Supporting information

One-pot synthesis of highly sintering- and coking-resistant Ni nanoparticles encapsulated in dendritic mesoporous SiO$_2$
for methane dry reforming

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Chemicals

All chemicals and reagents were obtained from commercial suppliers and used without further purification: Nickel(II) nitrate hexahydrate, Tetraethyl orthosilicate (TEOS), n-Hexane, quartz sand were purchased from Sinopharm Chemical Reagent Co., Ltd. Nickelocene, triethanolamine (TEA) were obtained from Aladdin Reagent Co., Ltd. 25% aqueous Hexadecyltrimethylammonium chloride (CTAC) solution was supplied by Aldridge. Air, methane, carbon dioxide, hydrogen and nitrogen gases (99.999 vol. %) were supplied by Shanghai Pujiang Specialty Gases Co., Ltd.

Catalyst synthesis methods

Synthesis of Ni/SiO2 (OP)

A typical synthesis of Ni/SiO2 (OP) was performed as following: First, 12 mL CTAC solution (25 wt%) and 0.12 mL TEA solution (10 wt.%) were added into 18 mL deionized water and stirred gently at 60 °C for 1 h in a 100-mL round bottom flask. Next, 10 mL n-hexane solution dissolved in 2.4 mL TEOS and 0.1 g nickelocene were carefully added into the water-CTAC-TEA solution and, the solution was kept at 60 °C in an oil bath under magnetic stirring with a stirring rate of ca. 150 rpm. The reaction was then kept at a constant temperature with a continuous stirring for 12 h. Then, the upper-phase n-hexane solution was completely removed and the product was collected by centrifugation and washed several times with ethanol to remove the residual reactants. The collected products were then dried at 60 °C overnight and calcined in flowing air (flow rate of 100 mL/min) at 550 °C for 4 h to remove the organic template. Finally, a NiO/SiO2 (OP) powder was obtained prior to use.

Synthesis of Ni/SiO2 (IM)

Ni/SiO2 (IM) was prepared by incipient wetness impregnation. First, the silica microsphere support was synthesized by the same method as that of Ni/SiO2 (OP), except that no nickelocene was used. Then, 2.403 g of nickel (II) nitrate hexahydrate were dissolved into 50 mL deionized water to obtain a transparent nickel (II) nitrate solution. Next, 5 mL aqueous nickel (II) nitrate solution was slowly dropped onto the silica microspheres (1.00 g), and the slurry was continuously stirred at ambient temperature overnight. Afterwards, the as-formed catalyst was dried at 60 °C overnight and finally calcined in flowing air (flow rate of 100 mL/min) at 550 °C for 4 h. Finally, a powder catalyst NiO/SiO2 (IM) was obtained prior to use.

Catalyst Characterization.

The Ni contents were quantified by inductively coupled plasma atomic emission spectroscopy (ICP–AES) performed on a Thermo IRIS Intrepid II XSP emission spectrometer after dissolving the catalyst in the HF solution.

The specific surface area and pore size distribution were performed by N2 adsorption at 77 K on a BELSORP-MAX instrument after activating the samples under vacuum at 573 K for 10 h.

Powder X-ray diffraction (XRD) patterns were measured on Rigaku Ultima IV X-ray diffractometer utilizing Cu Kα radiation (λ = 1.5405 Å) operated at 35 kV and 25 mA.

Transmission electron microscopy (TEM) images were performed on a FEI Tecnai G2F30 microscope working at 300 kV.

Scanning electron microscopy (SEM) was shooting by the Hitachi S-4800 microscope.
operating at 20 kV.

The temperature programmed reduction (H\textsubscript{2}-TPR) analysis of catalysts was performed by Micromeritics tp5080 apparatus using a 3% H\textsubscript{2}/He mixture (flowing rate: 30 mL\cdot min\textsuperscript{-1}) and at a heating rate of 10 °C\cdot min\textsuperscript{-1} with a thermal conductor detector (TCD).

TGA measurement was performed on METTLER TOLEDO to investigate the type and amount of coke formation on the used catalysts. The temperature was increased from 25 °C to 800 °C at a rate of 10 °C\cdot min\textsuperscript{-1}.

The X-ray photoelectron spectroscopies (XPS) spectra were obtained using Al K\textalpha (hv = 1486.6 eV) radiation on a Thermo Scientific K-Alpha spectrometer. Charging effects were corrected using the C 1s peak due to adventitious carbon with EB fixed at 284.8 eV.

**Catalytic tests**

Dry reforming of methane (DRM) reaction experiments were conducted in a quartz tube reactor with an inner diameter of 8 mm under atmospheric pressure. 0.1 g calcined catalyst (40–60 mesh) were diluted with 0.5 g quartz sand. Before reaction, the catalyst was reduced at 700 °C for 2 h under a pure H\textsubscript{2} atmosphere followed by a N\textsubscript{2} purging, and then the mixture of CO\textsubscript{2} and CH\textsubscript{4} (CH\textsubscript{4}:CO\textsubscript{2} = 1:1, total flow rate of 66.67 mL/min) was introduced. The composition of the product gases was analyzed using an online gas chromatograph (Shimadzu GC 2014, Japan) equipped with a TDX-1 packed column and a thermal conductivity detector.

\[
\text{Conversion of CH}_{4} = \frac{n(\text{CH}_{4})_{\text{in}} - n(\text{CH}_{4})_{\text{out}}}{n(\text{CH}_{4})_{\text{in}}} \times 100\%
\]

\[
\text{Conversion of CO}_{2} = \frac{n(\text{CO}_{2})_{\text{in}} - n(\text{CO}_{2})_{\text{out}}}{n(\text{CO}_{2})_{\text{in}}} \times 100\%
\]

\(n\) represent the mole of the substance.

TOF refers to the sum of converted mole of CH\textsubscript{4} and CO\textsubscript{2} per mole of surface Ni particles per hour.

**Computational methods**

All calculations were based on the density functional theory implemented in the Vienna Ab-initio Simulation Package (VASP). Electronic exchange and correlation were included through the generalized gradient approximation in the Perdew–Burke–Ernzerhof form. The projector-augmented wave method was used to describe the electronic interaction. Spin-unpolarized calculations were adopted with a plane-wave kinetic-energy cutoff of 400 eV. The Brillouin zone was represented by a Gonkhorst–Pack special k-point mesh of size 2 × 2 × 1 for geometry optimization and energy calculation. All structures were optimized until the maximum force component on each atom was less than 0.02 eV\text\textalpha. The formation energy of carbon cluster on the Ni catalyst is defined as

\[
E_{f} = E_{\text{tot}} - E_{\text{sub}} - N_{C} \times E_{C_{\text{in G}}}
\]

in which \(E_{\text{tot}}\) is the energy of carbon adsorbed Ni catalyst, \(E_{\text{sub}}\) is the energy of Ni catalyst, \(N_{C}\) is the number of the carbon atoms, and \(E_{C_{\text{in G}}}\) is the energy of a C atom in graphene.

A Ni\textsubscript{55} cluster can be a representative of the Ni cluster confined in the mesoporous SiO\textsubscript{2} of 2–3 nm in size considering the non-crystalline structure of the confined Ni cluster (Fig. 2c), and such a model has been widely used in previous studies.\textsuperscript{[1–4]} The Ni (111) surface can represent the Ni particles grown on the outside of the mesoporous SiO\textsubscript{2} with a diameter of 18 nm because the Ni (111) surface can be observed for these Ni nano-particles (Fig. 2d).
Fig. S1 The recorded state of synthesis of Ni/SiO$_2$ (OP) during variation of reaction times.

Fig. S2 XPS spectra of Ni/SiO$_2$ (OP) and Ni/SiO$_2$ (IM) before calcination.
Fig. S3 SEM images of (a) Ni/SiO₂ (IM) and (b) Ni/SiO₂ (OP).

Fig. S4 TEM image of Ni/SiO₂ (OP) and its microsphere distribution.

Fig. S5 N₂ adsorption–desorption isotherm of Ni/SiO₂ (OP).
Fig. S6 Line-scanning analysis of sliced Ni/SiO$_2$ (OP)

Fig. S7 TEM image of Ni/SiO$_2$ (IM) and its Ni NP size distributions.
Fig. S8 XRD patterns of the calcined NiO/SiO$_2$ (IM) and NiO/SiO$_2$ (OP) samples.

Fig. S9 Thermodynamic equilibrium plots for DRM at 1 atm, from 0-1000 °C and at inlet feed ratio of CO$_2$/CH$_4$ = 1. These plots were created by using Gibbs free energy minimization algorithm on HSC Chemistry 7.1 software.
Fig. S10 Increased $\text{H}_2/\text{CO}$ ratios at 700 °C over the IM- and OP- Ni/SiO$_2$ catalysts. Reaction conditions: $P = 1$ atm, 0.1 g of catalyst, CH$_4$ = 33.3 mL/min, CO$_2$ = 33.3 mL/min, GHSV = 40000 mL/g/h.

Fig. S11 TEM images of Ni/SiO$_2$ (IM) after reaction at 700 °C for 60 h.

Fig. S12 TEM images of Ni/SiO$_2$ (OP) after reaction at 700 °C for 200 h.
Fig. S13 Raman spectra of Ni/SiO$_2$ (OP) and Ni/SiO$_2$ (IM) after reaction.
Table S1. The comparison of Ni/SiO$_2$ performances used for dry reforming reactions.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction conditions</th>
<th>Initial CH$_4$ Conversion (%)</th>
<th>Reported duration time</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/SiO$_2$</td>
<td>40000 ml/g/h, 700 °C, 1 atm</td>
<td>72</td>
<td>200 h at 700 °C</td>
<td>This work</td>
</tr>
<tr>
<td>Ni/SBA-15</td>
<td>7500 ml/g/h, 700 °C, 1 atm</td>
<td>77</td>
<td>20 h at 750 °C</td>
<td>5</td>
</tr>
<tr>
<td>Ni/BN@mSiO$_2$</td>
<td>15000 ml/g/h, 700 °C, 1 atm</td>
<td>73</td>
<td>100 h at 750 °C</td>
<td>6</td>
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<tr>
<td>NiPt@Hol S-1</td>
<td>72000 ml/g/h, 800 °C, 1 atm</td>
<td>76</td>
<td>6 h at 800 °C</td>
<td>7</td>
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<tr>
<td>Ceria-zirconia doped Ni/SBA-15</td>
<td>20000 ml/g/h, 600 °C, 1 atm</td>
<td>63</td>
<td>24 h at 600 °C</td>
<td>8</td>
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<tr>
<td>Ni-MgO-Al$_2$O$_3$@m-SiO$_2$</td>
<td>7500 ml/g/h, 700 °C, 1 atm</td>
<td>60</td>
<td>8 h at 750 °C</td>
<td>9</td>
</tr>
</tbody>
</table>

References