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CO_2 to methanol conversion using hydride terminated porous silicon nanoparticles.

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Experimental

Materials: Tetraethoxysilane (TEOS, 99%, Sigma-Aldrich), ammonium hydroxide (NH_4OH, 28%, Caledon), magnesium powder (Mg, 99%, BDH), potassium chloride (KCl, 99%, Sigma-Aldrich), ethanol (ACS grade, Sigma-Aldrich), hydrofluoric acid (HF, 49% solution, J. T. Baker), hydrochloric acid (HCl, 37%, Sigma-Aldrich), acid purified sand (50-70 mesh particles, Sigma-Aldrich), nitric acid (HNO_3, 70%, Sigma-Aldrich), deuterated water (Deutero), and sodium acetate (Sigma-Aldrich) were used as received.

Synthesis of silicon nanoparticles. Stöber silica particles were synthesized *via* base catalyzed sol-gel method. 5.0 mL (45 mmol) TEOS was added to a reaction flask containing ethanol (40.0 mL) and deionized water (10.0 mL). NH_4OH solution (28 %, 3.0 mL) was added to the TEOS mixture and the reaction was stirred for three hours. The white precipitate was collected by vacuum filtration and washed with deionized water and ethanol multiple times (4 × 25 mL). The solid was transferred to a vacuum oven and was kept there for 24 hours at 70 $^{\circ}$C to drive off any residual water and ethanol.

1.00 g (16.8 mmol) of the dried silica particles were manually mixed with 0.88 g (36.8 mmol) of magnesium powder, 1.00 g of potassium chloride salt and transferred to an alumina boat. The mixture was heated to 650 ^{o}C at a rate of 10 ^{o}C/min in a tube furnace under argon atmosphere and maintained at that temperature for 6 hours followed by cooling to the room temperature. The resulting product was treated with 1.0 M aqueous HCl (100 mL) solution for two hours to remove magnesium oxide and potassium chloride salts. The silicon particles were then collected by vacuum filtration and sonicated in 1.0 M HCl (10 mL) for 15 min. The particles were recollected by vacuum filtration and washed multiple times with distilled water. It was then dried in vacuum oven overnight at 70°C.

Hydride termination of silicon surfaces. Silicon nanoparticles (0.25 g) were suspended in 1:1 mixture (5.0 mL) of water and ethanol. 49% HF (1.0 mL) was added to the nanoparticle slurry followed by 100 µL of concentrated HNO_3 acid. The reaction mixture was vigorously stirred for 10 min. The hydrophobic hydride terminated silicon nanoparticles were extracted using 50 mL toluene. The Si-NC/toluene mixture were centrifuged at 4000 rpm for 10 min and the toluene supernatant was decanted leaving a precipitate of hydride terminated silicon nanoparticles. The particles were washed with toluene twice and used for further reaction immediately with minimum exposure to ambient atmosphere.

Reaction of hydride silicon nanoparticles with carbon dioxide. The hydride terminated silicon nanoparticles (~ 0.25 g) dispersed in 10.0 mL toluene were transferred to a 50 mL Bergoh high pressure steel autoclave. The reaction vessel was evacuated and refilled with Argon thrice and finally filled with 10 bar CO_2. The reaction mixture was heated at 150 ^oC for 3 hours. The reaction flask was cooled to room temperature and the pressure was released. The reaction mixture was centrifuged and the precipitate was isolated. The brown solid was reacted with 2.00 mL deuterated water and catalytic amounts of DCl for 30 min. The reaction mixture was centrifuged again and the D_2O layer was extracted. 0.45 mL of the extracted D_2O was transferred to an NMR tube and 0.05 mL of 10 mM sodium acetate solution In D_2O) was added to the mixture as an internal standard.

***In-situ* IR experiments**. *In-situ* IR experiments were performed using a React-IR/MultiMax four-autoclave system from Mettler-Toledo with 50 mL steel autoclaves equipped with a diamond window, a mechanic stirring and an electronic thermostat. The autoclaves were cleaned extensively with boiling acetone, dichloromethane, and toluene sequentially. After heating to 130 ºC in vacuum for several hours the reactor was cooled down and flushed with argon atmosphere prior to use. The reaction mixtures (0.25 g of hydride terminated Si nanoparticles dispersed in 10.0 mL toluene) were added via syringe through a valve in presence of an argon stream and the stirrer was set to 800 rpm. The autoclave was evacuated and refilled with CO_2 until the required pressure was reached. The temperature was measured using a thermostat attached to the reactor. The collected data was edited using the iC-IR 4.1 from Mettler Toledo software. Background noise was measured prior to each measurement and subtracted from the dataset.

Reduction of sand to Si. 0.25 g of the sand particles were manually mixed with 0.22 g (9.2 mmol) of magnesium powder, 1.00 g of potassium chloride salt and transferred to an alumina boat. The mixture was heated to 800 ^{o}C at a rate of 10 ^{o}C/min in a tube furnace under argon atmosphere and maintained at that temperature for 24 hours followed by cooling to the room temperature. The resulting product was treated with 1.0 M aqueous HCl (25 mL) solution for two hours to remove magnesium oxide and potassium chloride salts. The silicon particles were then collected by vacuum filtration and sonicated in 1.0 M HCl (10 mL) for 15 min. The particles were recollected by vacuum filtration and washed multiple times with distilled water. It was then dried in vacuum oven overnight at 70°C.

Reaction of sand derived Si with CO_2. Silicon particles (0.1 g) obtained from sand were suspended in 1:1 mixture (5.0 mL) of water and ethanol. 49% HF (1.0 mL) was added to the nanoparticle slurry followed by 500 µL of concentrated HNO_3 acid. The reaction mixture was vigorously stirred for 15 min. The suspension was centrifuged at 3000 rpm for 5 min and the supernatant was decanted and quenched with saturated $CaCl_2$ solution immediately. The precipitate was washed with toluene twice. It was finally redispered in toluene (10 mL) and transferred a 50 mL Bergoh high pressure steel autoclave. The reaction vessel was evacuated and refilled with Argon thrice and finally filled with 10 bar CO_2. The reaction mixture was heated at 150 ^{o}C for 3 hours. The reaction flask was cooled to room temperature and the pressure was released. The reaction mixture was transferred to a separatory funnel and 2.00 mL deuterated water was added to it. The separatory funnel was shaken for 30 seconds and the D_2O layer was extracted. 0.45 mL of the extracted D_2O was transferred to an NMR tube and 0.05 mL of 10 mM sodium acetate solution In D_2O) was added to the mixture as an internal standard.

Characterization

Infrared spectroscopy. Fourier transform infrared (FTIR) spectra were collected with a Bruker Vertex 70 FTIR using a Platinum ATR set-up.

NMR spectroscopy. NMR spectra were recorded on a Bruker AV-300 and AV-500C spectrometer. ^{1}H and ^{13}C NMR spectroscopic shifts δ are reported in ppm relative to the residual solvent signal. Unless otherwise stated, the spectra were recorded at 298 K.

Scanning Electron Microscopy. Scanning electron microscopy (SEM) images were recorded in a Field Emission Scanning Electron Microscope, JEOL 6301F. Ethanolic dispersions of the samples were directly deposited onto the aluminium pin stubs. All SEM images were recorded using secondary electron imaging with an accelerating voltage of 5.0.

Transmission Electron Microscopy. Transmission electron microscopy (TEM) analyses were performed using a JOEL-2010 (LaB_6 filament) with an accelerating voltage of 200 keV. The samples were prepared by drop coating solutions of composite dispersed in ethanol onto a carbon coated copper grid (400 mesh) and allowing the solvent to evaporate in air. The particle sizes were measured using Image J software.

Powder X-ray Diffraction. X-ray powder diffraction (XRD) patterns were collected using an INEL XRG 3000 X-Ray diffractometer with CuK_α radiation (λ = 1.54 Å).

BET and BJH measurements. Nitrogen adsorption-desorption isotherms were collected using Sorptomatic 1900 instrument from Porotec. The data was fit using Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) theory.

X-ray Photoelectron Spectroscopy. XPS analyses were performed using a Kratos Axis Ultra instrument operating in energy spectrum mode at 210 W. The base pressure and operating chamber pressure were maintained at 10^{-7} Pa. A monochromatic Al K_α source (λ = 8.34 Å) was used to irradiate samples, and spectra were obtained with an electron takeoff angle of 90°. To minimize sample charging the charge neutralizer filament was used as appropriate. Survey spectra were collected using an elliptical spot with major and minor axis lengths of 2 and 1 mm, respectively, and 160 eV pass energy with a step of 0.33 eV. CasaXPS software (VAMAS) was used to interpret high-resolution (HR) XP spectra. All spectra were internally calibrated to the C 1s emission (284.8 eV). After calibration, the background was subtracted using a Shirley-type background to remove most of the extrinsic loss structure. The full width at half maximum (FWHM) for all the fitted peaks was maintained below 1.2 eV.

GC-MS. To identify the gas phase products an Agilent 7820A GC coupled with a 5977E MS with a heated cold quadrupole detector and a capillary CarbonPLOT column was used.

Figure S1. Pore size distribution (BJH analysis) in (A) Stöber silica and (B) porous Si-NPs.

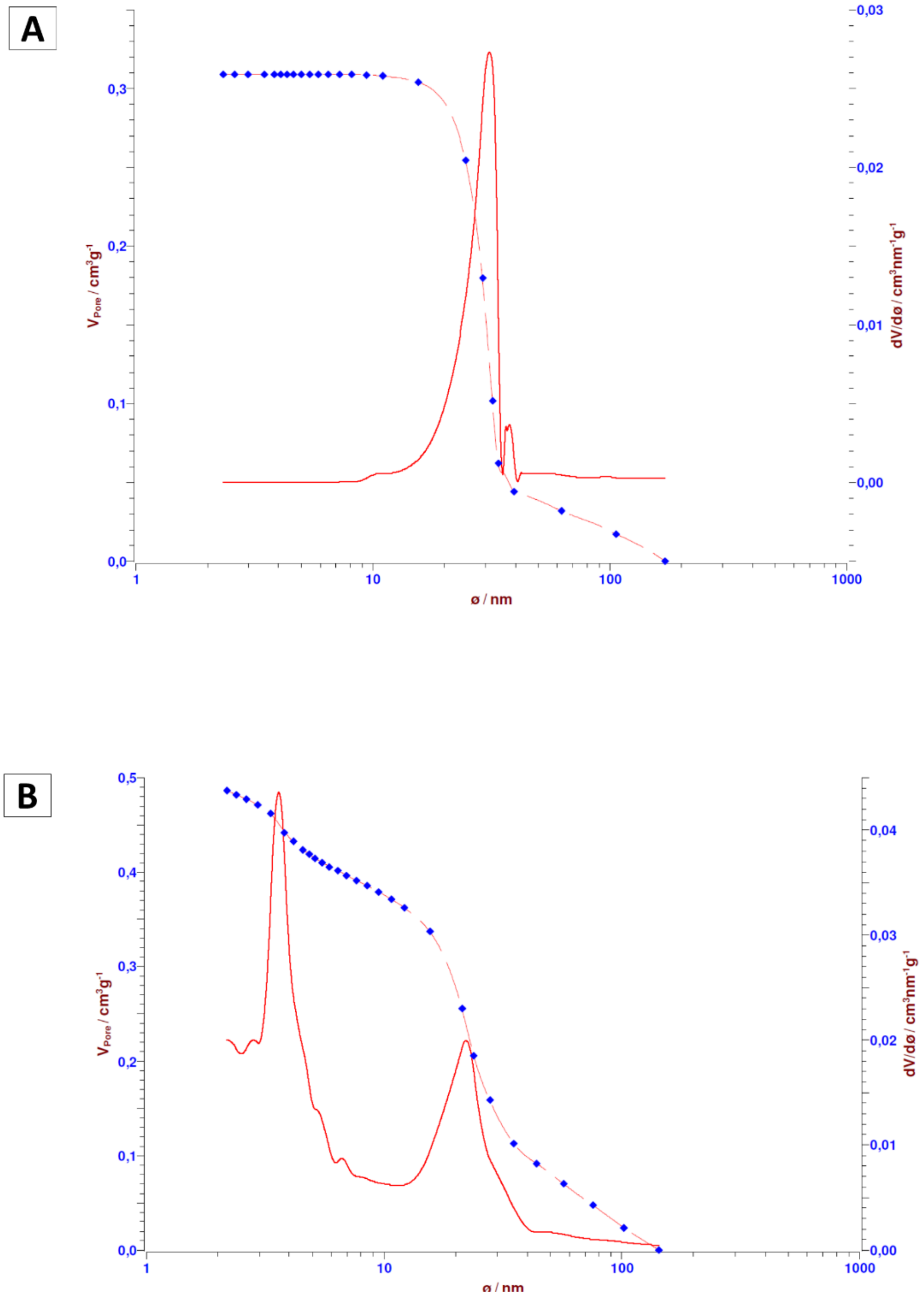

Figure S2. FT-IR spectrum of hydride terminated porous Si-NPs.

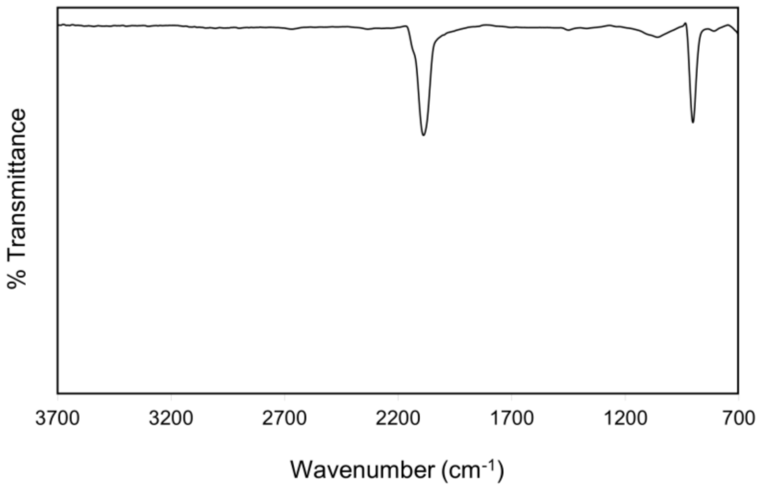

Figure S3. In-situ IR spectrum of CO_2 stretches as a function of time.

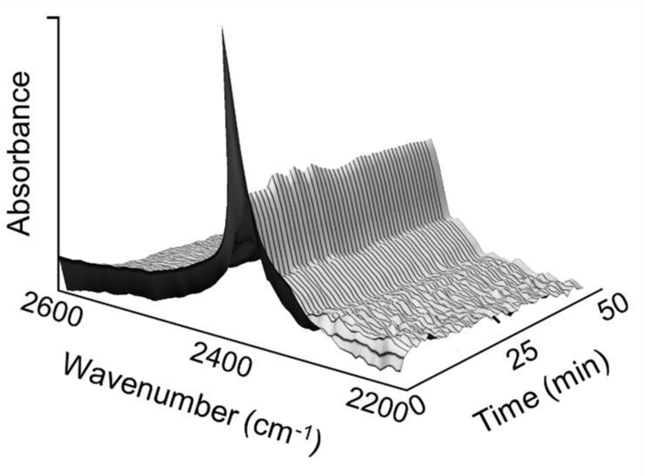

Figure S4. CO_2 IR absorbance intensity vs. time during the reduction reaction. The reaction reached room temperature at t = 55 min.

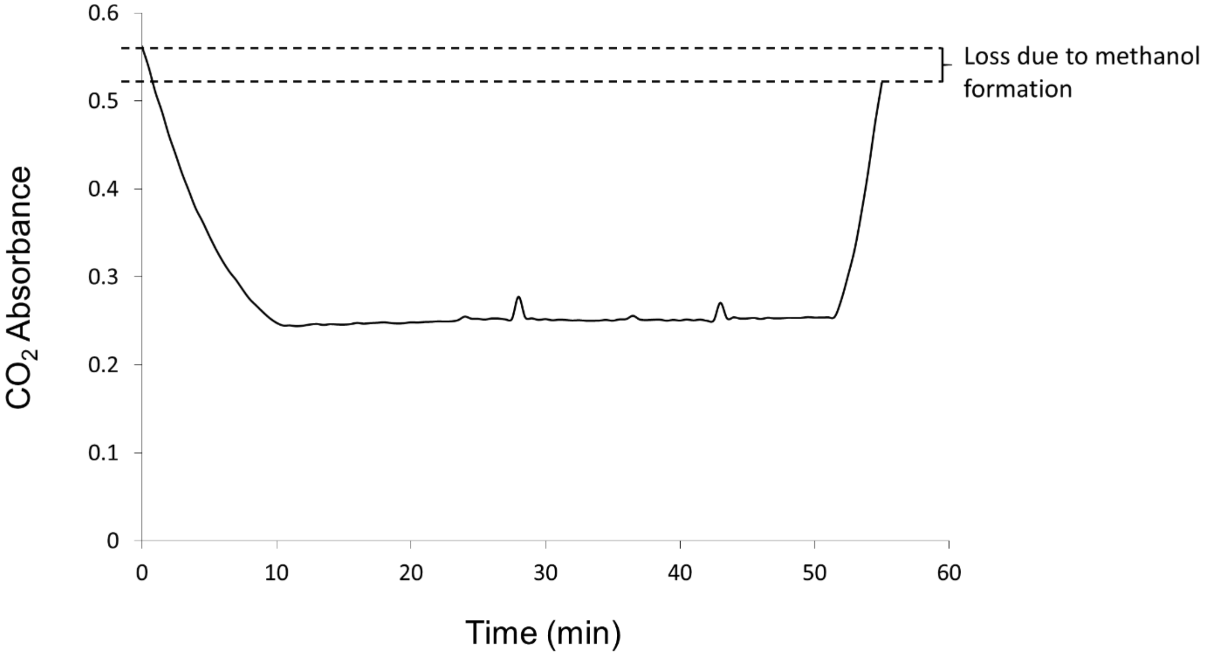

Figure S5. FT-IR spectrum of methoxy terminated porous Si-NPs.

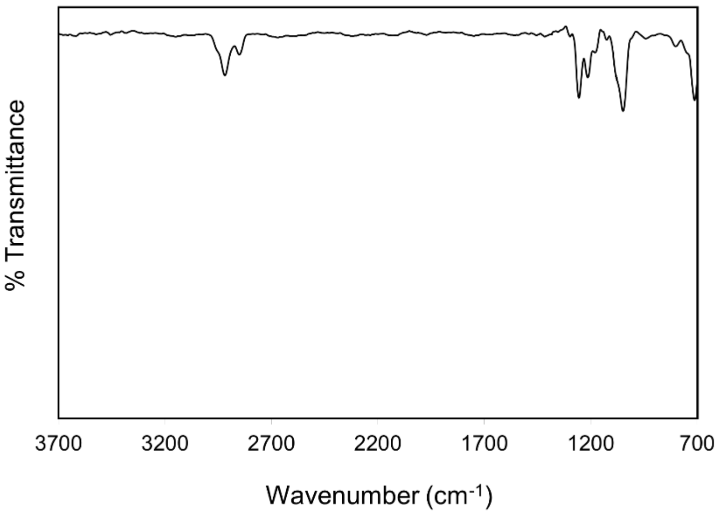

Figure S6. Representative ^{1}H and ^{13}C NMR spectra of the D_2O extractions.

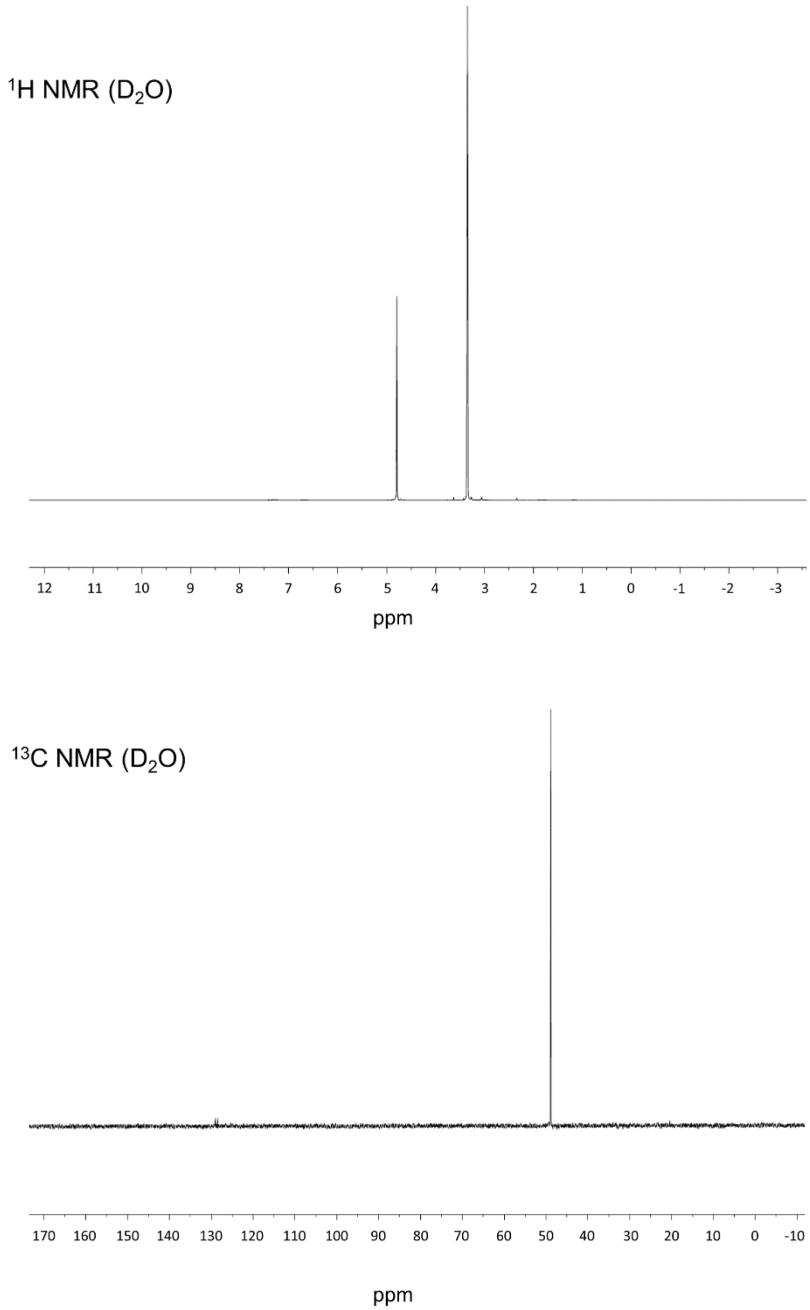

Figure S7. FT-IR of the Si-NPs after D_2O extraction.

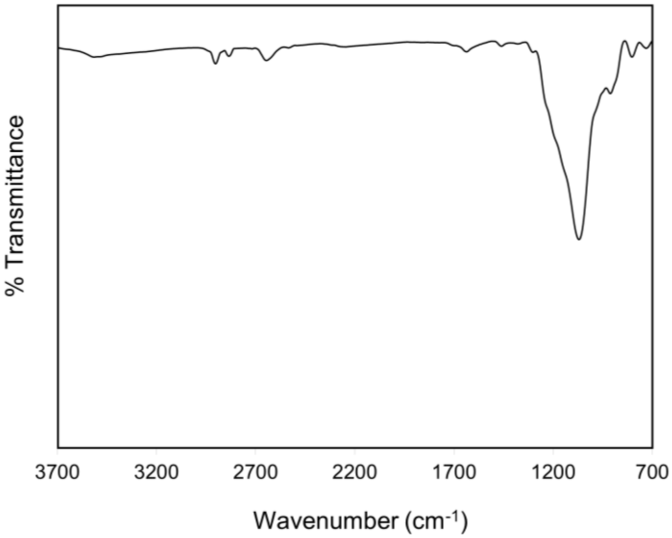

Figure S8. High resolution X-ray photoelectron spectra (Si 2p) of Si-NPs reacted with CO_2 at 150°C and pressures (A) 15 bars, (B) 10 bars, and (C) 5 bars.

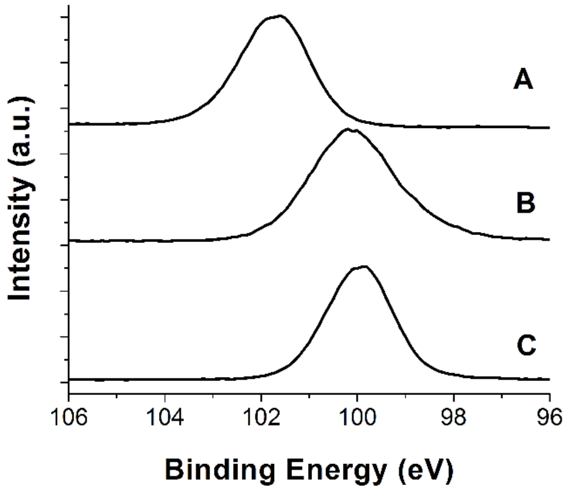

Figure S9. Methanol yields as a function of Si-NP mass.

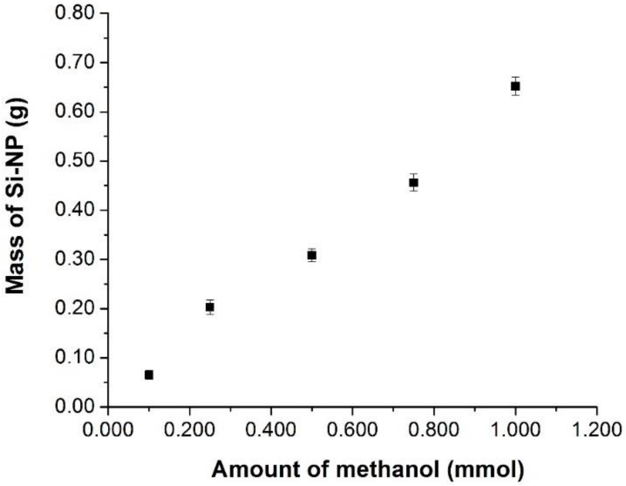

Figure S10. Powder XRD pattern of Si particles obtained *via* magnesiothermic reduction of (A) Stöber silica particles and (B) sand.