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Electronic Supplementary Material

Ammonia-Assisted Synthesis towards a Phyllosilicate-Derived High-Dispersed and Long-Lived Ni/SiO_2 Catalyst

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1. Catalyst characterization

Transmission electron microscopy (TEM) images were taken on an FEI Tecnai-F30 FEG instrument at an acceleration voltage of 300 kV.

X-ray powder diffraction (XRD) analysis was performed on a Panalytical X'pert PRO diffractometer scanning 2θ from 10° to 90°. Cu Kα radiation obtained at 35 kV and 15 mA was used as the X-ray source.

X-ray photoelectron spectroscopy (XPS) analysis was performed on a Quantum 2000 Scanning ESCA Microprobe instrument (Physical Electronics) using Al-K_α radiation as the X-ray source. The spectra were corrected using the C 1s signal located at 284.6 eV.

The reducibility of the catalysts was studied by H_2 temperature-programmed reduction (H_2-TPR), which was conducted in a quartz tube with 50 mg sample, raised the temperature from 100 to 900 °C with a heating rate of 10 °C/min under a 5% H_2/Ar mixture flowing at 30 mL/min. Hydrogen consumption was monitored by a online gas chromatography equipped with a thermal conductivity detector (TCD) after removing the water formed.

The Ni dispersion and surface area was determined by H_2 pulse chemisorption on the ASAP 2920 apparatus. The catalyst (200 mg) was reduced at 750 °C for 1 h under hydrogen flow. After reduction, the catalyst was purged with carrier gas (Ar) at 750 °C for 0.5 h, and then it was cooled down to 50 °C under Ar. H_2 pulses were injected until the eluted peak area of consecutive pulse was constant. The active surface area of Ni was calculated from the volume of H_2 adsorbed by assuming a H/Ni stoichiometry of 1 and a surface area of 6.5×10^{-20} m^2 per Ni atom. The percentage reduction of nickel to the metal was determined after hydrogen chemisorption by evacuating the sample to 450 °C followed by measuring the uptake of pure oxygen at 400 °C. It was assumed that in the reduced catalysts all unreduced nickel was in the form of NiO and that all metallic nickel would be oxidized to NiO in the presence of oxygen at 400 ^oC. Comparison of the needed actual oxygen uptake if all of the nickel were assumed to be initially in the metallic state constituted the basis for calculating the percentage reduction to the metal.

Thermogravimetric (TG) analysis was carried out on a NETZSCH TG 209F1 instrument. The dried catalysts were heated from 30 to 900 ^oC in flowing air stream (20 ml/min) at a heating rate of 10 ^oC/min.

2. Catalyst performance evaluation

The reaction of the partial oxidation of methane to syngas was carried out in a fixed-bed quartz reactor (i.d. = 5mm) at atmospheric pressure. Before reaction, the catalyst was reduced at 700 ^oC in H_2 flow (30 mL•min^{-1}) for 1 h. After the pre-treatment, feed gases consist of CH_4/O_2 with a molar ratio of 2.5/1 were allowed to flow through the catalyst bed at GHSV = 1.0×10^5 mL•g^{-1}•h^{-1}. The reactants (CH_4 and O_2) and products (CO, H_2 and CO_2) were analyzed with an on-line gas chromatography equipped with a thermal conductivity detector (TCD) and a TDX-01 column. An ice-cold trap was set between the reactor exit and the GC sampling valve to remove the water formed during reaction.

3. Results

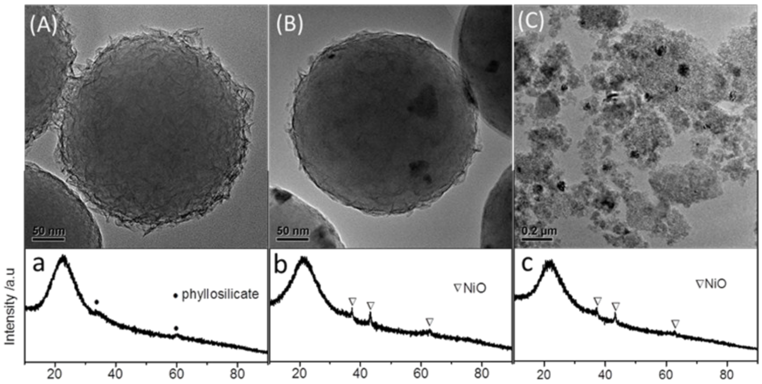

Figure. S1 TEM images and XRD patterns of Ni/SiO_2 samples after calcination with different silica source. A, a: dried Stöber SiO_2; B, b: Stöber SiO_2 after heat treatment at 600 ^oC for 1 h; C, c: commercial silica gel.

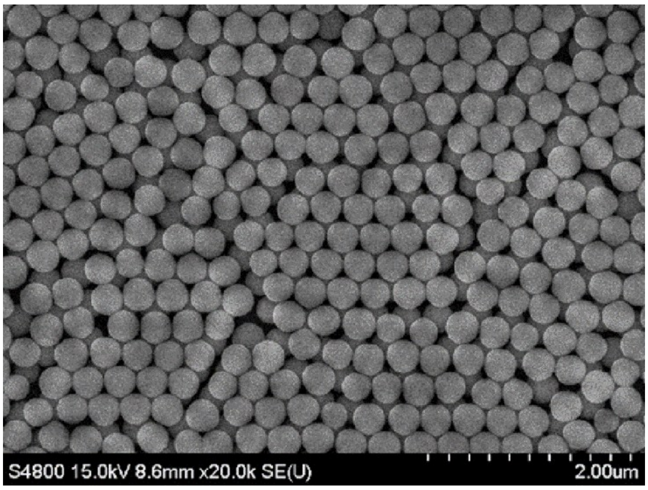

Figure. S2 SEM image of SiO_2 nanoparticles prepared by a modified Stöber method.

Table S1. The values of H_2 uptake, percentage reduction, percentage dispersion, nickel active surface area, and crystallite size for catalysts studied.

catalysts	H_2 uptake ($cm^3g^{-1}_{cat}$)	reduction extent[c] (%)	dispersion (%)	metal surface area ($m^2g^{-1}_{Ni}$)	crystallite size (nm)
Ni/SiO_2[a]	0.86	97	9.8	63.7	9.9
Ni/SiO_2[b]	0.22	99	2.4	16.1	40.1

[a] the catalyst prepared by ammonia-assisted impregnation method

[b] the catalyst prepared by conventional impregnation method without adding ammonia

[c] Reduction extent of nickel determined based on O_2 uptake at 400 °C [Bartholomew, et al., *J. Catal.*, 1976, 45, 41].

In Figure S3, the corresponding intense MS signal peak with m/z = 18 of water appears at temperatures below 100 °C is assigned to the physically absorbed water. The MS signal peaks with m/z =18, 30 and 44 of H_2O, N_2O and CO_2 at around 200 °C are assigned to the remove of crystal water, and the decomposition of the residual ammonium ions, carbonate ions. The MS signal peak of water between 400 and 700 °C is assigned to the reaction products between Ni 1:1 PS and the silica.

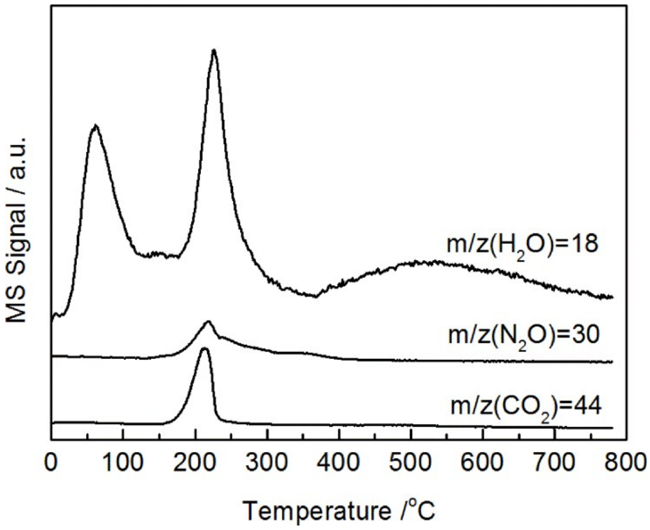

Figure. S3 Profiles of m/z = 18, 30 and 44 measured by mass spectrometer during calcination of 1:1 phyllosilicates sample in air.

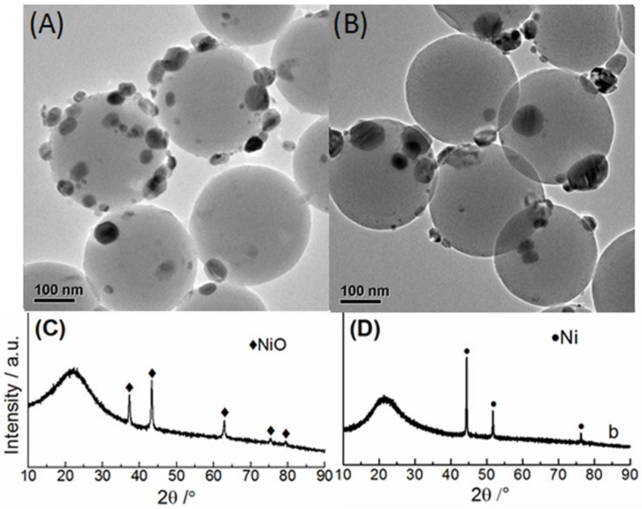

Figure S4. TEM images (A,B) and XRD patterns (C,D) of Ni/SiO_2 catalyst prepared by the conventional impregnation method without adding ammonia. (A,C) catalysts after calcination; (B,D) catalysts after reduction.

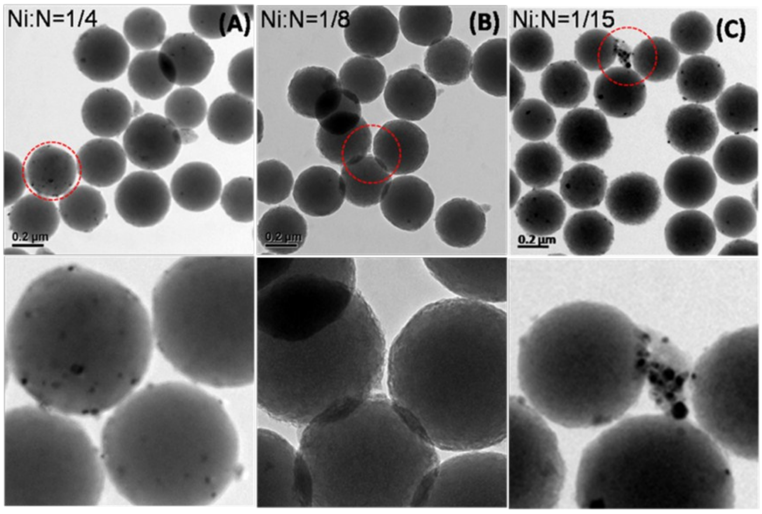

Figure. S5 TEM images of Ni-phyllosilicates/SiO_2 catalysts prepared with different amount of ammonia: (A) Ni/ NH_4OH=1/4; (B) Ni/ NH_4OH=1/8; (C) Ni/ NH_4OH=1/15.

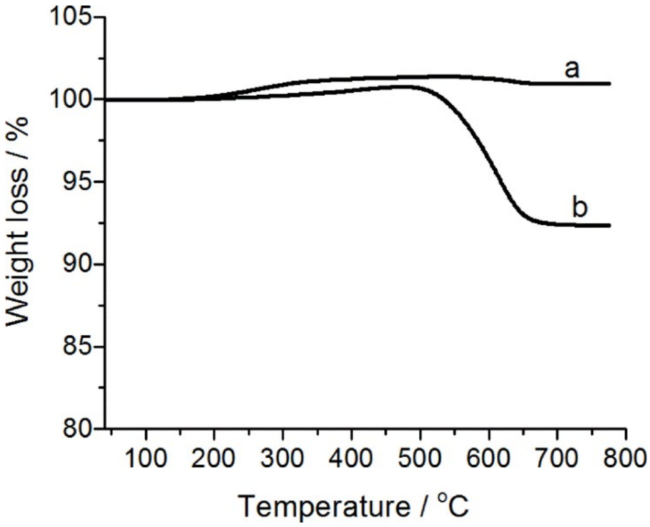

Figure. S6 TG profiles of the 5.0% wt% Ni/SiO_2 catalysts prepared by different methods after 50 h POM reaction at 700 ^oC. (a) Prepared by the ammonia-assisted impregnation method; (b) prepared by conventional impregnation method without adding ammonia.