Electronic Supplementary Information (ESI):

Hexagonal Boron Nitride supported mesoSiO$_2$-confined Ni Catalysts for Dry Reforming of Methane

Yang Cao, Meirong Lu, Jianhui Fang, Liyi Shi and Dengsong Zhang*

Department of Chemistry, Research Center of Nano Science and Technology, Shanghai University, Shanghai 200444, P. R. China.

Fax: 86 21 66136079; E-mail: dszhang@shu.edu.cn
Experimental section

1. Reagents and materials

The hexagonal boron nitride (h-BN) was purchased from Saint-Gobain Ceramic Materials and the other chemical materials were purchased from Sinopharm Chemical Reagent Company China. Deionized water was used for all applications.

2. Catalyst preparation

Synthesis of Ni/BN@mSiO$_2$ catalyst

The h-BN (0.4 g) and Ni precursor (Ni(NO$_3$)$_3$·6H$_2$O 0.15 g) were dispersed in the mixture solution of ethanol (120 mL) and deionized water (160 mL) using a sonic bath for 3 h. Then the cetyltrimethylammonium bromide (CTAB 0.6 g) and concentrated ammonium hydroxide (NH$_3$·H$_2$O 28 wt% 1.8 mL) were added respectively under vigorous stirring. After being stirred 30 min, a mixture solution of ethanol solution (2.4 g) and tetraethyl orthosilicate (TEOS 0.6 g) was added into the solution dropwise in 30 min under vigorous stirring. As the reaction proceeds at room temperature, a homogeneous pale green colloidal solution was obtained under continuous stirring. After stirring for 6 h, washed the samples with deionized water and ethanol, then collected by centrifugation and finally dried overnight at 90 °C. The as-prepared samples were calcined at 600 °C for 4 h under air atmosphere and reduced under the H$_2$ at 800 °C, the obtained catalysts denoted as Ni/BN@mSiO$_2$. The loading of Ni was at 5.31 wt% determined by ICP analysis.

Synthesis of Ni/mSiO$_2$@BN catalyst

The synthesis of Ni/mSiO$_2$@BN catalyst mainly includes two aspects, the synthesis of mSiO$_2$@BN support and the impregnation process of Ni species. The synthesis of mSiO$_2$@BN support is similar to that for mesoSiO$_2$ coating, except the addition of Ni precursor. The h-BN (0.4 g) were dispersed in ethanol solution using a sonic bath for 3 h. Then the CTAB (0.6 g) and NH$_3$·H$_2$O (28 wt% 1.8 mL) were added respectively under vigorous stirring. After being stirred 30 min, a mixture solution of ethanol solution (2.4 g) and TEOS (0.6 g) was added into the solution dropwise in 30 min under vigorous stirring. After stirring for 6 h, washed the samples with deionized water and ethanol, then collected by centrifugation and finally dried overnight at 90 °C and the support were obtained by the calcination at 600 °C for 4 h. Then, a certain amount of Ni precursor (Ni(NO$_3$)$_3$·6H$_2$O) was impregnated on the obtained BN@mSiO$_2$ support using a sonic
bath for 3 h and a rotary evaporator. Finally, the as-prepared sample was calcined and reduced under the same conditions as above mentioned. The obtained catalyst was denoted as Ni/mSiO$_2$@BN and the loading of Ni was at 6.23 wt % determined by ICP analysis.

**Synthesis of Ni/BN catalyst and Ni/SiO$_2$ catalyst**

The Ni/BN catalyst and Ni/SiO$_2$ catalyst were prepared by impregnation process as above mentioned. The supports were h-BN and SiO$_2$ respectively. The loading of Ni over the Ni/BN catalyst and Ni/SiO$_2$ catalyst were at 5.60 wt % and 6.43 wt %, respectively.

3. Characterization

**Materials Characterization**

The detailed morphology of samples was performed using transmission electron microscopy (TEM) and high resolution TEM (HRTEM) on JEOL JEM-200CX. The microscope was also equipped with energy dispersive X-ray spectroscopy (EDS) detector for elemental distribution of the catalyst. Elemental composition was obtained by inductively coupled plasma-atomic emission spectrometer (ICP-AES). The hydrogen chemisorption and N$_2$ adsorption-desorption isotherm were carried out on Quantachrome instrument. The specific surface areas and pore size distribution of the catalyst were obtained using BET equation and BJH method, respectively. The XRD pattern was carried out on a Rigaku D/MAX-RB X-ray diffractometer with Cu K$_\alpha$ radiation. X-ray photoelectron spectroscopy (XPS) was performed using a RBD upgraded PHI-5000C ESCA system.

**Surface Adsorption and Desorption**

The H$_2$-temperature programmed reduction (H$_2$-TPR) was carried out to demonstrate the redox ability of the catalysts. First, the catalysts (80 mg) were pretreatment at 300 °C for 30 min under the N$_2$ atmosphere, and then reduced in 10 vol% H$_2$ of N$_2$ (30mL·min$^{-1}$) atmosphere from room temperature to 800°C at a ramp rate of 10°C·min$^{-1}$.

*In situ* diffuse reflectance infrared transform spectroscopy (DRIFTs) was performed on a Nicolet 6700 spectrometer with a Harrick Scientific DRIFT cell and a mercury-cadmium-telluride (MCT) detector to illustrate the study of the catalysts behavior during the DRM reaction. Firstly, the catalysts were purged with N$_2$ (50 mL·min$^{-1}$) at 300 °C, then cooled down to get the background spectrum. In a typical experiment, the catalysts were exposed to CO$_2$ (45 mL·min$^{-1}$) atmosphere at 500 °C for 1 h and then stop the adsorption of CO$_2$. Next, introduce CH$_4$ (45
mL·min⁻¹) steam to illustrate the transformation of the intermediate species with CH₄ introducing. In comparison, treat the CO₂ pre-adsorbed catalyst with flowing CH₄ stream, and also treat the CH₄ pre-adsorbed catalyst with flowing CO₂ stream, to examine the active species. In another experiment designed to illustrate the process of the DRM reaction, the catalysts were exposed to CO₂ (45 mL·min⁻¹) and CH₄ (45 mL·min⁻¹) for 1 h at 500 °C. The DRM reaction at 500 °C for 1 h has been measured for 3 cycles. Of each cycle the catalysts were purged with N₂ (50 mL·min⁻¹) at 500 °C for 30 min.

The thermogravimetric (TG) was performed on NETZSCH STA 449 F1 to illustrate the deposited carbon. The carbonized catalysts were heated in 40 vol% O₂ of N₂ flow (30mL·min⁻¹) from room temperature to 800 °C at a ramp rate of 10 °C·min⁻¹.

**Catalyst test**

The catalytic tests were conducted in a quartz fixed-bed tubular reactor loaded with 120 mg catalysts. The feed, a mixture of CH₄ and CO₂ (CO₂/CH₄=1) was introduced at a gas hourly space velocity (GHSV) of 15000 mL·(gh)⁻¹. The products were analyzed by a gas chromatograph (GC) equipped with thermal conductivity detector (TCD). The catalytic stability was carried out at 750 °C for 20 h and 100 h, respectively. The catalytic activity was carried out and the temperature range of the test is from 450 °C to 800 °C.

The thermodynamic equilibrium is calculated by Equilibrium Composition Block of HSC software, version 6.0 consisting of DRM and RWGS reaction.
For the Ni/mSiO$_2$@BN catalyst, the Ni particles mainly loaded on the surface of mesoSiO$_2$ coating. In addition, the Ni particle sizes of the Ni/mSiO$_2$@BN, Ni/BN and Ni/SiO$_2$ catalysts are much bigger than the Ni/BN@mSiO$_2$ catalyst.
**Fig. S2** EDX analyses in Fig. S2 showed that the body of the Ni/BN@mSiO$_2$ catalyst was composed of elements B, N, O, Ni and Si and the corresponding atom content were shown in the inserted table.
Fig. S3 FT-IR spectra of the samples.

The surface properties of the dried and calcined samples were determined by FT-IR in Fig. S3. The band at 3437 cm\(^{-1}\) can be assigned to the H-bonded OH groups and the band at 1380 cm\(^{-1}\) suggested the existence of the BN species.\(^1\) The C-H bands at 2926 cm\(^{-1}\) and 1638 cm\(^{-1}\) were detected over the dried samples corresponded to the treatment of an impregnation via ethanol. In addition, the Si-OH and Si-H bands at 956 cm\(^{-1}\) and 616 cm\(^{-1}\) were observed.\(^2\) Meanwhile, the Si-O-Si bands at 1056 cm\(^{-1}\), 796 cm\(^{-1}\) and 435 cm\(^{-1}\) were strong, on the one hand, illustrating the interaction of the silica species and h-BN nanosheets. Because the h-BN supported Ni species could interact with H-bonded Si-OH species, forming the Si-OH coating. These findings further confirm the structure of the BN-templated conjugated mesoSiO\(_2\) species.
Fig. S4 XRD patterns of the reduced catalysts.
Fig. S5 a) H$_2$-TPR profiles, b) Ni 2p XPS spectra and c) B 1s XPS spectra of the reduced catalysts.
Fig. S6 Temperature dependence of CO$_2$ conversions over the reduced catalysts.
Fig. S7  a) TEM, b) HRTEM images, c) the size distribution of Ni particles after 20 h test and d) TEM, e) HRTEM images, f) the size distribution of Ni particles after 100 h stability test over the Ni/BN@mSiO$_2$ catalyst. TEM images of g) Ni/mSiO$_2$@BN; h) Ni/BN; i) Ni/SiO$_2$ catalysts after 20 h stability test.
Fig. S8 shows the TG profiles and DSC curves of the spent catalysts after 20 h stability test.

As DRM reaction is operated at high temperatures, the formation of coke by means of CH₄ decomposition is favored, and CO disproportionation is less favored at such temperatures. Previous studies reported that CH₄ decomposition mainly generates highly reactive carbon species Cₓ. Most of the Cₓ species can be gasified by reactions with H₂O, CO₂, or hydrogen, but some are converted into less active Cᵧ. The Cᵧ would be further gasified, but may encapsulate on the surface or encapsulate the Ni species, leading to the deactivation of the catalysts. Therefore, coke formation is a result of the balance between the coke formation and gasification. Notably, DSC curve of the Ni/BN@mSiO₂ catalyst shows a peak ranged from 200 °C to 300 °C which can be assigned to the active carbon species. While, DSC curves of the Ni/mSiO₂@BN, Ni/BN and Ni/SiO₂ show a broad peak ranged from 550 °C to 700 °C which can be assigned to the carbon nanotube and graphite carbon. These types of carbon can deposit on the surface of Ni sites, leading to the deactivation of the catalysts.
First, the catalysts were pre-adsorbed by CO$_2$ at 500 °C for 1 h, the \textit{in situ} DRIFTs were collected as presented in Fig. S9. The strong feature at 2350-2280 cm$^{-1}$ region can be attributed to the absorbed CO$_2$ and the band at 3550-3750 cm$^{-1}$ region can be assigned to the OH vibrations of the surface OH groups linked by H-bonds.$^{1a,3}$ It can be noticed that no feature peaks were detected before the adsorption of CO$_2$ and the OH groups appeared following the introduction of CO$_2$. Both theoretical calculations and experimental research have reported that h-BN as hydrogen adsorbent showed a high H$_2$ uptake capacity via chemisorption or physisorption.$^4$ After the reduction treatment in the H$_2$ atmosphere, the h-BN support can bound to amount of H atoms possibility but it is difficult to detect the strongly bounded H atoms. In addition, the h-BN support can be able to capture CO$_2$ effectively.$^5$ Therefore, the activation of CO$_2$ can occur on both active Ni sites and Ni-BN interface, the formed active species can react with the surface B-H to form B-OH intermediates. Both the adsorbed CO$_2$ species and B-OH intermediates can be clearly observed on the Ni/BN@mSiO$_2$ and Ni/BN catalysts. The synergistic effect of the active Ni sites and the Ni-BN interface can effectively promote the activation of CO$_2$ and CH$_4$ during the DRM reaction.

\textbf{Fig. S9} \textit{In situ} DRIFTs of a) the Ni/BN@mSiO$_2$ catalyst and b) the Ni/BN catalyst after the catalysts were pre-adsorbed CO$_2$ at 500 °C for 1h.
Fig. S10 Evolution of *in situ* DRIFTs after CO$_2$ adsorption at 500 °C. *In situ* DRIFTs of transient reactions over a) the Ni/BN@mSiO$_2$ catalyst and b) the Ni/BN catalyst after the catalysts were exposed to CH$_4$ species; (C) consumption of B-OH species upon passing CH$_4$ over the Ni/BN@mSiO$_2$ and Ni/BN catalysts.

As shown in Fig. S10a-b, the intensity of the B-OH peaks over the Ni/BN@mSiO$_2$ catalyst decreases at a more rapid rate compared with the Ni/BN catalyst. The normalized intensity of the B-OH intermediates changed with time over the Ni/BN@mSiO$_2$ and Ni/BN catalysts are shown in Fig. S10c. Of the B-OH peaks at 3735 cm$^{-1}$, 3704 cm$^{-1}$, 3626 cm$^{-1}$ and 3592 cm$^{-1}$, the main peak at 3735 cm$^{-1}$ is used to illustrate the reactivity of B-OH intermediates over the different catalysts. The intensity of B-OH intermediates decreases as time going by, suggesting that the adsorbed B-OH species can react with CH$_4$ and contributes to the DRM activity. We supposed that the active CH$_x$ species derived from CH$_4$ decomposition can react with OH species, and then form the CH$_x$O species on the surface of support. Specially, this reaction process can contribute to the transport of the CH$_x$ species from the Ni sites to the surface of support, providing more Ni sites for the CH$_4$ activation. Therefore, the decreased B-OH species can be due that the reaction between the CH$_x$ species derived from CH$_4$ decomposition and B-OH species.
Fig. S11 Evolution of *in situ* DRIFTs over the Ni/BN@mSiO$_2$ catalyst after CO$_2$ adsorption at 500 °C with flowing CH$_4$ stream for a) 1 min and b) 30 min; after CH$_4$ adsorption at 500 °C with flowing CO$_2$ stream for c) 1 min and d) 30 min.

The Ni/BN@mSiO$_2$ catalyst was pre-adsorbed CO$_2$ at 500 °C for 1 h and then introduce the CH$_4$ stream simultaneously (Fig. S11a). The intensity of the B-OH peaks over the Ni/BN@mSiO$_2$ catalyst decreases rapidly with flowing CH$_4$ stream, suggesting that the adsorbed B-OH species can react with CH$_4$ as discussed. Notably, the intensity of the B-OH species maintains after 1 min (Fig. S11b), which is a result of the balance between the consumption and generation of B-OH species. In comparison, the Ni/BN@mSiO$_2$ catalyst was pre-adsorbed CH$_4$ at 500 °C for 1 h and then introduce the CO$_2$ stream simultaneously. As shown in Fig S11c, B-OH peaks do not appear after the adsorption of CH$_4$ for 1 h. While the B-OH peaks appears and increased rapidly with flowing CO$_2$ stream, and the intensity of B-OH species also maintains after 1 min (Fig. S11d). In addition, it can be notice that the intensities of B-OH species with different pre-adsorption are different. The CH$_4$ pre-adsorbed catalyst with flowing CO$_2$ stream shows the higher intensity of B-OH species. It may be due to that CH$_4$ decomposition can occur on the Ni sites and generate H species and H$_2$. While, h-BN as hydrogen adsorbent can absorb abundant H and H$_2$ species, contributing to the formation of B-OH species.
Fig. S12 *In situ* DRIFTS of the DRM reaction at 500 °C for 1 min the over a) Ni/BN@mSiO$_2$ and b) Ni/BN catalysts; c) formation of active species upon passing CH$_4$ and CO$_2$ over the Ni/BN@mSiO$_2$ and Ni/BN catalysts; *in situ* DRIFTs of the DRM reaction at 500 °C for 1 h over the d) Ni/BN@mSiO$_2$ catalyst and e) Ni/BN catalyst.
Three cycles of DRM reaction have been examined to illustrate the regenerability of B-OH species. As shown in Fig. S13, the B-OH species can be formed with flowing CO$_2$ and CH$_4$ stream, and the B-OH peaks disappear with N$_2$ purging. Notably, the B-OH species can be regenerated on the surface of the Ni/BN@mSiO$_2$ catalyst with flowing CO$_2$ and CH$_4$ stream for each cycle.
Table S1. Surface Ni exposure from H₂ chemisorption

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Ni dispersion</th>
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</thead>
<tbody>
<tr>
<td>Ni/BN@mSiO₂</td>
<td>9.74 %</td>
</tr>
<tr>
<td>Ni/mSiO₂@BN</td>
<td>1.32 %</td>
</tr>
<tr>
<td>Ni/SiO₂</td>
<td>1.15 %</td>
</tr>
</tbody>
</table>

The Ni dispersions of the Ni/BN@mSiO₂, Ni/mSiO₂@BN and Ni/SiO₂ catalysts are 9.74 %, 1.32 % and 1.15 %, respectively. But the Ni dispersion of the Ni/BN catalyst can not be measured. Both theoretical calculations and experimental research have reported that h-BN as hydrogen adsorbent showed a high H₂ uptake capacity via chemisorption or physisorption. After the reduction treatment in the H₂ atmosphere, the h-BN support can bound to amount of H atoms possibility. Therefore, the high H₂ uptake capacity of the h-BN can influence the measurement of the hydrogen chemisorption.
Table S2. TOF value obtained from H\textsubscript{2} chemisorption

<table>
<thead>
<tr>
<th>Time</th>
<th>Ni\textsuperscript{a} (wt %)</th>
<th>Ni Dispersion\textsuperscript{b} (%)</th>
<th>Conversion (CH\textsubscript{4})\textsuperscript{c} (%)</th>
<th>TOF\textsubscript{CH4}\textsuperscript{d} (h\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 min</td>
<td>9.74</td>
<td>13.82</td>
<td>3782</td>
<td></td>
</tr>
<tr>
<td>360 min</td>
<td>5.31</td>
<td>9.02</td>
<td>12.07</td>
<td>3565</td>
</tr>
</tbody>
</table>

Condition: 50mg of catalysts, CH\textsubscript{4}:CO\textsubscript{2} = 1:1, 45 mL/min per reactor, Temperature: 550 °C.

\textsuperscript{a} Determined by ICP

\textsuperscript{b} Determined by H\textsubscript{2} chemisorption

\textsuperscript{c} CH\textsubscript{4} conversion at 15 min and 360 min of the DRM reaction

\textsuperscript{d} In mole\textsubscript{CH4}.h\textsuperscript{-1}.mole\textsuperscript{-1} suf\textsubscript{Ni}
Reference


