**Experimental Section:**

1. Preparation of catalysts

   a. Synthesis of LDH nanoplates.

   The LDH nanoplates were synthesized by a modified hydrothermal method. Briefly, 20 mL of mixed salt solution containing Mg(NO₃)₂ (5.14 mmol), Ni(NO₃)₂ (0.86 mmol) and Al(NO₃)₃ (2.0 mmol) was quickly added into 80 mL of NaOH aqueous solution (0.15 M) under vigorous stirring, followed by 10-15 min stirring. The pure LDH slurry was obtained via centrifugation and washed twice with deionized water, and then suspended in 80 mL of deionized water. This aqueous suspension was transferred into a 100 mL Teflon autoclave, sealed and maintained at 120 °C for 5 h. After the reaction was completed, water was removed from the resulting sol product by conducting reduced pressure distillation. The final NiMgAl-NO₃ LDH nanoplates were dried at 60 °C. Besides, the MgAl-NO₃ LDH nanoplates were also fabricated by the same method.

   b. Synthesis of the modular catalysts.

   The core-shell Ni-MgO-Al₂O₃@m-SiO₂ modular catalysts were synthesized by a surfactant-assistant sol–gel coating method. Briefly, 0.20 g of the obtained LDH NPs were first dispersed in the solution containing 160mL of deionized water H₂O, 120 mL of ethanol, 0.60 g of CTAB and 1.80 mL of NH₃•H₂O with ultrasonic for 1h. Then 0.60 g of TEOS was added dropwise to the mixture with vigorously stirring. After the reaction for 6 h, the product was collected after the centrifugation and washed with distilled water and with ethanol for three times, then dried at 60 °C for 24 h. The modular catalysts, noted as IR-Ni-MO@m-SiO₂, were obtained via the calcination at 600 °C for 4 h and the in-situ reduction at 700 °C for 1 h. The mass fraction of nickel element is 5.84 % determined by ICP analysis.

   c. Synthesis of the IM-Ni-MO@m-SiO₂ catalysts

   First, MgAl-LDH@m-SiO₂ was fabricated by the above way. Then, a certain amount of Ni(NO₃)₂•H₂O was impregnated on the MgAl-LDH@m-SiO₂. After the
drying and calcination, the sample was reduced at 700 °C for 1 h. The obtained catalysts were IM-Ni-MO@m-SiO₂. The amount of Ni in the IM-Ni-MO@m-SiO₂ catalysts was kept the same as that in the modular catalysts.

d. Synthesis of the IR-Ni-MO catalysts

The NiMgAl-LDH powder was calcined at 600 °C for 4 h, then the sample was in-situ reduced at 700 °C for 1 h. The IR-Ni-MO catalysts were obtained.

2. Characterization

Analytical performance of determination for Ni by inductively coupled plasma-atomic emission spectrometer (ICP-AES) with charge injection device (CID) was investigated on a Plasma-400.

The XRD measurements were performed with a Rigaku D/MAX-RB X-ray diffractometer by using Cu Kα (40 kV, 40 mA) radiation and a secondary beam graphite monochromator. The Scherrer equation was used to estimate the mean crystallite size based on the diffraction peaks of (100) facet of Ni particles.

The morphologies were observed by a TEM (JEOL JEM-200CX). The high-resolution transmission electron microscopy (HRTEM), bright-filed TEM (BF-TEM), and high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) was conducted to characterize the detailed morphology of catalysts employing a JEM-2100F TEM 200 kV. The microscope was also fitted with a liquid nitrogen cooled EDS detector for elemental analysis.

N₂ adsorption-desorption measured was with a Quantachrome NOVOE 4000e analyzer by nitrogen adsorption at 77 K. The samples were degassed at 300 °C for 4 h before measurements. The BrunauerEmmettTeller (BET) method was utilized to calculate the specific surface areas and the pore volume, and the pore size distributions were derived from the adsorption branches of isotherms by using the Barrett Joyneer Halenda (BJH) model.

The H₂-TPR measurements were carried out in a quartz tube reactor equipped with a thermal conductivity detector (TCD). First of all, the catalysts (80 mg) were pretreated at 300 °C for 30 min in a flowing stream of high-purity nitrogen. After cooling to room temperature, a 10% H₂ of N₂ gas mixture (40 mL/min) was introduced and the programing temperature was controlled from room temperature to 900 °C with a rate of 10 °C/min.

The CO₂-TPD tests were also carried out to study the basicity of catalysts, First, the catalysts (120 mg) were pretreated at 300 °C for 30 min in a flowing stream of high-purity helium. After cooling to 50 °C, the samples were saturated with CO₂ for 1h and flushed with He for 30 min to remove physisorbed CO₂. Then, the temperature was increased at a ramp of 10 °C/min to 700 °C in He, and the desorbed products were monitored by the TCD detector.

The TPO measurements were carried out with the same procedure of H₂-TPR. The difference was that the amount of the used catalysts was 50 mg and a 10% O₂ of N₂ gas mixture was applied.

TGA/TGA (SHIMADZU DTG-60H) was used to investigate the amount of coke formation on the used catalysts. The temperature was increased from room
temperature to 1000 °C at a rate of 10 °C·min⁻¹.

3. DRM test

The CO₂ reforming of methane reactions was carried out in a fixed bed reactor with a quartz tube (inner diameter of 8 mm). The quartz tube was filled with 0.12 g of catalysts (40-60 mesh) and fed a mixture of CH₄ and CO₂ (CH₄:CO₂ = 1:1, 15 mL/min per reactor). The catalytic tests were carried out from 450 to 800 °C with a heating rate of 5 °C/min. The effluent product gases were cooled in an ice-water bath and analyzed by online gas chromatography with a TCD, using a TDX-01 packed column. The durability tests were also carried out at 750 °C for 480 min.
Fig. S1. Schematic procedure for the preparation of the IM-Ni-MO@m-SiO₂ catalysts.
Fig. S2. XRD patterns of: (1) MgAl-LDH, (2) IR-NiO-MO@m-SiO₂, and (3) IM-Ni-MO@m-SiO₂

For the catalysts before reduction, the weak peaks at 2θ = 37°, 43° and 64° can be ascribed to the presence of mixed oxides and/or solid solution (Ni-Mg-O) phase.[s2] However, it is not possible to differentiate between mixed oxides, due to the overlapping of their peaks. Besides, the peaks located at 31.3°, 44.8°, 59.4°, 65.4° are assigned to the MgAl₂O₄ and/or NiAl₂O₄ spinel phase.[s3] Compared with the IR-NiO-MO@m-SiO₂, the peaks corresponding to spinel phase on IM-NiO-MO@m-SiO₂ are more obvious. The formation of spinel phase needs a high temperature (above 500°C) and the decomposition temperature after the impregnation of Ni(NO₃)₂ is low, so it can be determined that the spinel phase on IM-NiO-MO@m-SiO₂ is MgAl₂O₄.[s4] Therefore, Ni species on IM-NiO-MO@m-SiO₂ may be composed of NiO species dispersed on the supports; While, Ni species on IR-NiO-MO@m-SiO₂ may consist of NiO, NiAl₂O₄ and Ni-Mg-O solid solution.[2]
Fig. S3. TEM images of the NiMgAl-LDH (A), IR-NiO-MO@m-SiO₂ (B), IR-Ni-MO@m-SiO₂ (C) and IM-Ni-MO@m-SiO₂ (D) catalysts (inset: schematic diagrams and the size distributions of Ni NPs).

The size of the IM-Ni-MO@m-SiO₂ catalysts shows ~40×120 nm. The difference results from the different size of LDH nanoplates before the coating of mesporous SiO₂. The size of nickel NPs is non-uniform and largely concentrated in a range of 13-15 nm. Besides, most of nickel NPs exist in the mesoporous silica shells layer.
Fig.S4. BF-TEM micrograph, and EDS mapping and spectrum of the IR-Ni-MO@\textit{m}-SiO$_2$ catalysts.
Fig. S5. N$_2$ adsorption-desorption isotherms and the mesopore size distributions (the inset) of the two catalysts.

The silica shells can be fabricated after the removal of CTAB templates. The mesoporous channels are readily accessible, favoring the adsorption and release of reactant gas.\textsuperscript{[s5]} The mesopore size distribution exhibits a maximum centered at 3.62 nm and 3.38 nm on the IR-Ni-MO@$m$-SiO$_2$ and IM-Ni-MO@$m$-SiO$_2$ catalysts, respectively (Fig. 5, inset). The presence of 20–30 nm in the pore size distribution on the modular catalysts is due to interstices between the primary particles.\textsuperscript{[s6]} For the IM-Ni-MO@$m$-SiO$_2$ catalysts, the impregnated Ni NPs occupy part of the confined space inside the mesoporous channels, resulting in the smaller pore size.
Table S1. Textural properties of different samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{BET}$ (m$^2$/g)</th>
<th>$V_{mes}$ (mL/g)</th>
<th>$D_{pore}$ (nm)</th>
<th>Ni Particle size $^a$</th>
<th>Carbon Deposition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IM-NiO-MO@m-SiO$_2$</td>
<td>251.77</td>
<td>0.254</td>
<td>3.358</td>
<td>N.A.</td>
<td>N.A.</td>
</tr>
<tr>
<td>IR-NiO-MO@m-SiO$_2$</td>
<td>368.29</td>
<td>0.222</td>
<td>3.597</td>
<td>N.A.</td>
<td>N.A.</td>
</tr>
<tr>
<td>IM-Ni-MO@m-SiO$_2$</td>
<td>194.27</td>
<td>0.249</td>
<td>3.379</td>
<td>10.5</td>
<td>12.0</td>
</tr>
<tr>
<td>IR-Ni-MO@m-SiO$_2$</td>
<td>413.09</td>
<td>0.231</td>
<td>3.619</td>
<td>8.2</td>
<td>8.5</td>
</tr>
</tbody>
</table>

$^a$. Determined by the Scherrer’s equation.

The BET surface areas of the IM-NiO-MO@m-SiO$_2$ and IR-NiO-MO@m-SiO$_2$ are 251.77 m$^2$/g and 368.29 m$^2$/g, respectively. The vast difference is caused by the size distinction of LDH nanoplates, as confirmed in TEM images. After the reduction, the variation of the BET surface areas for the two catalysts is different. For the IM-Ni-MO@m-SiO$_2$ catalysts, the reduction of Ni NPs plugs part of the mesporous channels, causing the decrease of BET surface areas. While, the reduction of Ni NPs on the modular catalysts can produce some porosity and cavities, which can enhance the BET surface areas and pore volume. The larger BET surface areas and pore volume are helpful for the absorption and storage of reactant gas, which can generate an excellent catalytic activity.
The surface interaction between NiO and MO@SiO₂ supports was evaluated by H₂-TPR experiments (Fig. S6A). For the IM-NiO-MO@SiO₂, according to the fact confirmed in the TEM image and the previous literatures, three reduction peaks are mainly assigned to NiO species in interaction with the mesoporous SiO₂ supports. The fact further confirms that only one confinement of mesoporous SiO₂ exists in the IM-Ni-MO@SiO₂ catalysts. However, the TPR profile of the IR-NiO-MO@SiO₂ shows two peaks, a weak reduction peak at 300–500 °C and an intense reduction peak at 745 °C. The first broad weak is due to the reduction of bulk NiO species or weakly interactive NiO species with mixed oxide supports. The second reduction peak at 850–870 °C is attributed to the NiO species in strong interaction with support, which are generally considered as the formed Ni-Mg-O solid solution and/or NiAl₂O₄ spinel phase, which are the main sources of metallic Ni NPs. Though the reduction of these stable Ni²⁺ species needs a high temperature, the obtained highly dispersed Ni⁰ species show a strong interaction with the mixed oxide supports.

The strength of basic sites in the catalysts is also detected by the CO₂-TPD
measurements (Fig. S6B). The small desorption peak around 100 °C might be derived from the weakly chemisorbed CO$_2$ on the weak basic sites, and the broad peak between 350-650 °C can be assigned to the moderately and strongly chemisorbed CO$_2$ on the basic sites. It is generally acknowledged that the strong basic sites are remarkably related to the existence of MgO. For the modular catalysts, the larger specific surface areas can increase the exposure of MgO species. Therefore, compared with the IM-Ni-MO@m-SiO$_2$ catalysts, the TPD profile shifts to the higher temperature and its intensity are higher, suggesting the more and stronger basicity on the catalysts.
Fig S7 XRD patterns of the used catalysts after long-term stability tests. (a. IR-Ni-MO@m-SiO$_2$, b. IM-Ni-MO@m-SiO$_2$, c. IR-Ni-MO.)

The used IR-Ni-MO catalysts display the distinct diffraction peaks belong to graphite carbon, suggesting the high coke deposition.
Fig. S8. TEM images of the used IR-Ni-MO@m-SiO₂ catalysts (A) and IM-Ni-MO@m-SiO₂ catalysts (B) (inset: the size distributions of Ni NPs).
The TPO profile of the used IR-Ni-MO@\textit{m}-SiO\textsubscript{2} catalysts shows a small peak centered at around 700 °C, whereas that of the IM-Ni-MO@\textit{m}-SiO\textsubscript{2} catalysts exhibits a small broad peak from 200 °C to 700 °C and a larger one at 700-800°C. According to the literatures, carbon nanotubes or filamentous carbon oxidized at a high temperature mainly response for the carbon deposition.\textsuperscript{[7a, 8]}
References


