Supplementary Information

Tunable colloidal Ni nanoparticles confined and redistributed in mesoporous silica for CO₂ methanation

Wilbert L. Vrijburg,^a Jolanda W.A. van Helden,^a Arno J.F. van Hoof,^a Heiner Friedrich,^a Esther Groeneveld,^b Evgeny A. Pidko,^{*,a,#} Emiel J.M. Hensen^{*,a}

^a Laboratory of Inorganic Materials and Catalysis, Schuit Institute of Catalysis, Eindhoven University of

Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

^b BASF Nederland B.V., De Meern, The Netherlands

[#] Present address: Inorganic Systems Engineering group, Department of Chemical Engineering, Delft University of Technology, Van der Maasweg 9, 2629 HZ, Delft, The Netherlands

* Corresponding authors. Email: e.j.m.hensen@tue.nl (E.J.M.H.), e.a.pidko@tudelft.nl (E.A.P.)

Supplementary Information

1.1.1 Synthesis of colloidal NiNPs with Ni(acac)₂ using an external reducing agent

To obtain the smallest particles (seeds), 257 mg Ni(acac)₂ (1 mmol), 15 mL oleylamine (OAm) and 0.32 mL oleic acid (OAc, 1 mmol) were added to a 250 mL two-neck round-bottomed flask equipped with a magnetic stirring bar. The mixture was brought under inert conditions by flushing with Ar and degassed at 110 °C for 30 min to removed oxygen and water. A green-blue solution was obtained. In a second flask, 0.44 g borane tert-butyl amine complex (BTB, 5 mmol) was dissolved in 2 mL OAm and degassed. The Ni(acac)₂ solution was cooled to 90 °C and the BTB solution was subsequently injected into the Ni(acac)₂ solution. The mixture went black within 30 s, signalling the reduction of the Ni²⁺ to metallic Ni. The synthesis continued for 1 h, after which the reaction was quenched by adding 17 mL toluene and cooled to room temperature. Nanoparticles were collected by adding acetone followed by centrifugation (5000 rpm, 10 min). Particles were washed 3 times with a toluene/acetone mixture.

1.1.2 Synthesis of colloidal NiNPs via seed-mediated growth

In a typical seed-mediated growth synthesis procedure, seeds were first synthesized at 90 °C using the procedure outlined in section above with a BTB/Ni ratio of 5. The seed-mediated growth approach was

defined by the injection temperature and growth temperature (mild vs. hot). The "hot" injection and growth approach is discussed in the main article.

1.1.2.1 Mild injection growth

Next to the seed formation, 514 or 1028 mg of Ni(acac)₂ (2 or 4 mmol) was added to another round-bottom flask with magnetic stirring bar. Next, respectively 10 or 20 mL of octadecene (ODE) and 0.64 or 1.3 mL of OAc (2 or 4 mmol) were added to ensure that the concentration of the Ni(acac)₂ solution remained constant. The Ni(acac)₂ solution was heated to 110 °C with an oil bath and degassed over 30 min, resulting a green solution.

After 1 h of seed formation at 90 °C, the addition of the Ni(acac)₂ solution was started. The temperature of the reaction was 90 °C. The additional Ni(acac)₂ solution was added dropwise to seeds via a canula with slight over-pressure. The addition took typically 20 to 40 min. The reaction was terminated after 18 h of reaction (overnight) by removing the heat source and quenching with toluene (1:1 mixture of reaction mixture and toluene). The NiNPs were collected with addition of acetone followed by centrifugation (5000 rpm, 10 min). The particles were washed three times with a mixture of 5 mL toluene and 45 mL acetone and collected with centrifugation. The particles were dried under vacuum overnight.

1.1.2.2 Hot injection growth

Next to the seed formation, 514 or 1028 mg of Ni(acac)₂ (2 or 4 mmol) was added to another round-bottom flask with magnetic stirring bar. Next, respectively 10 or 20 mL of octadecene (ODE) and 0.64 or 1.3 mL of OAc (2 or 4 mmol) were added to ensure that the concentration of the Ni(acac)₂ solution remained constant. The Ni(acac)₂ solution was heated to 110 °C with an oil bath and degassed over 30 min, resulting a green solution.

After 1 h of seed formation at 90 °C, the heat source was changed to a heating mantle with a thermocouple. The reaction mixture was than heated quickly to 220 °C. Than the addition of the Ni(acac)₂ solution was started. The added Ni(acac)₂ solution was added dropwise to seeds via a canula with slight over-pressure. The addition took typically 20 to 40 min. The reaction was terminated after 1.5 h of reaction (the time needed for addition was included in the 1.5 h) by removing the heat source and quenching with toluene (1:1 mixture of reaction mixture and toluene). The NiNPs were collected with addition of acetone followed by centrifugation (5000 rpm, 10 min). The particles were washed three times with a mixture of 5 mL toluene and 45 mL acetone and collected with centrifugation. The particles were dried under vacuum overnight.

TEM colloidal NiNPs



Figure S1: TEM images of colloidal NiNPs prepared using seed-mediated growth methods. Initial particles were produced with BTB/Ni = 5 at 90 °C. Either (a) 2 equivalents of Ni²⁺ (yield = 125mg) or (b) 4 equivalents Ni²⁺ (yield = 370 mg) were added to the initial particles.

Figure S1 shows the TEM images of NiNPs produced by seed formation at 90 °C, and growth at 90 °C by addition of 2 (Figure S1a) and 4 (Figure S1b) equivalents Ni²⁺. These data show that the growth of these particles at 90 °C is not significant. The yields obtained from the addition of 4 equivalents were almost double that from the addition of 2 equivalents. This indicates that the reducing agent is limiting the possibility to grow the nanoparticles. The addition of extra Ni(acac)₂ leads to new seeds forming locally. These seeds grow to reach a final particle size identical to the initial colloidal suspension.

1.1.3 XPS colloidal NiNPs

Procedure	Sample	% Ni(0)	% Ni(2+)
	description		
1	Ni(53)	46.8	53.2
2	Ni(4.4)	22.2	77.8
3	Ni(6.3)	11.8	88.2
4	Ni(7.9)	39.2	60.8

Table S1: XPS derived Ni⁰ and Ni²⁺ relative percentages for colloidal NiNPs after exposure to air.

XPS measurements were used to determine the ratio of Ni²⁺ and Ni⁰ on the NiNP surface after synthesis and exposure to air (Table S1). Figure S2 shows XP spectra of the carbon 1s region. Fresh NiNPs prepared via direct thermal decomposition (procedure 1 in article) were etched with Ar⁺ ions to verify the presence of Ni carbide within the crystal structure. Etching revealed the presence of a Ni-carbide peak at 283.5 eV, confirming that the XRD patterns were from hcp-Ni₃C and not hcp-Ni. In contrast, NiNPs synthesized via procedures **2-4** did not exhibit a Ni-C contribution after etching (Figure S3).



Figure S2: XP spectra in carbon 1s region of NiNP prepared via thermal decomposition (procedure 1) showing Ni-C contribution (green, 283.5 eV) increase after Ar^+ sputtering between 60-180 s.



Figure S3: XP spectra of carbon 1s region after 180 s Ar⁺ sputtering of (a) Ni(4.4) (procedure **2**), (b) Ni(6.3) (procedure **3**), and (c) Ni(7.9) (procedure **4**). All fitted spectra did not show a contribution from Ni-C.

1.1.4 Direct deposition on SiO₂



Figure S4: (a) Ar-normalized CH_4 signal (16/40) highlighting the decomposition of the organic ligands during temperature-programmed reduction up to 550 °C. (b) Temperature-programmed benzene hydrogenation comparing the catalytic activity of calcined and uncalcined NiNPs prepared via direct deposition.

Directly deposited NiNPs were reduced in 10 vol% H_2 in He to remove organic ligands and fully reduce the supported NiNPs. To ensure that the ligand decomposed under these conditions, the reduction of NiNPs supported on SiO₂ was followed by mass spectrometer (MS). Methane (CH₄) evolution was observed between 400-550 °C, indicating the decomposition of the organic ligands (Figure S4a). To verify whether calcination improved the activity of catalysts prepared via direct deposition, a sample of supported NiNPs was first calcined at 350 °C (20 vol% O₂ in N₂), to remove the organic ligand, followed by reduction at 450 °C (10 vol% H₂ in He). Figure S4b shows that a single reduction step led to higher catalytic activity for supported NiNPs prepared via direct deposition.

1.1.5 Encapsulated NiNPs in mesoporous SiO₂

Thermogravimetric analysis (TGA) was employed to determine the decomposition temperature of the capping/templating agents after drying. Representative TGA profiles are given in Figure S4. BET surface areas and pore volumes were determined with N₂ physisorption (Figure S5).



Figure S5: TGA profiles and derivative plots for representative encapsulated Ni(x)@SiO₂ catalysts.



Figure S6: N_2 physisorption results showing adsorption and desorption isotherms and (inset) pore size distribution calculated from the adsorption branch of the isotherm.



Figure S7: HAADF-STEM image of calcined Ni(7.2)@SiO₂ showing NiO platelets.

Calcined Ni@SiO₂ catalyst was studied with HAADF-STEM to see how the oxidic phase disperses. Nickel phyllosilicate like platelets were observed after Ni(7.2)@SiO₂ was calcined at 500 °C as shown in Figure S6.



Figure S8: HAADF-STEM images of (a) Ni(4.4)@SiO₂, (b) Ni(5.0)@SiO₂, (c) Ni(6.8)@SiO₂, and (d) Ni(7.2)@SiO₂ after CO₂ methanation.

All spent catalysts were studied with HAADF-STEM (Figure S7) after being exposed to CO_2 methanation conditions between 200-400 °C, followed by a 70 h stability test at 350 °C. Figure S7a highlights how encapsulated particles (circled) retained their original particle size, whereas NiNPs that were not well encapsulated could still sinter. The HAADF-STEM results confirmed that encapsulated NiNPs in all catalysts retained their original particle size.