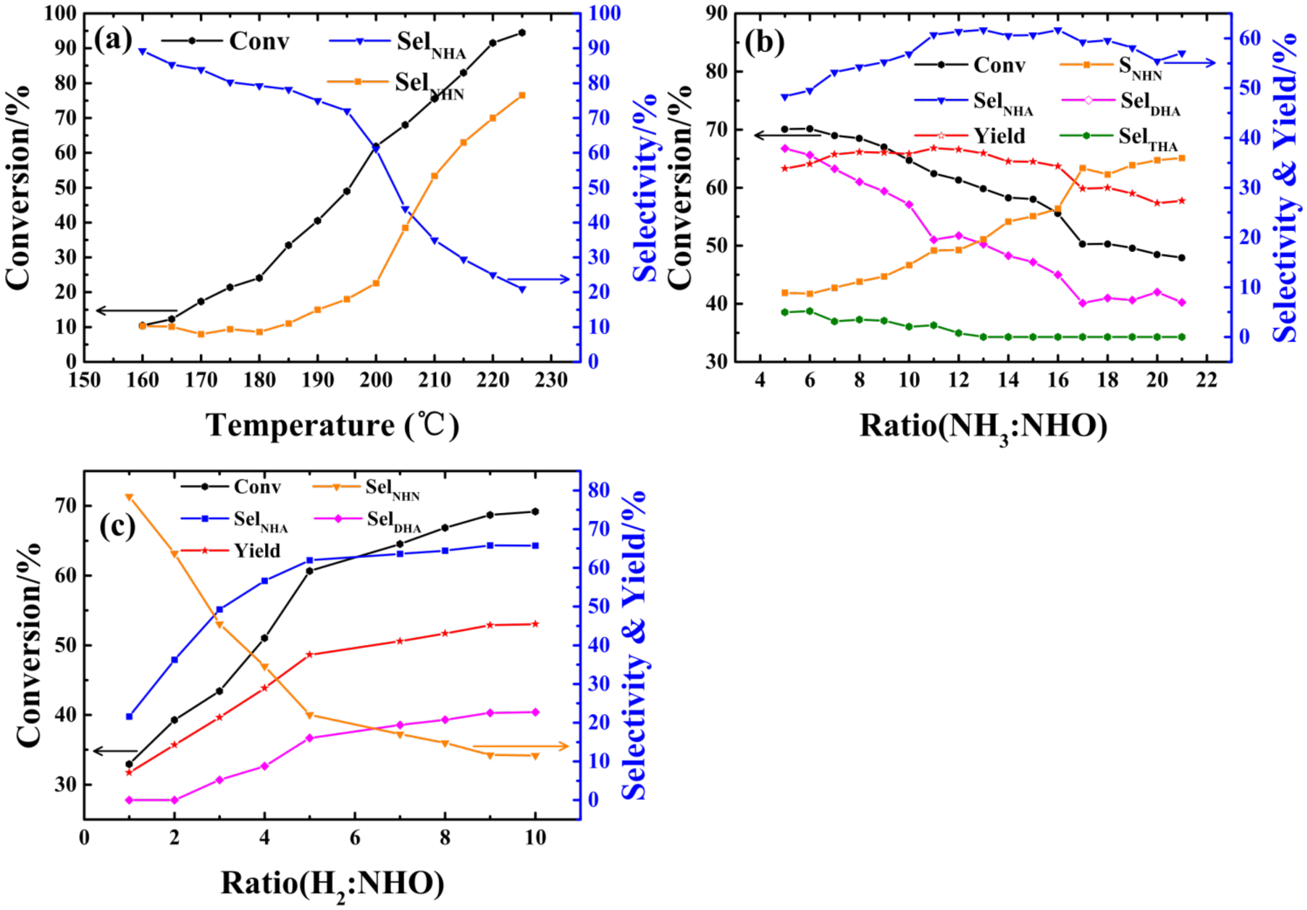

Fig. S5. Influence of reaction parameters on the hexanol conversion and the selectivity over Ni-xCe catalyst: (a) Reaction temperature, (b) Ratio(NH_3: hexanol), (c) Ratio(H_2: hexanol). Common reaction conditions: 200 °C, 0.1 MPa, GHSV= 7.91 min^{-1}, Ratio(NH_3: hexanol)= 10:1, Ratio(H_2: hexanol)= 9:1, 0.25 g cat.

8. The structures of the catalysts with and without cerium

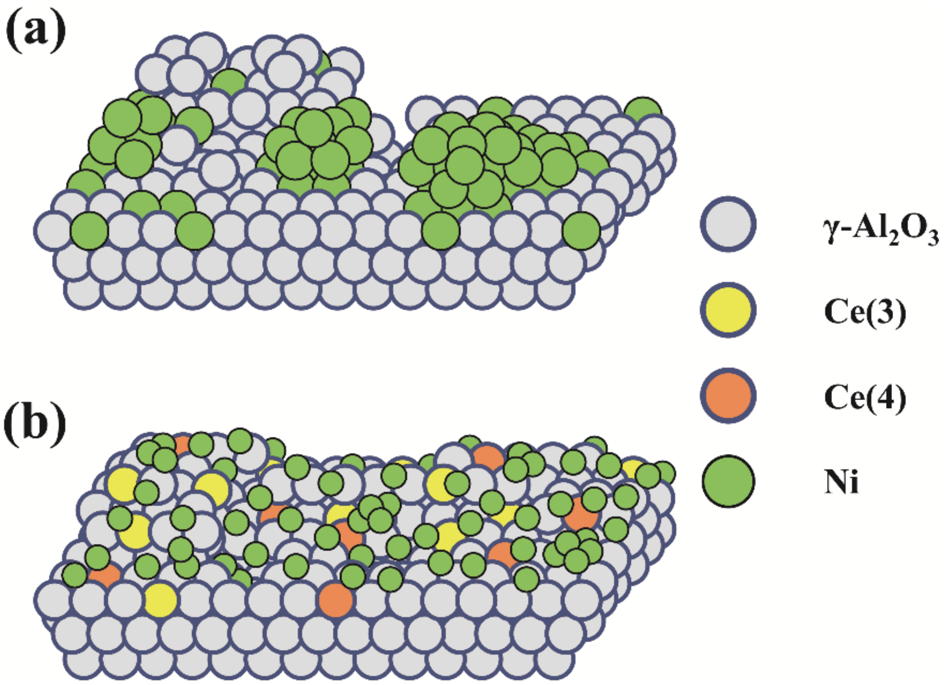

Fig. S6. Proposed structures for (a) Ni-0Ce and (b) Ni-2Ce.