

## Electronic Supporting Information

### Highly dispersed nickel catalysts via facile pyrolysis generated protective carbon layer

Sonali Das,<sup>a</sup> Ashok Jangam,<sup>a</sup> Yonghua Du,<sup>b</sup> Kus Hidajat<sup>a</sup> and Sibudjing Kawi\*<sup>a</sup>

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<sup>a</sup> Department of Chemical and Biomolecular Engineering, National University of Singapore, Singapore 119260, Republic of Singapore. Email: [chekawis@nus.edu.sg](mailto:chekawis@nus.edu.sg)

<sup>b</sup> Institute of Chemical and Engineering Sciences, A\*STAR, 1 Pesek Road, Jurong Island, 627833, Singapore

## 1. Experimental Section

### 1.1. Catalyst Synthesis

All chemicals were purchased from Sigma Aldrich and used without further pre-treatment. Ni/SiO<sub>2</sub> catalysts with a nominal Ni loading of 10 % were synthesized by impregnation method using Nickel (II) acetylacetonate as a metal precursor and Stöber silica (specific surface area of 17.5 m<sup>2</sup>/g as measured by BET analysis) as support and subjected to different treatments to synthesize the Ni/SiO<sub>2</sub> (calcination) and Ni/SiO<sub>2</sub> (pyrolysis) catalysts.

Synthesis of support Stöber silica:

The SiO<sub>2</sub> support was synthesized by modified Stöber method. A solution of 8 ml TEOS in 280 ml ethanol was added to 8.4 ml NH<sub>4</sub>OH solution (25%) in 50 ml DI water and stirred for 24 hours. The solution was subsequently centrifuged, washed with water and ethanol and dried at 60°C to get Stöber silica support.

Synthesis of Ni/SiO<sub>2</sub> (calcination):

1 g of dried Stöber SiO<sub>2</sub> support was added to 2.5 ml solution containing 0.435 g Nickel (II) acetylacetonate and stirred at 50°C until drying. The impregnated catalyst was dried overnight at 100°C and subsequently calcined at 600°C for 2 hours to remove the organic components, and the synthesized catalyst was called Ni/SiO<sub>2</sub> (calcination). The catalyst was reduced under H<sub>2</sub> flow (20 ml/min) for one hour at 600°C *in situ* before reaction and is referred to as Ni/SiO<sub>2</sub> (calcination) – reduced catalyst.

Synthesis of Ni/SiO<sub>2</sub> (pyrolysis):

1 g of dried Stöber SiO<sub>2</sub> support was added to 2.5 ml solution containing 0.435 g Nickel (II) acetylacetonate and stirred at 50°C until drying. The impregnated catalyst was dried overnight at 100°C and subsequently was heated to 450°C for 30 minutes under inert atmosphere to pyrolyze the acetylacetonate component, and the synthesized catalyst was called Ni/SiO<sub>2</sub> (pyrolysis). The catalyst was reduced under H<sub>2</sub> flow (20 ml/min) *in situ* for one hour at 600°C before reaction and is referred to as Ni/SiO<sub>2</sub> (pyrolysis) – reduced catalyst.

For comparison, Ni/SiO<sub>2</sub>-nitrate catalyst was also synthesized by following the same procedure and using Nickel nitrate hexahydrate as precursor. During impregnation, 2.5 ml solution containing 0.492 g Nickel nitrate hexahydrate was added to 1 g Stöber SiO<sub>2</sub> support. All the other steps remain same as that for the Nickel (II) acetylacetonate precursor.

## 1.2. Catalyst Characterization

TEM measurement was done to investigate catalyst morphology by a JEOL JEM-2100 transmission electron microscope (TEM). The STEM characterization was conducted on a JEM-ARM200F (JEOL) equipped with a cold field emission gun, an ASCOR aberration corrector, operated at 200 kV.

The X-ray diffraction (XRD) pattern of each sample was measured on a Shimadzu XRD-6000 diffractometer using Cu K $\alpha$  radiation. All the catalysts were scanned at  $2\theta$  range between  $20^\circ$  to  $80^\circ$  (rate of  $2^\circ/\text{min}$ ).

The metal dispersion measurement on catalyst was done on a Thermo Scientific TPDRO 1100 series by a Hydrogen chemisorption method. 100 mg sample was first reduced by treating with a 5% hydrogen in nitrogen flow (30 ml/min) with a temperature ramp up to  $600^\circ\text{C}$  and held for 1 h. The reduced sample was then cooled under nitrogen flow to  $40^\circ\text{C}$  and treated with 10 pulses of hydrogen of known volume. The moles of hydrogen chemisorbed was used to calculate the moles of surface nickel on the catalyst assuming that one hydrogen atom is adsorbed on one surface nickel atom. The average size of nickel crystallites was calculated from the equation  $d = (6 \times 10^3) / (g_{\text{Ni}} \times S_{\text{Ni}})$ , where  $g_{\text{Ni}}$  is the density of nickel and  $S_{\text{Ni}}$  is the surface area of nickel ( $\text{m}^2/g_{\text{Ni}}$ ), assuming that nickel crystallites are spherical, and the surface area occupied by one atom of hydrogen equals to  $0.065 \text{ nm}^2$ .

IR spectrum for impregnated Ni/SiO<sub>2</sub> sample after drying and thermal annealing under inert conditions [Ni/SiO<sub>2</sub> (pyrolysis)] was recorded in a Bruker FTIR Vertex 70 Spectrometer equipped with a diamond ATR.

The structural characterization of carbon on the synthesized catalyst was analyzed using Xplora Plus Microscope Raman (HORIBA, Japan) using a laser beam excitation of  $\lambda = 632.81 \text{ nm}$ . The quantity of carbon residue on the synthesized and spent catalyst after CO methanation reaction was measured by thermo-gravimetric analysis (TGA) coupled with DTA (differential thermal analysis) on a Shimadzu DTG-60 thermogravimetric analyser. A fixed weight of spent catalyst was used heated in static air to  $850^\circ\text{C}$  with a ramping rate of  $10^\circ\text{C}/\text{min}$  and its weight was monitored with temperature.

*In-situ* Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) experiment was conducted in a Bruker FTIR Vertex 70 spectrometer using Harrick Praying Mantis DRIFTS gas cell equipped with ZnSe windows and a controlled gas system. The Ni/SiO<sub>2</sub>

(pyrolysis) catalyst was synthesized *in situ* in the DRIFTS cell by heating the supported catalyst precursor at 450°C under 30 ml/min He flow, to prevent Ni oxidation by exposure to air. The Ni/SiO<sub>2</sub> (calcination) catalyst was reduced *in situ* at 600°C under 30 ml/min H<sub>2</sub> flow. Prior to CO adsorption, the remaining gas in the cell was flushed with 20 ml/min Helium flow for 1 hour at 50°C, following which a background scan was taken. A mixture of CO and He was then introduced into the cell (CO/He = 2/20 ml/min) and the IR spectra were collected at 250°C after 10 minutes to allow CO saturation<sup>1</sup>. The spectra were taken 32 times each with a resolution of 4 cm<sup>-1</sup>.

The XAS experiments were carried out at XAFCA beamline of Singapore Synchrotron Light Source. The samples were measured under transmission mode and Ni standard foil was applied for the energy calibration.

### 1.3. Catalyst Evaluation

Thermal stability of the Ni/SiO<sub>2</sub> (pyrolysis) catalyst was tested by subjecting the catalyst to air flow (10 ml/min) and H<sub>2</sub> flow (10 ml/min) at 600°C for 6 hours each, following which the samples were examined by TEM and XRD analysis. After thermal treatment with air, the sample was reduced again in H<sub>2</sub> at 600°C for 1 hour to convert NiO to Ni<sup>0</sup> before TEM and XRD analysis.

Catalyst performance in CO methanation was evaluated in the temperature range of 250°C – 500°C, 1 atm pressure, H<sub>2</sub>/ CO ratio of 3 and a GHSV of 120 L h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>. The catalyst was loaded in a 4mm ID quartz reactor. The Ni/SiO<sub>2</sub> (calcination) catalyst was reduced *in situ* in a stream of H<sub>2</sub> at 20 ml/min at 600°C for 1 hr prior to reaction. The Ni/SiO<sub>2</sub> (pyrolysis) catalyst was tested both (1) without reduction and (2) with an *in situ* reduction step in 20 ml/min H<sub>2</sub> at 600°C for 1 hr (referred to as the Ni/SiO<sub>2</sub> (pyrolysis)-reduced catalyst). The flow rates of the reactant gases were controlled by mass flow controllers and the composition of outlet gas was analysed online by a gas chromatograph (Agilent 7820A) equipped with a thermal conductivity detector (TCD). The CO conversion and CH<sub>4</sub> yield was calculated as follows, where F<sub>i, in</sub> and F<sub>i, out</sub> are the volumetric flowrates of CO and CH<sub>4</sub> at the inlet and outlet.

$$CO \text{ conversion, \%} = \frac{F_{CO,in} - F_{CO,out}}{F_{CO,in}} * 100$$

$$CH_4 \text{ yield, \%} = \frac{F_{CH_4,out}}{F_{CO,in}} * 100$$

## 2. Results

### 2.1. Fresh Catalyst Characterization

Table S1. Ni dispersion measurement by H<sub>2</sub> chemisorption.

<b>Catalyst</b>	<b>H<sub>2</sub> chemisorbed (mol H<sub>2</sub>/ g<sub>Ni</sub>)</b>	<b>Nickel Dispersion (wt%)</b>	<b>Estimated Ni particle size (nm) by H<sub>2</sub> chemisorption</b>
Ni/SiO <sub>2</sub> (calcination) – reduced	3.0 x 10 <sup>-4</sup>	3.6	26.8
Ni/SiO <sub>2</sub> (pyrolysis) – reduced	8.9 x 10 <sup>-4</sup>	10.4	9.3

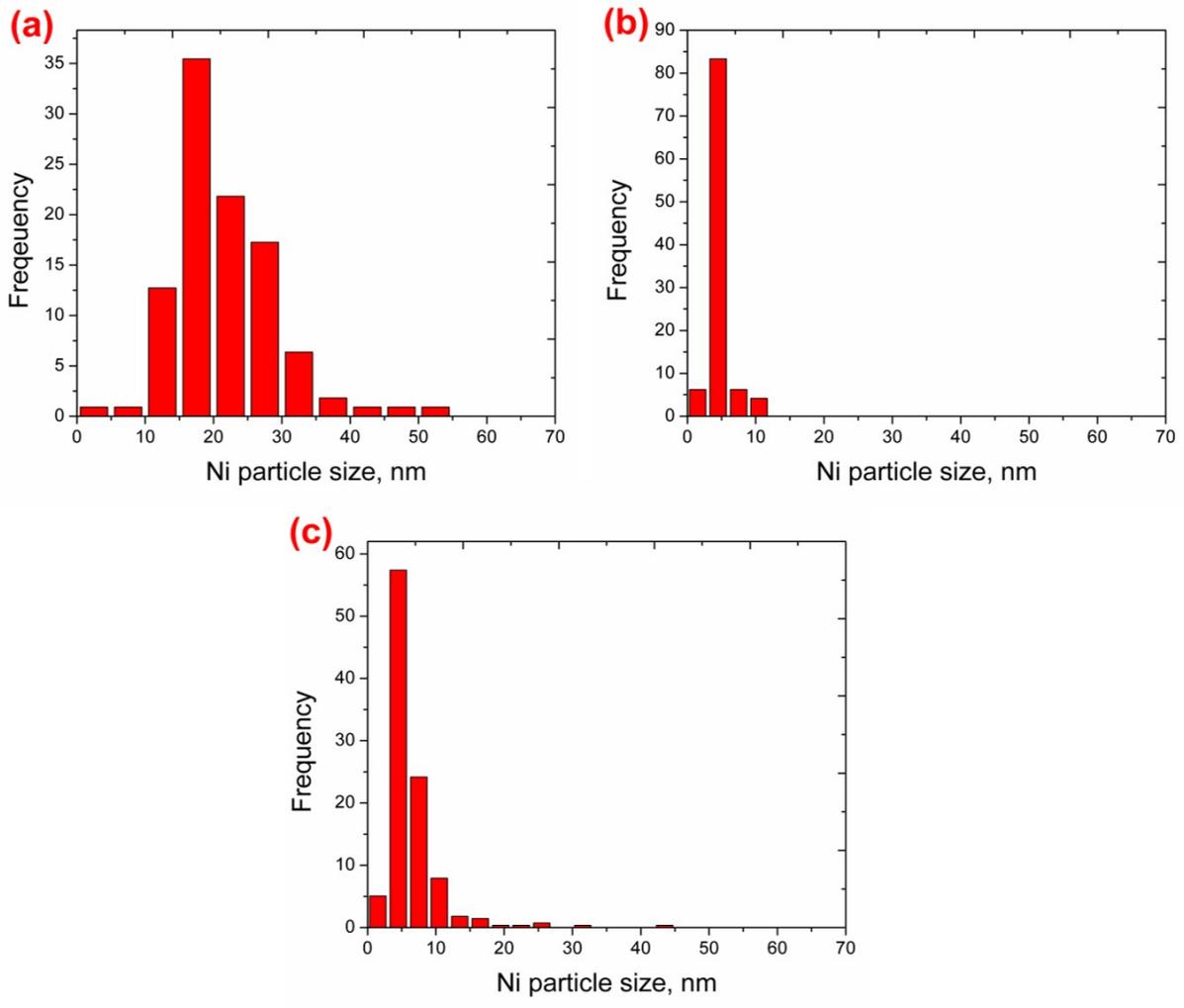


Figure S1. Ni particle size distribution in (a) Ni/SiO<sub>2</sub> (calcination) - reduced, (b) Ni/SiO<sub>2</sub> (pyrolysis), (c) Ni/SiO<sub>2</sub> (pyrolysis) – reduced

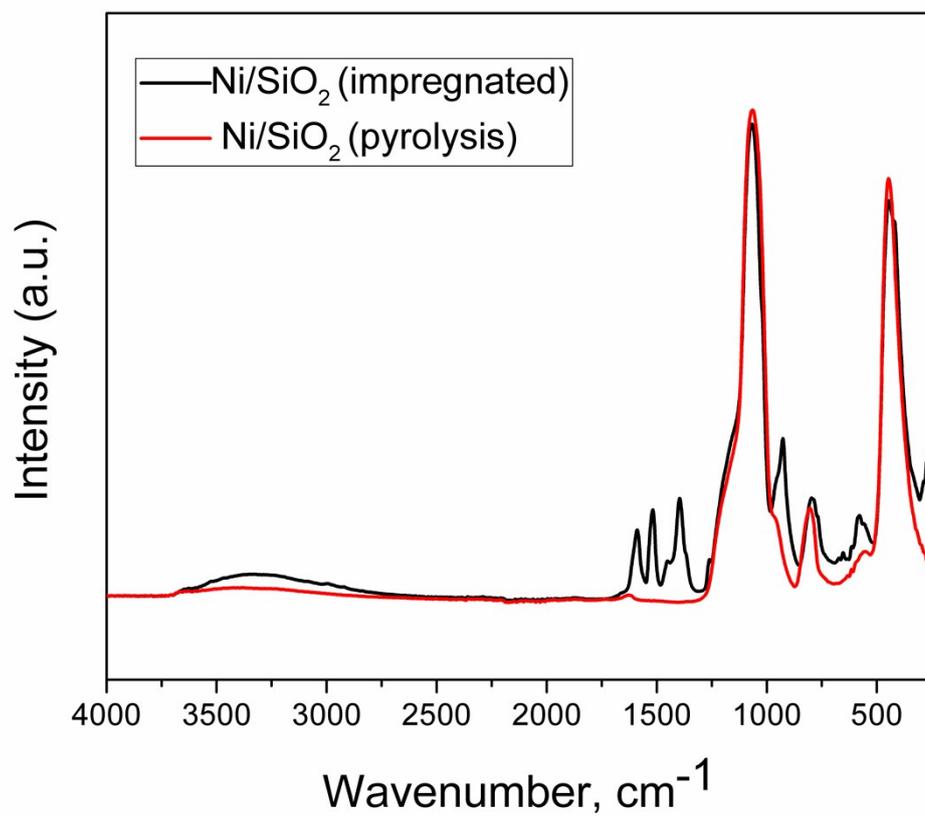
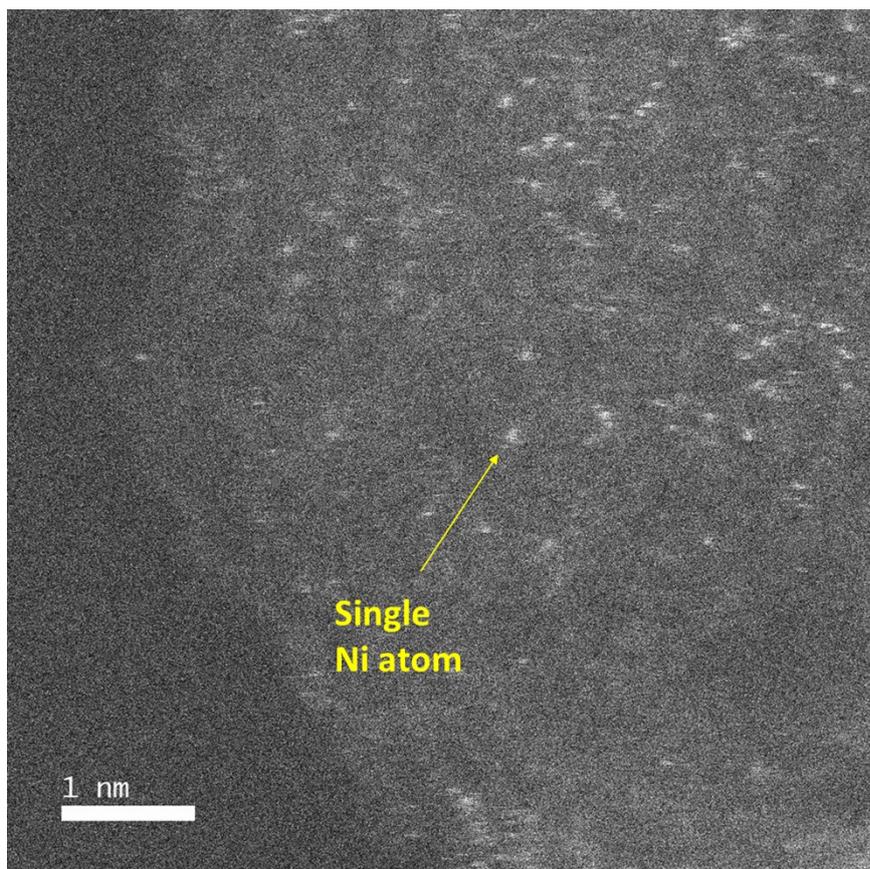


Figure S2. FTIR spectra of impregnated and dried Ni/SiO<sub>2</sub> before and after pyrolysis in inert atmosphere.



*Figure S3. HAADF-STEM image of Ni/SiO<sub>2</sub> (pyrolysis) showing single Ni atoms in the carbon matrix.*

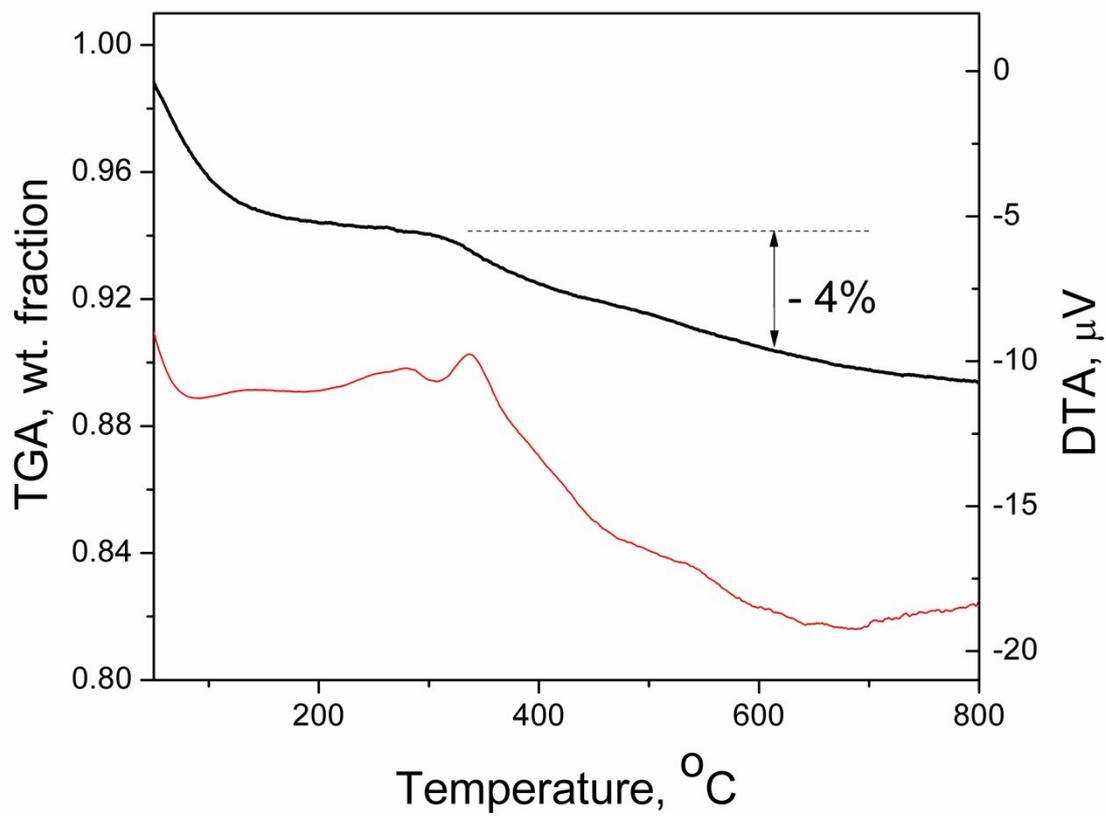
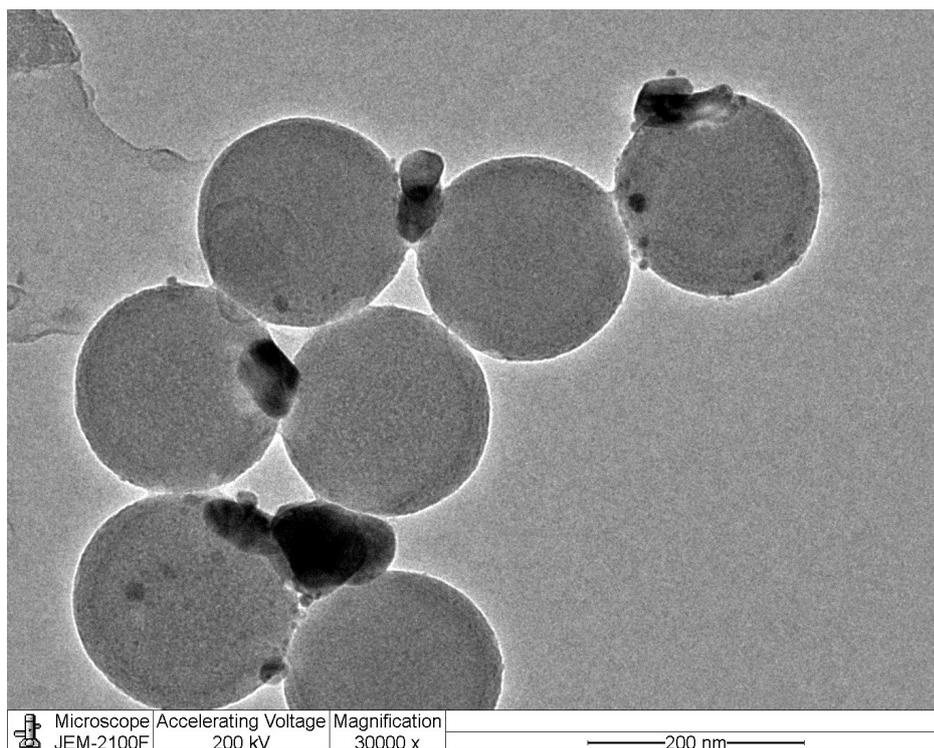


Figure S4. TGA/DTA profile of Ni/SiO<sub>2</sub> (pyrolysis) under air showing a weight loss in between 250°C – 400°C for the oxidation of residual carbon.



*Figure S5. TEM image of Ni/SiO<sub>2</sub> (pyrolysis) with nickel nitrate hexahydrate precursor. Catalyst was subjected to inert thermal treatment at 450°C for 30 mins after impregnation and drying.*

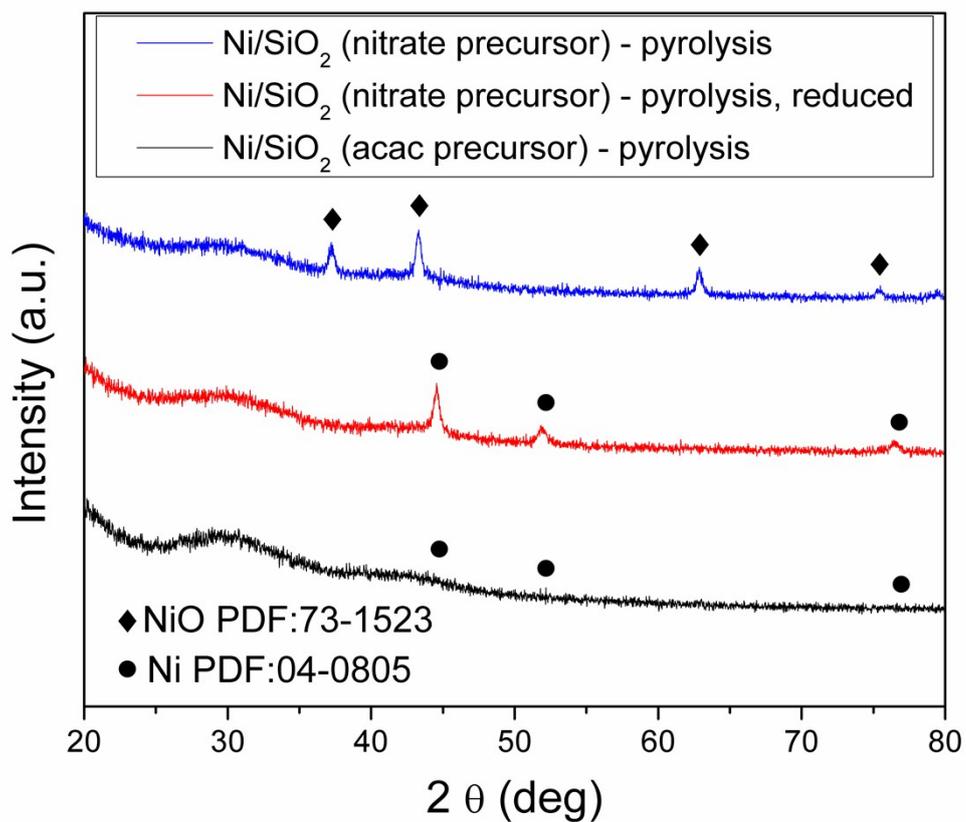


Figure S6. XRD profile for Ni/SiO<sub>2</sub> synthesized with nitrate precursor after pyrolysis and subsequent reduction, and prepared using acac precursor after pyrolysis. Pyrolysis conditions were set at 450°C for 30 mins under inert (He) atmosphere and reduction was carried out at 600°C for 1 hour under 20 ml/min H<sub>2</sub> flow.

## 2.2. Catalyst characterization post thermal stability test

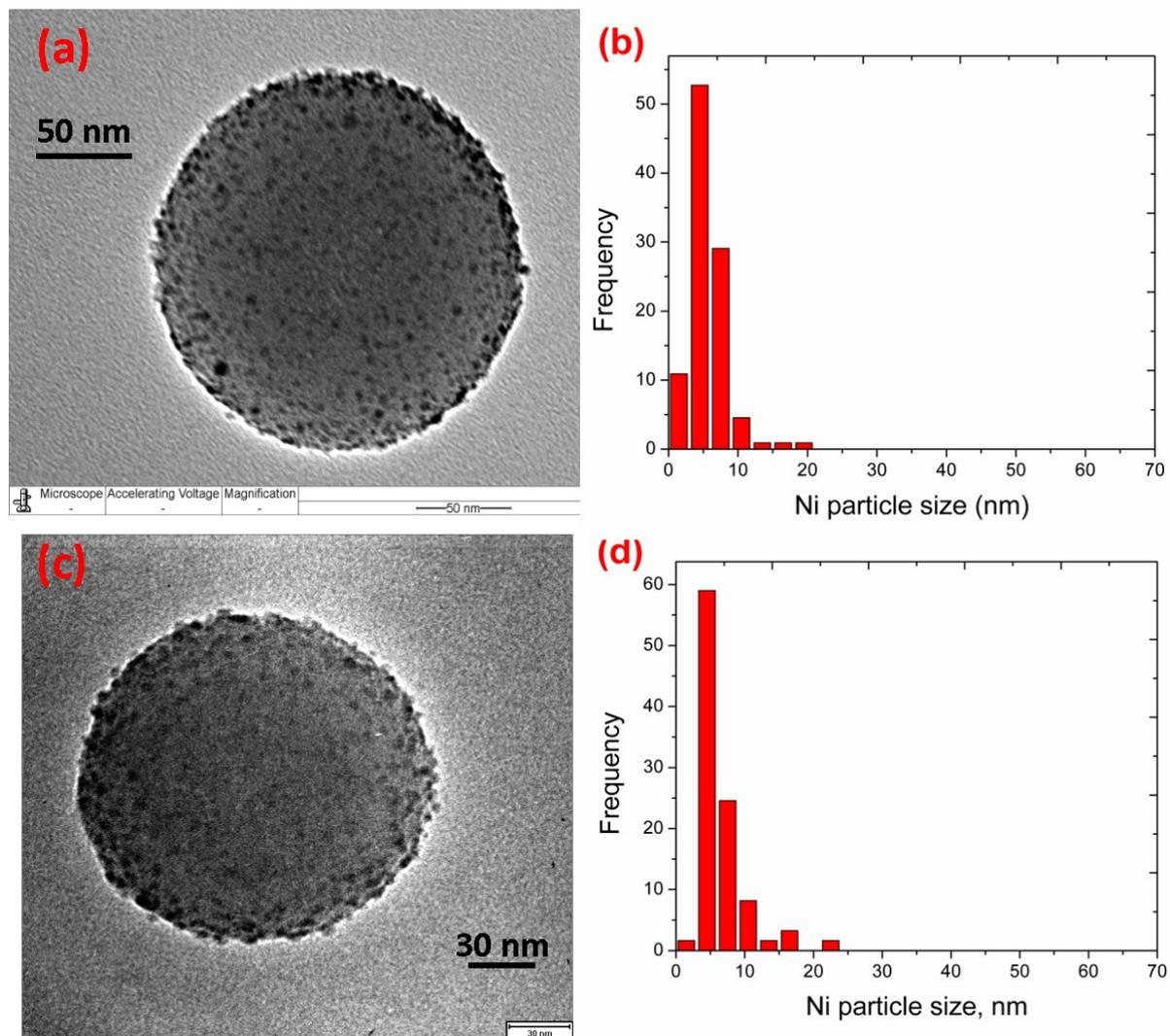


Figure S7. TEM image and particle size distribution of Ni-SiO<sub>2</sub> (pyrolysis) after exposure to (a, b) H<sub>2</sub> flow at 600°C for 6 hrs, (c, d) air flow at 600°C for 6 hrs and subsequent reduction at 600°C.

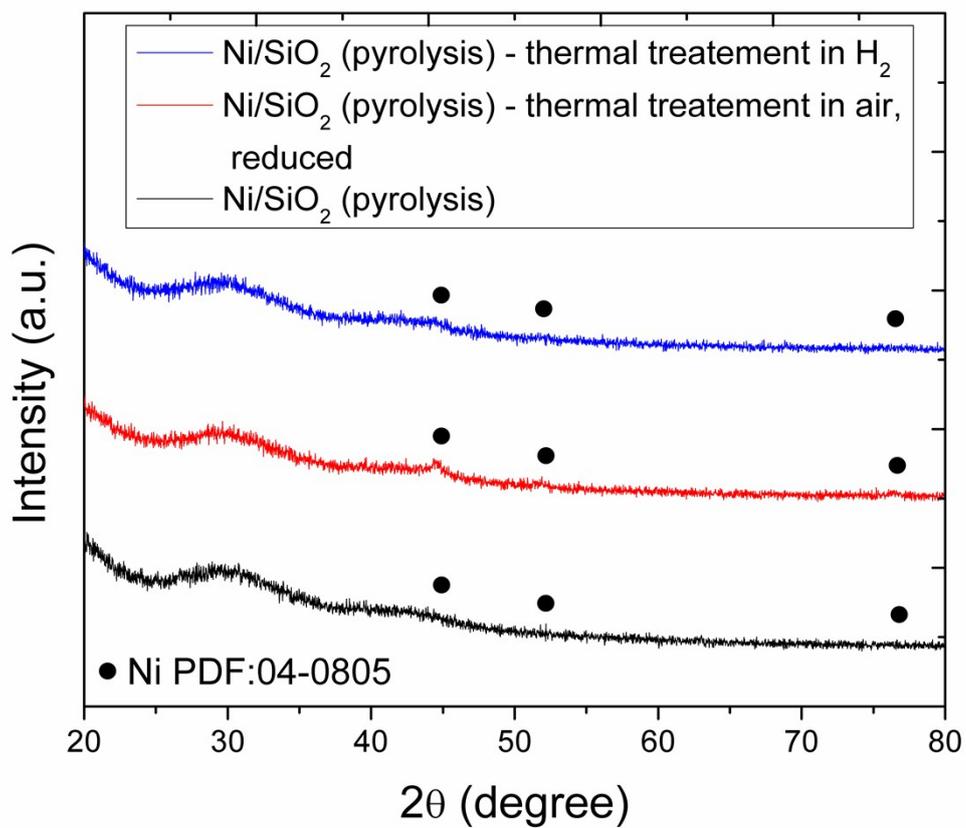


Figure S8. XRD profile of Ni-SiO<sub>2</sub> (pyrolysis) after exposure to H<sub>2</sub> flow at 600°C for 6 hrs, and air flow at 600°C for 6 hrs and subsequent reduction at 600°C

### 2.3. Catalyst Evaluation in CO methanation

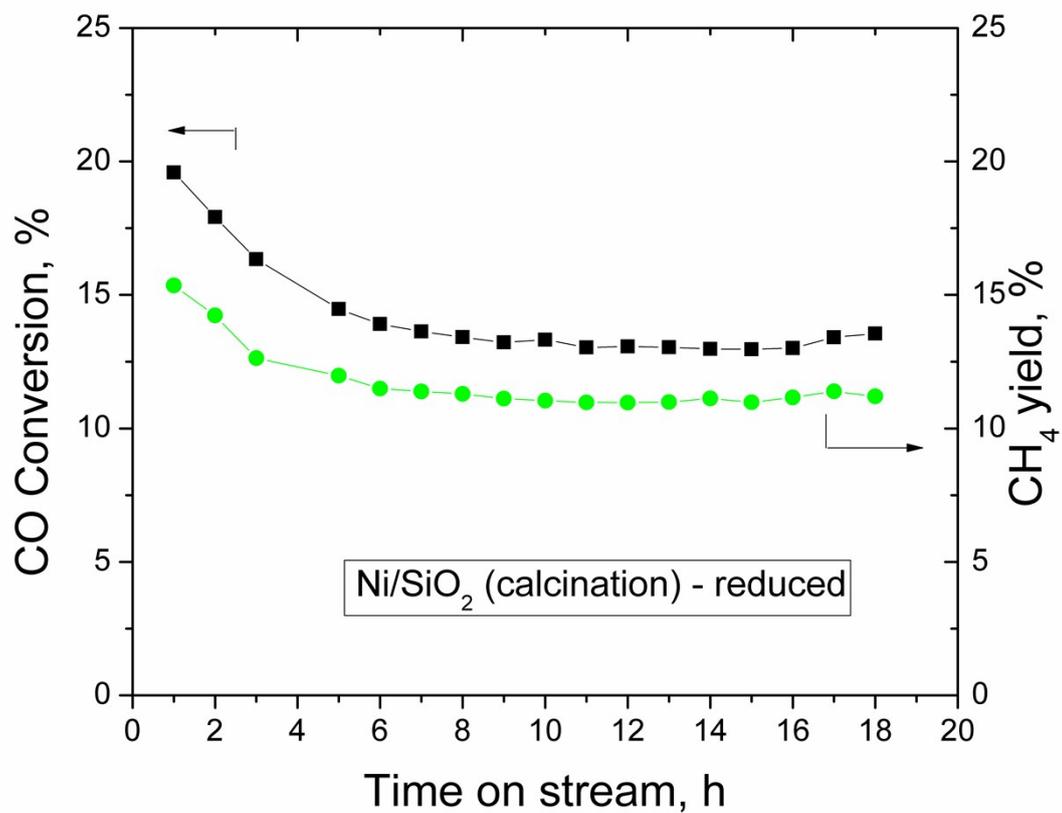


Figure S9. CO conversion and CH<sub>4</sub> yield over Ni/SiO<sub>2</sub> (calcination) at 400°C, GHSV = 120 L h<sup>-1</sup> gcat<sup>-1</sup>, 1 atm with time.

## 2.4. Spent Catalyst Characterization after CO methanation

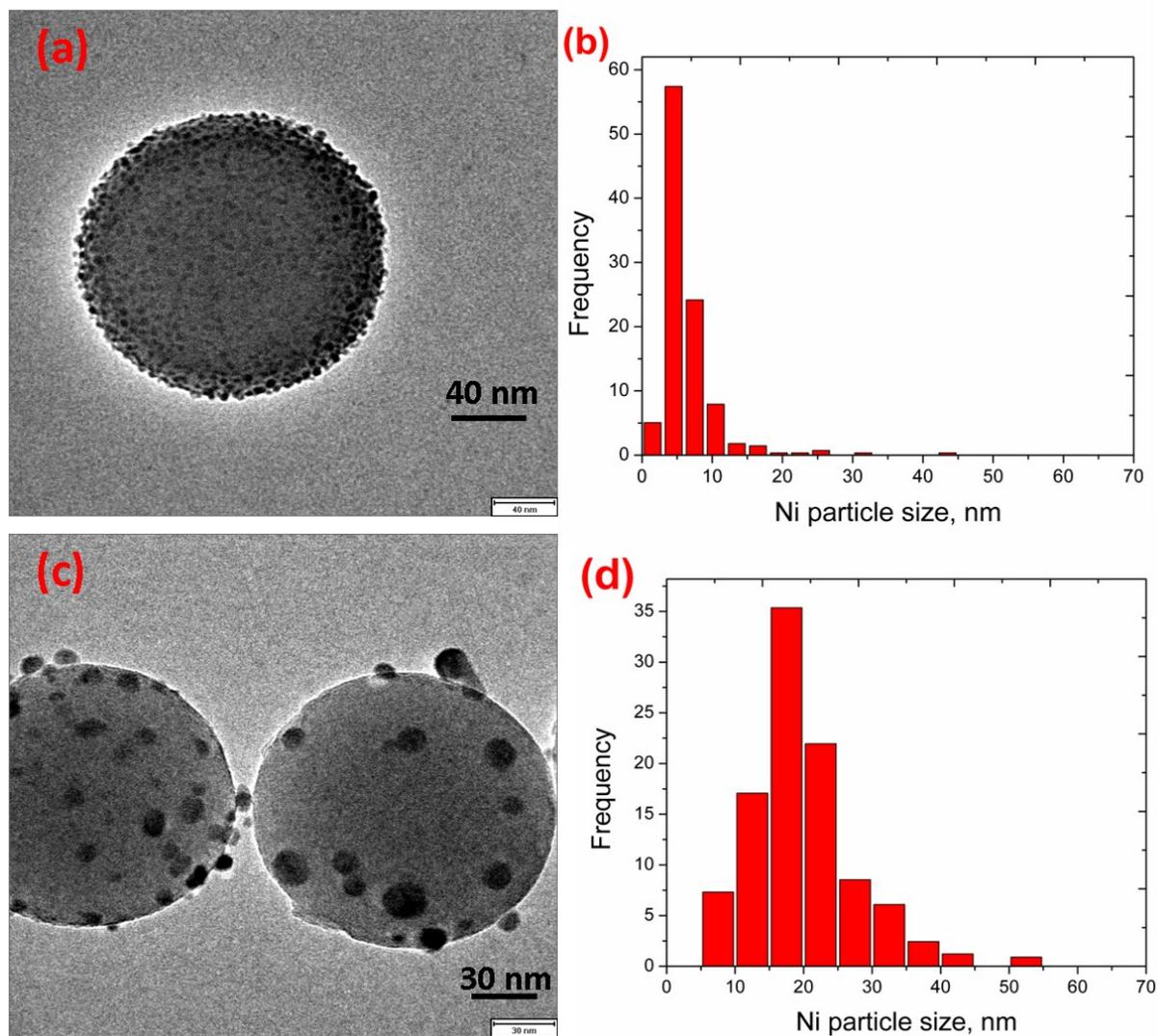


Figure S10. TEM image and Ni particle size distribution of (a, b) Ni/SiO<sub>2</sub> (pyrolysis) after CO methanation at 400°C for 92 h and (c, d) Ni/SiO<sub>2</sub> (calcination) after CO methanation at 400°C for 18 h.

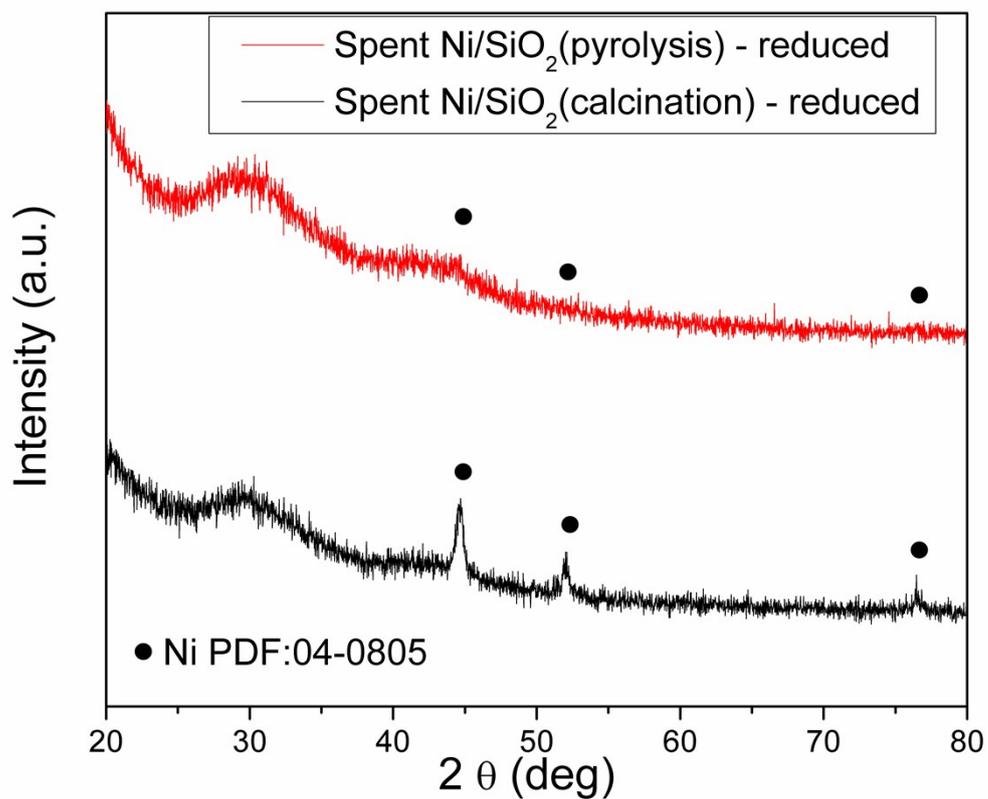


Figure S11. XRD profile of spent catalyst after CO methanation at 400°C - Ni/SiO<sub>2</sub> (pyrolysis) 92 h reaction and Ni/SiO<sub>2</sub> (calcination) 18 h reaction, GHSV = 120 L h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>. Both catalysts were reduced at 600 °C for 1 h under pure H<sub>2</sub> flow prior to reaction.

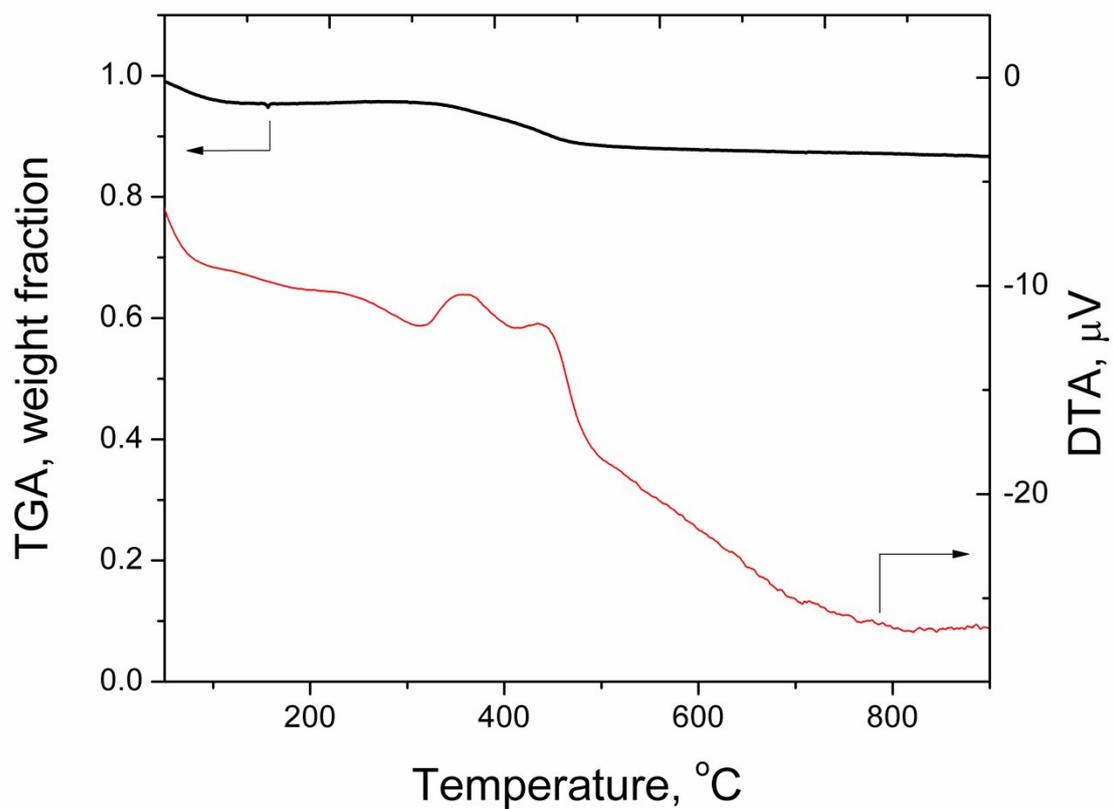


Figure S12. TGA-DTA profile for spent Ni/SiO<sub>2</sub> (pyrolysis) – reduced catalyst after 92 h CO methanation at 400°C, GHSV = 120 L h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>. The weight loss from 300°C – 400°C corresponds to oxidation of amorphous coke on the spent catalyst.

## 2.5. Characterization of Carbon Layer after CO methanation

The effect of CO methanation reaction atmosphere on the protective carbon layers on Ni in the Ni/SiO<sub>2</sub> (pyrolysis) catalyst was investigated using STEM and TGA measurements. CO methanation was carried out at 400°C for 6 hours on Ni/SiO<sub>2</sub> (pyrolysis) and Ni/SiO<sub>2</sub> (pyrolysis) – reduced catalysts at a GHSV = 120 L h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup> and the spent catalyst was characterized by STEM (Fig. S13) and TGA (Fig.S14)

For the Ni-SiO<sub>2</sub> (pyrolysis) catalyst, the spent catalyst clearly shows the presence of graphitic carbon layers on the Ni nanoparticles (Fig S13a,b), similar to that in the fresh catalyst, indicating that the carbon layers may be stable under the reaction conditions. However, the weight loss in TGA for the spent catalyst due to burning of carbon is ~ 1.2% (corresponding to exothermic DTA peak at 250-350°C) which is lower than that of the fresh catalyst (Fig.S4), indicating some carbon depletion. It should also be noted that coke deposition may happen even during the CO methanation reaction by Boudouard reaction. Overall, the presence of the carbon layers on the Ni nanoparticles under the CO methanation reaction atmosphere are observed, but some depletion or generation of coke may have happened under the reaction conditions.

For the Ni-SiO<sub>2</sub> (pyrolysis)-reduced catalyst, the fresh catalyst shows no carbon layer on Ni from STEM imaging (Fig.1f). Interestingly, some Ni nanoparticles were observed to be encapsulated with carbon in the spent catalyst, while other particles were bare (Fig S13c,d). TGA analysis of the spent Ni-SiO<sub>2</sub> (pyrolysis)-reduced catalyst showed a very low weight loss while the exothermic peak in DTA was barely perceptible, indicating low carbon content. This indicates that a very small amount of encapsulating carbon was formed during the course of CO methanation reaction, which was observed in STEM images.

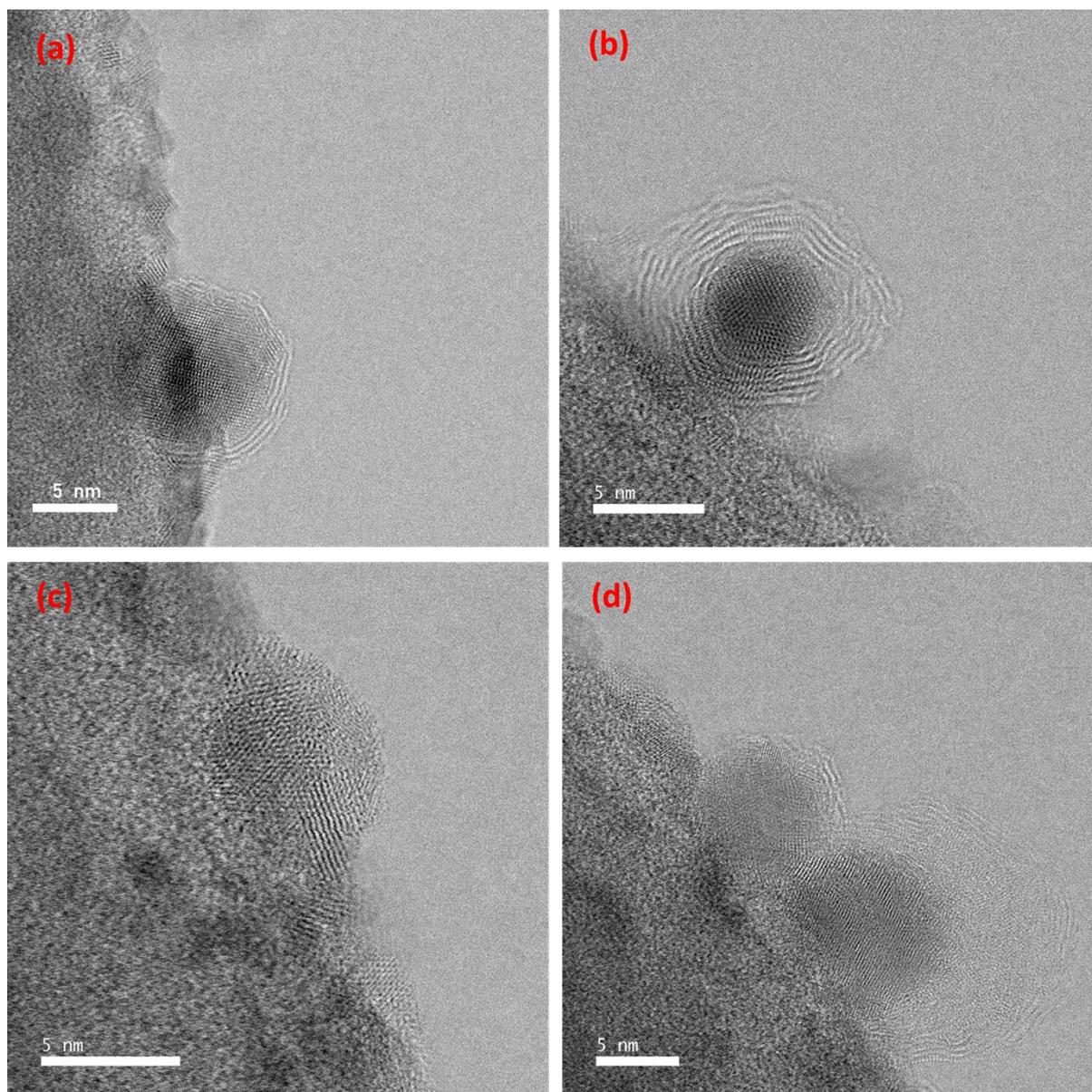


Figure S13. STEM images for (a, b) spent Ni/SiO<sub>2</sub> (pyrolysis) and (c, d) spent Ni/SiO<sub>2</sub> (pyrolysis) – reduced catalyst after 6 h CO methanation at 400°C, GHSV = 120 L h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>

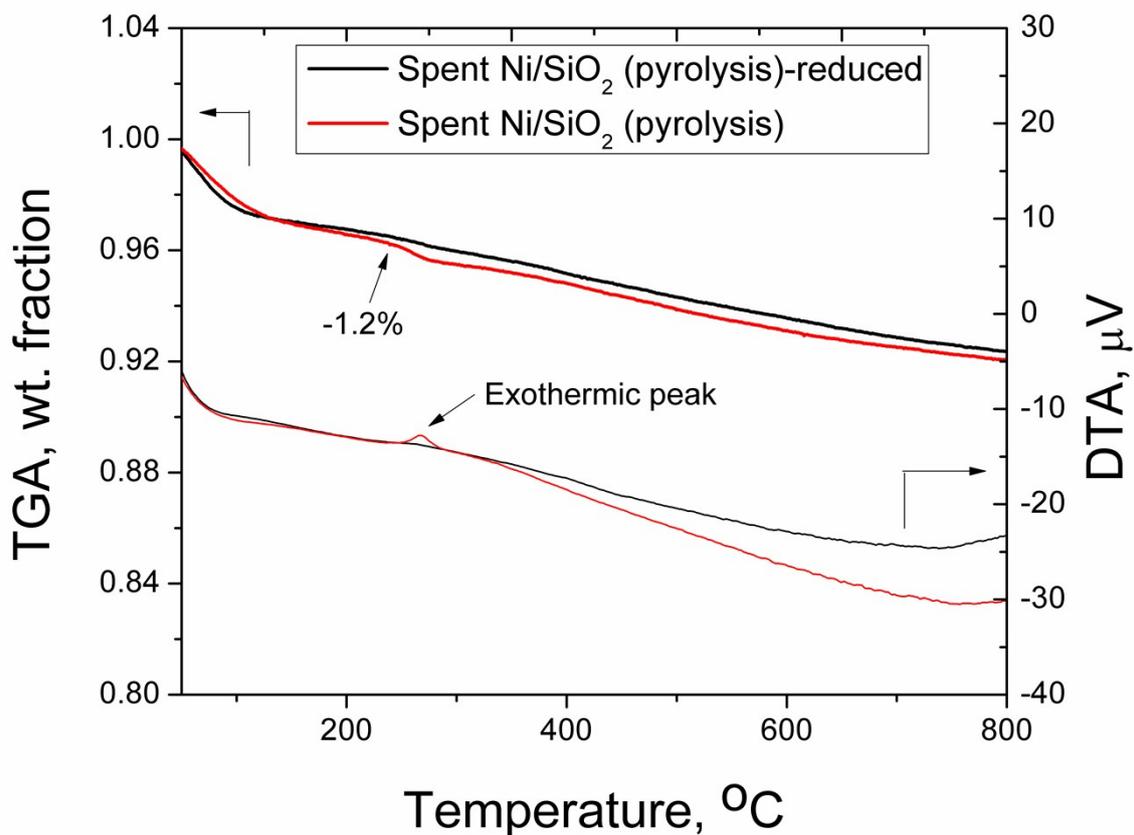


Figure S14. TGA-DTA profile for spent Ni/SiO<sub>2</sub> (pyrolysis) and Ni/SiO<sub>2</sub> (pyrolysis) – reduced catalyst after 6 h CO methanation at 400°C, GHSV = 120 L h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>

#### References:

1. E. T. Saw, U. Oemar, X. R. Tan, Y. Du, A. Borgna, K. Hidajat and S. Kawi, *Journal of Catalysis*, 2014, **314**, 32-46.