Electronic Supporting Information

Chemical transformation and morphology change of nickel-silica hybrid nanostructures via nickel phyllosilicates

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Experimental

Chemicals

Nickel(II) acetylacetonate (Ni(acac)$_2$, 95%), oleylamine (70%), trioctylphosphine (TOP, 90%), tetramethyl orthosilicate (TMOS, 98%), and igepal CO-630 were purchased from Aldrich. Ammonium hydroxide (NH_4OH, 28% in water) and cyclohexane (99.5%) were purchased from Junsei. The chemicals were used as received without further purification.

Synthesis of Ni nanoparticles. A mixture of Ni(acac)$_2$ (0.77g, 3.0 mmol) and TOP (4.0 mL, 9.0 mmol) in oleylamine (20 mL) was slowly heated from room temperature to 230 °C for 20 min under inert atmosphere, and allowed to stir at 230 °C for 40 min. After cooling the reaction mixture, the colloidal particles were separated by adding ethanol (40 mL) and centrifuging at 10,000 rpm for 20 min. Finally, the nickel nanoparticles were dispersed in cyclohexane.

Silica coating of Ni nanoparticles. Cyclohexane (25 mL) was mixed with igepal CO-630 (8 mL) and NH_4OH solution (1 mL) and stirred for 10 min. The nickel particle dispersion in cyclohexane (25 mL, 60 mM with respect to the precursor concentration) was added into the mixture and allowed to stir fast for 30 s. TMOS (1.0 mL) was added, and the resulting mixture was stirred for 60 min at room temperature. After 60 min, Ni@SiO$_2$ particles were precipitated by adding methanol (10 mL) and washed with ethanol thoroughly.

Synthesis of branched nickel phyllosilicate/SiO$_2$ and Ni/SiO$_2$ nanoparticles. Freshly prepared Ni@SiO$_2$ core-shell particle dispersion in de-ionized water (40 mL, 37.5 mM with respect to the precursor concentration) was refluxed for 2 h under a weak basic condition (pH = 9.6). The pH of the solution was actually resulted from the residual amount of ammonium hydroxide used in the silica coating process. After cooling the reaction mixture, the branched nickel phyllosilicate/SiO$_2$ particles were precipitated as a green power by centrifugation at 10,000 rpm for 20 min. For the synthesis of Ni/SiO$_2$ nanoparticles, the powders of the branched nickel phyllosilicate/SiO$_2$ particles were placed at the ceramic boat in the glass tube oven, and were slowly heated at a ramping rate of 5.5 ^{o}C/min up to 700 ^{o}C under a hydrogen flow of 200 cc/min. The particles were allowed at 700 ^{o}C for 10 h under the continuous hydrogen flow. After the reduction treatment, the resulting black powders were cooled down to room temperature, and were submerged into anhydrous ethanol (20 mL) under the hydrogen flow in order to prevent surface oxidation of the nickel particles. Finally, the Ni/SiO_2 powders were easily separated by a magnet force and dried completely under vacuum.

General procedure for hydrogenation transfer reactions of acetophenone. In a 25 mL stainless steel reactor, Ni/SiO_2 nanoparticles (2.0 mg, 1 mol% with respect to the substrate concentration), acetophenone (2.4 mL, 0.02 mmol), isopropanol (10 mL), and NaOH (0.40 g) were added, and the resulting mixture was stirred for 1 h at 100 ^oC. After the reaction, the nanoparticles were separated by centrifugation.

Characterization. The Ni/SiO_2 nanostructures were characterized by TEM (Omega EM912 operated at 120 kV, Korea Basic Science Institute), HRTEM (Philips F20 Tecnai operated at 200 kV, KAIST), and ED (attached to EM912). Samples were prepared by putting a few drops of the corresponding colloidal solutions on carbon coated copper grids (Ted Pellar, Inc). X-ray powder diffraction (XRD) patterns were recorded on a Rigaku D/MAX-RB(12 kW) diffractometer. Nitrogen sorption isotherms were measured at 77 K with a BELSORP mini-II (BEL Japan Inc.). Before measurements, the samples were degassed in a vacuum at 150 ^oC for 6 h. The nickel loading amounts were measured by MiniPal 2 energy dispersive X-ray fluorescence (EDXRF) spectrometer. The reaction products were analyzed by ^1H NMR using Varian Mercury Plus (300 MHz). Chemical shift values were recorded as parts per million relative to tetramethylsilane as an internal standard unless otherwise indicated, and coupling constants in Hertz.

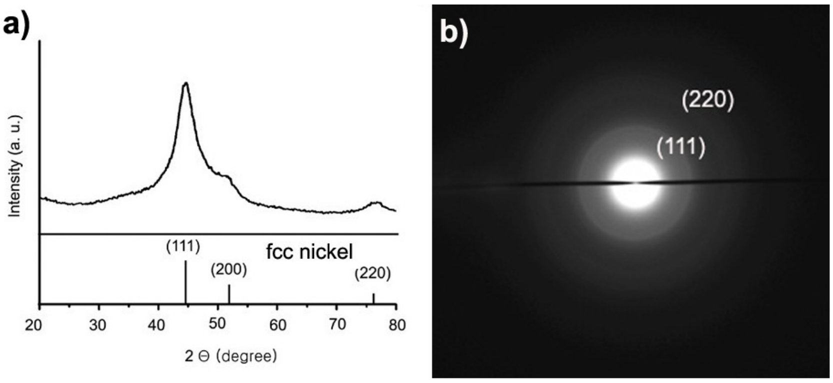

Figure S1. (a) XRD spectrum and (b) ED pattern of Ni nanoparticles.

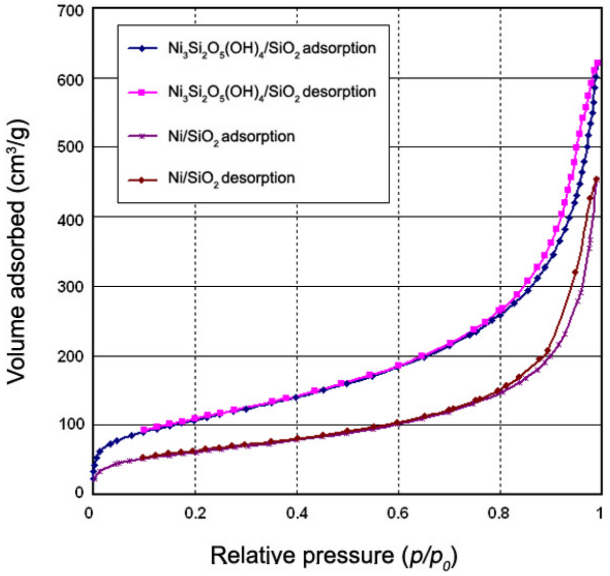

Figure S2. N_2 sorption isotherms of branched nickel phyllosilicate/SiO_2 and Ni/SiO_2 nanoparticles.

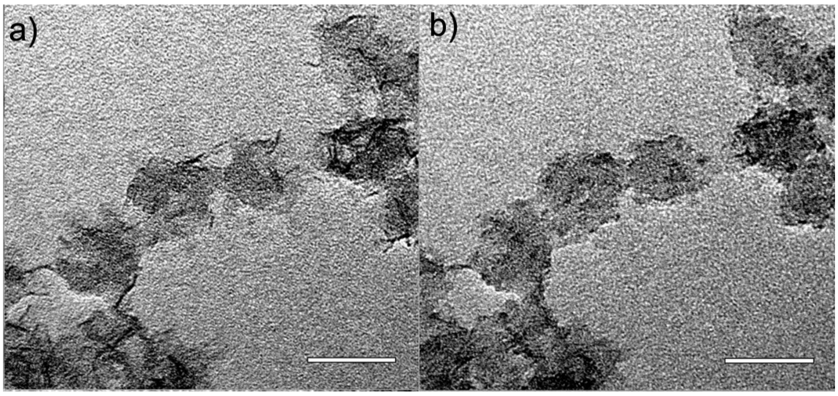

Figure S3. HRTEM images of nickel phyllosilicate/SiO_2 nanoparticles (a) before and (b) after the long time irradiation of electron beam in HRTEM apparatus. All bars represent 20 nm.

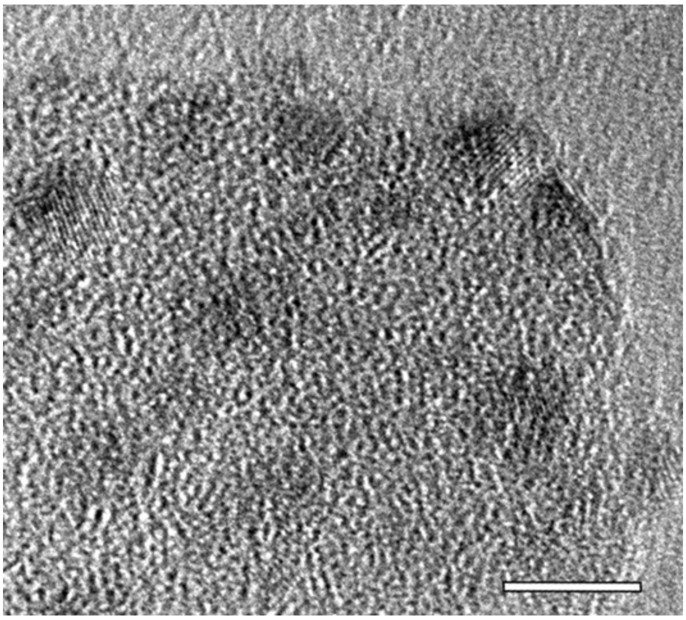

Figure S4. HRTEM image of tiny nickel nanoparticles on a silica sphere. The bar represents 5 nm.

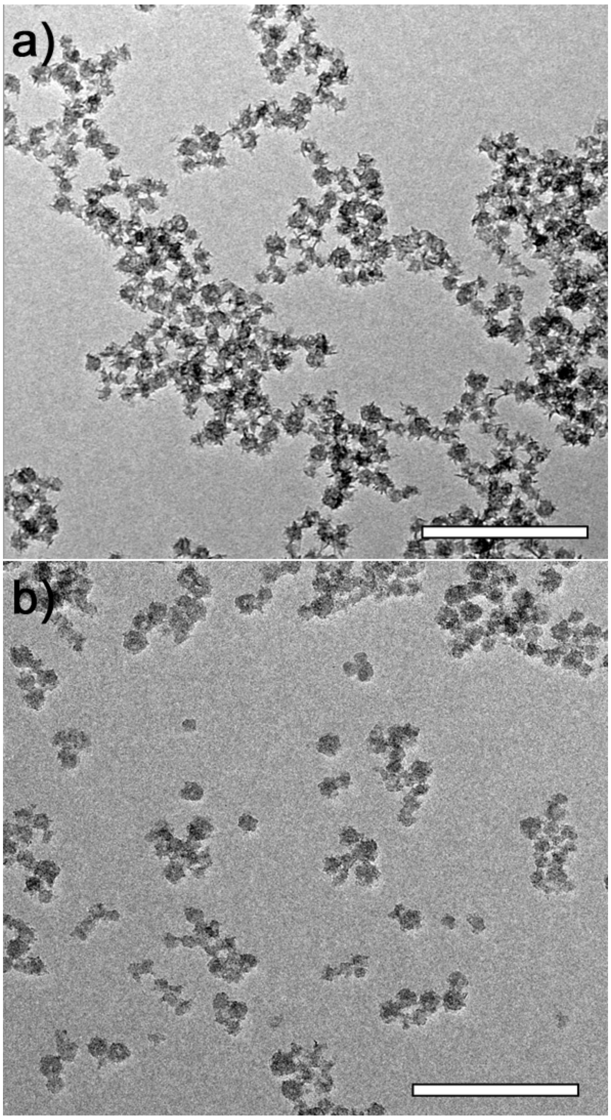

Figure S5. Low resolution TEM images of (a) branched nickel phyllosilicate/SiO_2 and (b) Ni/SiO_2 nanostructures. All bars represent 200 nm.

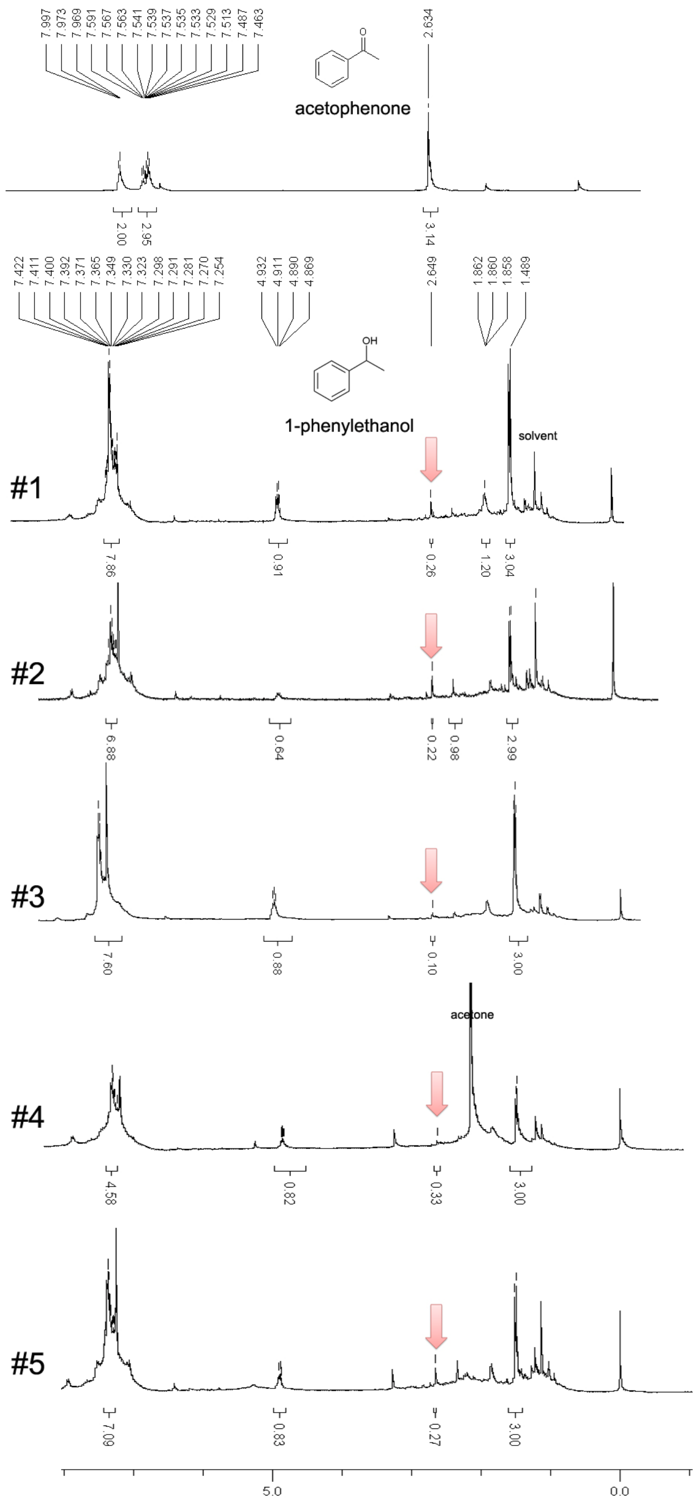

Figure S6. Reuse-test experiments. ^{1}H-NMR spectra of acetophenone and the products in successive five runs using the Ni/SiO_2 catalysts recovered from the reaction mixture. The red arrows indicate proton peaks of the methyl group in unreacted acetophenone.