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Facile immobilization of Ni nanoparticles into mesoporous MCM-41 channels for efficient methane dry reforming

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ABSTRACT

Development of dry reforming of methane and carbon dioxide is an effective route to convert industrial waste gases such as coke-oven gas and coal-to-oil gas into platform syngas. However, this process encounters severe problems of metal particle sintering and coke formation at high temperatures. In this work, we developed a new synthetic method for preparing confined Ni/MCM-41 catalysts, which impede the sintering of metal nanoparticles (NPs) and coke deposition at high temperatures, enabling them to be successfully applied to methane dry reforming. The method results in high activity and stability of the catalyst at 700 °C for 200 h. The Ni precursor is immersed in ethanol and impregnated into MCM-41 by the peculiar capillary action of hexagonal straight mesopores. By this method, 10 wt% Ni NPs ($d = 2$ nm) is equably confined to the mesoporous channels with strong metal-support interactions, as confirmed by HRTEM, TEM mapping, H₂-TPR, and XRD measurements. Such a confined structure has a significant effect on the inhibition of metal NP agglomeration and carbon deposition during methane dry reforming, as evidenced by TEM, Raman, TGA, and TPO measurements of used Ni/MCM-41 catalysts. In contrast, unconfined Ni/MCM-41 catalysts, with Ni NPs located on the pore exteriors, are rapidly deactivated after 12 h due to the blocked contact between the active metal centers and the gas feedstock. Additionally, a fast increase in the Ni NP size and the formation of substantial carbon nanotubes on the unconfined catalyst surface are seen. This work offers a facile approach for the synthesis of anti-sintering, carbon-resistant confined Ni catalysts that can operate at high temperatures.

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1. Introduction

Methane can be converted by reforming or partial oxidation into syngas, a mix of carbon monoxide and hydrogen, which can be further transformed into valuable fuels and chemicals such as alkanes, olefins, alcohols, and ethylene glycol [1].

Steam reforming (SR) of methane: $\text{CH}_4 + \text{H}_2\text{O} = \text{CO} + 3\text{H}_2$;

$$\Delta H_{298\text{ K}} = 206 \text{ kJ} \cdot \text{mol}^{-1} \quad (1)$$

Partial oxidation (PO) of methane: $\text{CH}_4 + 1/2\text{O}_2 = \text{CO} + 2\text{H}_2$;

$$\Delta H_{298\text{ K}} = -36 \text{ kJ} \cdot \text{mol}^{-1} \quad (2)$$

Dry reforming of methane (DRM): $\text{CH}_4 + \text{CO}_2 = 2\text{CO} + 2\text{H}_2$;

$$\Delta H_{298\text{ K}} = 247 \text{ kJ} \cdot \text{mol}^{-1} \quad (3)$$

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DRM converts the inert, small greenhouse gas molecules of methane and carbon dioxide into syngas with a H_2/CO ratio ≈ 1 . High temperatures (650 to 1000 °C) are required for the DRM since it is a highly endothermic reaction [2]. The reaction initiates methane dissociation on the metal surface to afford C^* and H^* and CO_2 dissociation to form CO^* and O^* . The C–C bonds from C^* forming graphitized carbon via polymerization are highly favored if the combination of C^* and O^* is impeded. The former would cover the active metal surface, preventing further contact of the reactants and active centers, leading to fast catalyst deactivation [3]. As a result, the activation of CO_2 would be a strong determinant of the catalyst lifetime. Additionally, metal nanoparticle (NP) aggregation is thermodynamically favorable at high reaction temperatures, further lowering the catalyst activity [4].

The inexpensive metallic Ni is commonly used in the DRM due to its ability to dissociate methane [5]. To facilitate the dissociation of CO_2 , alkaline earth oxides such as MgO, BaO, and CaO can be added for strengthening the adsorption of CO_2 [6–8]; alternatively, oxides such as CeO_2 , ZrO_2 , and La_2O_3 , which have oxygen vacancies, can be incorporated to trap CO_2 [9–11]. It should be noted that in bimetallic NiFe catalysts, Fe activates CO_2 by reducing it to CO and FeO. Then, FeO can convert the dissociated C^* to CO and Fe via a redox reaction. This leads to a good combination of CO_2 activation and C^* deposit removal at high temperatures [12].

The sintering of metallic Ni at the high temperatures used in the DRM is another challenge, and the synthesis of confined metal catalysts would be a solution to such a problem. Metallic Ni can be embedded into the lattice of $NiAl_2O_4$ [13] or $LaNiO_3$ [14], or confined to mesoporous supports such as ZrO_2 , SiO_2 , Al_2O_3 , and hydrotalcite [15–18]. By increasing the calcination temperature to 900 °C, Ni can be embedded into the $NiAl_2O_4$ lattice, which significantly suppresses the sintering of Ni NPs and carbon deposition (60 h DRM test) compared to the case of the unconfined samples [13]. In addition, a layer of coated SiO_2 (3.3–15.1 nm) on the external surface of the Ni NPs forms a core-shell catalyst, extending the catalyst lifetime for the DRM to 90 h [19]. If SiO_2 is coated on the exterior of Ni-Mg-Al hydrotalcite, this secondary confinement highly enhances the catalyst stability for the DRM at 750 °C [20]. Additionally, our group synthesized a Ni/ SiO_2 sample with confined Ni NPs (2 nm) in mesoporous SiO_2 channels by a one-pot process [21]. This sample showed high DRM performance at 700 °C for 200 h. Furthermore, density functional theory (DFT) calculations showed that carbon atoms on small-sized Ni clusters exist in the form of single adsorbed atoms, but those adsorbed onto larger-sized Ni clusters can easily form nanotubes, rendering the Ni clusters inactive.

Well-ordered, stable mesoporous silica materials such as SBA-15 and MCM-41 are considered to be promising supports for the growth of metal NPs due to the confinement effects imposed by their uniform channels [22,23]. Xie et al. [24] impregnated dispersive Ni NPs into the channels of SBA-15 from an ethylene glycol solution, so that stable reactivity was achieved at 750 °C for 20 h. MCM-41 is a two-dimensional hexagonal mesoporous SiO_2 with straight channels. In this work,

we used the capillary action induced by the hexagonal mesoporous straight channels to impregnate the material with Ni salt-ethanol solution, leading to uniform and dispersive Ni NPs in the mesopores of MCM-41. Such a confined catalyst highly rendered metal sintering and carbon deposition at 700 °C and showed long-term (200 h) high activity for the DRM reaction.

2. Experimental

2.1. Chemicals

All chemicals and reagents were obtained from commercial suppliers and used without further purification. Nickel(II) nitrate hexahydrate, tetraethyl orthosilicate (TEOS), ethyl alcohol (>99.7%), and quartz sand were purchased from Sinopharm Chemical Reagent Co., Ltd. Nickelocene, triethanolamine (TEA), and 25% aqueous hexadecyltrimethylammonium chloride (CTAC) solution were obtained from Aladdin Reagent Co., Ltd. Aluminum sulfate octadecahydrate (>98%) and ammonium hydroxide solution (28% NH_3 in H_2O) were obtained from Sigma-Aldrich Co., Ltd. Air, methane, carbon dioxide, hydrogen, and nitrogen gases (99.999 vol%) were supplied by Shanghai Pujiang Specialty Gases Co., Ltd.

2.2. Synthesis

According to our previously developed method [25], the typical preparation of [Si]MCM-41 material was performed as follows: CTAC was mixed with TEOS and ammonium hydroxide solution in a volume ratio of 1:1:1 in 500 mL of demineralized water and stirred at room temperature to form a white gel. The gel was completely mixed with vigorous stirring for 1 h. The resulting solid was collected by filtration, washed with distilled water, and then dried in an oven at 80 °C. Finally, the obtained MCM-41 material was calcined at 550 °C at a heating rate of 1 °C·min⁻¹, in static air for 6 h.

The Ni/MCM-41 catalysts were prepared by an impregnation method. Calcined [Si]MCM-41 was used for preparing nickel NPs on the inner surface (denoted as $Ni_{in}/MCM-41$), while uncalcined [Si]MCM-41 with templates were used for preparing nickel NPs on the outer surface (denoted as $Ni_{out}/MCM-41$). The typical synthesis was carried out as follows. First, $Ni(NO_3)_2 \cdot 6H_2O$ was dissolved in ethanol to form a 1.0 mol/L solution, and then, MCM-41 powder was added to the nickel precursor solution with stirring. Slow evaporation of the mixture was carried out at 80 °C, and the obtained solid was calcined in a muffle furnace at 550 °C for 4 h at a heating rate of 1 °C·min⁻¹, in static air.

For the synthesis of NPs on both the inner and outer surfaces (denoted as $Ni_{in\&out}/MCM-41$), the calcined [Si]MCM-41 was used as the carrier, with the Ni precursor salt dissolved in an ethanol/water (5:1) mixture. Impregnation, air-calcination, and hydrogen-reduction procedures were carried out in a similar manner to those already mentioned.

2.3. Catalyst characterization

Inductively coupled plasma-atomic emission spectroscopy (ICP-AES; Thermo IRIS Intrepid II XSP emission spectrometer) was used for the quantification of Ni on catalysts pre-dissolved in hydrofluoric acid (HF).

Specific surface area and pore size distributions were obtained by N₂ adsorption at –196 °C on a BELSORP-MAX instrument, under vacuum at 300 °C for 10 h after sample activation.

Powder X-ray diffraction (XRD) patterns were obtained using a Rigaku Ultima IV X-ray diffractometer, utilizing Cu K α radiation ($\lambda = 1.5405 \text{ \AA}$) and operating at 35 kV and 25 mA.

Transmission electron microscopy (TEM) images were obtained using an FEI Tecnai G2F30 microscope working at 300 kV. Scanning electron microscopy (SEM) was performed on a Hitachi S-4800 microscope operating at 20 kV.

Temperature-programmed reduction (H₂-TPR) analysis of the catalysts was performed with a Micromeritics tp5080 apparatus at a heating rate of 10 °C·min^{–1}, a thermal conductivity detector (TCD), and a 3% H₂/N₂ mixture (flow rate: 30 mL·min^{–1}).

The dispersion of Ni was measured by CO adsorption. First, the catalysts (100 mg) were pre-treated at 700 °C for 2 h in a flowing stream of high-purity H₂, followed by N₂ purging. After cooling to room temperature, a CO pulse was introduced through a six-way valve equipped with a 10 μ L loop. An ice-water bath was used to reduce the temperature of value to 0 °C. Unadsorbed CO was detected using a TCD.

The dispersion of Ni (D) was calculated based on the volume of chemisorbed CO using the following simplified equation:

$$D = \frac{V_{ad} \times M_{Ni} \times SF}{V_m \times m_{cat} \times X_{Ni,ICP}} \times 100\%$$

Where V_{ad} (mL) denotes the volume of chemisorbed CO measured in the CO adsorption procedure, under standard temperature and pressure (STP) conditions; m_{cat} is the mass of the sample (g); M_{Ni} is the molecular weight of Ni (58.69 g·mol^{–1}); $X_{Ni,ICP}$ is the weight fraction of Ni in the sample, as determined by ICP; SF is the stoichiometric factor (the Ni:CO molar ratio in the chemisorption), which is taken as 1; and V_m is the molar volume of CO (22414 mL·mol^{–1}), at STP.

Thermogravimetric analysis (TGA; METTLER TOLEDO) was used to explore the type and amount of coke formed on the used catalysts. During the analysis, the temperature was increased from 25 °C to 800 °C at a rate of 10 °C·min^{–1}.

X-ray photoelectron spectroscopy (XPS) profiles were obtained using Al K α ($h\nu = 1486.6 \text{ eV}$) radiation on a Thermo Scientific K α spectrometer. Charging effects were corrected using the C1s peak (adventitious carbon contamination) with BE fixed at 284.8 eV.

Temperature-programmed oxidation (TPO) measurements were carried out in a quartz tube reactor equipped with a TCD. The catalysts (30 mg) were pre-treated at 300 °C for 30 min in a flowing stream of high-purity He. After cooling to room temperature, a 10% O₂ in N₂ gas mixture (50 mL·min^{–1}) was introduced. The programming temperature was controlled from room temperature to 800 °C at a rate of 10 °C·min^{–1}.

2.4. Catalytic activity and stability tests

Catalytic activity measurements for DRM over the Ni/MCM-41 catalysts were performed in a fixed-bed reactor with an internal diameter of 8 mm. A 0.1 g sample of each calcined catalyst (40–60 mesh) was mixed with 0.5 g of quartz sand. The catalysts were reduced *in situ* with pure H₂ (30 mL·min^{–1}) at 700 °C for 2 h, followed by N₂ purging. Then, a mixture of CO₂ and CH₄ (CH₄:CO₂ = 1:1, total flow rate of 75 mL·min^{–1}) was introduced. Catalytic performance was evaluated from 450 to 800 °C. The products CO, H₂, CH₄, and CO₂ from the outlet were separated by a packed column (TDX-01) and then analyzed by an on-line gas chromatograph (Shimadzu, GC-2014) equipped with a TCD. Conversions of CH₄ and CO₂, turnover frequency (TOF) of CH₄, selectivity of H₂ and CO, as well as the molar ratio of H₂/CO, were determined using the corresponding flow rates at the inlet and outlet.

$$\text{CH}_4 \text{ conversion: } C_{\text{CH}_4} = \frac{F_{\text{CH}_4,\text{in}} - F_{\text{CH}_4,\text{out}}}{F_{\text{CH}_4,\text{in}}} \times 100\%$$

$$\text{CO}_2 \text{ conversion: } C_{\text{CO}_2} = \frac{F_{\text{CO}_2,\text{in}} - F_{\text{CO}_2,\text{out}}}{F_{\text{CO}_2,\text{in}}} \times 100\%$$

$$\text{Molar ratio of H}_2/\text{CO: } \frac{n_{\text{H}_2}}{n_{\text{CO}}} = \frac{F_{\text{H}_2,\text{out}}}{F_{\text{CO},\text{out}}} \times 100\%$$

$$\text{TOF of CH}_4: \text{TOF}_{\text{CH}_4} = \frac{\text{The number of molar of CH}_4 \text{ converted per hour}}{\text{The number of molar of surface Ni}}$$

3. Results and discussion

3.1. Synthesis and characterization of Ni/MCM-41 samples

MCM-41 was synthesized by our previously reported one-step method [25]. TEOS was used as the silicon source, CTAC was used as the template, and ammonium hydroxide solution acted as the base. The resulting solid was collected after synthesis at ambient temperature. The synthesized MCM-41 was characterized by N₂ adsorption-desorption, XRD, SEM, and TEM to determine the texture, long-range order, and morphology (Fig. S1 and Table S1). The TEM image of the MCM-41 material clearly showed a typical regular mesoporous structure with hexagonal pores. The SEM image showed a uniform particle shape, with particle sizes in the range of 50 to 200 nm. XRD patterns showed wall thicknesses (the difference between the average pore size and the unit cell parameter) of 0.91 nm, which was similar to the literature values [26]. The N₂ sorption results revealed a specific surface area of 1042 m²·g^{–1}, pore volume of 0.897 cm³·g^{–1}, and mesoporous pore diameter of 3.44 nm.

A schematic for the preparation of the Ni_{in}/MCM-41 catalyst is displayed in Fig. 1. First, the calcined MCM-41 was dried in vacuum at 100 °C for 12 h to remove adsorbed water in the mesopores. Then, the MCM-41 powder was added to an ethanol solution of nickel nitrate with stirring. Nickel nitrate was uniformly dispersed into the mesopores owing to the capillary action of the MCM-41 mesopores with ethanol solution. After calcination in air and reduction in hydrogen the Ni_{in}/MCM-41 catalyst with uniformly dispersed Ni particles and 10 wt% Ni loading into the mesopores was obtained. For comparison, we prepared an ~10 wt% Ni_{out}/MCM-41 catalyst with external Ni

Fig. 1. Schematic diagram of the synthesis strategy of Ni_{in}/MCM-41.

NPs by direct impregnation without removing the template of MCM-41 in the mesopores. An ethanol-water mixture was used as the solvent, and the 10 wt% Ni_{in&out}/MCM-41 sample with Ni NPs on both internal and external surface areas of MCM-41 was obtained.

The N₂ adsorption-desorption isotherms and the corresponding Barrett-Joyner-Halenda (BJH) pore size distribution curves for the Ni/MCM-41 catalysts are depicted in Fig. 2. All the samples showed type IV isotherms, which are indicative of a mesoporous structure, according to the IUPAC classification. The specific surface areas of Ni_{in}/MCM-41, Ni_{in&out}/MCM-41, and Ni_{out}/MCM-41 were 537, 629, and 734 m²·g⁻¹, respectively. The pore volumes of the three catalysts were 0.505, 0.676, and 0.737 cm³·g⁻¹, respectively, which were smaller than that of the MCM-41 support (0.897 cm³·g⁻¹). This may be due to the blocking of some mesopores by the Ni NPs, suggesting that the Ni NPs were at least partly encapsulated into the mesopores. The pore size distributions, evaluated by the BJH model, corresponded to narrow and uniform mesopores (2.64–2.76 nm) for all Ni/MCM-41 catalysts (Table 1). It should be noted that among the three Ni/MCM-41 samples, Ni_{in}/MCM-41 had a much smaller pore volume (0.505 cm³·g⁻¹) and pore diameter (2.64 nm), which implied that a substantially larger number of Ni NPs were confined in the hexagonal mesopores of MCM-41.

Characterization by XPS, TEM, and EDX mapping was performed to explore the fine structures of the Ni NPs and supports on the three Ni/MCM-41 catalysts (Fig. 3 and Figs. S2 and

Fig. 2. N₂ adsorption-desorption isotherms of Ni_{in}/MCM-41, Ni_{in&out}/MCM-41 and Ni_{out}/MCM-41.

Table 1

The physicochemical properties of the various fresh Ni/MCM-41 catalysts determined by N₂ sorption.

Sample	S_{BET} (m ² ·g ⁻¹)	V (cm ³ ·g ⁻¹)	d (nm)
Ni _{in} /MCM-41	537	0.505	2.64
Ni _{in&out} /MCM-41	629	0.672	2.66
Ni _{out} /MCM-41	734	0.737	2.76

S3). The presence of reduced Ni⁰ metal in all three Ni/MCM-41 samples was confirmed by XPS. Characteristic peaks of Ni 2p_{3/2} and Ni 2p_{1/2} appeared at 852.7 and 870.4 eV, respectively. Figs. 3(a) and 3(b) show the high-resolution TEM images of Ni_{in}/MCM-41, as viewed from two different growth directions (α - and z -axis). These results clearly showed that Ni NPs were uniformly confined in the hexagonal channels and mesopores of MCM-41, with the average diameter of the Ni NPs being 3.0 nm. In line with the TEM images, the EDX mapping image of Ni_{in}/MCM-41 (Fig. 3(c)) showed the Ni element was uniformly distributed in the pores of the MCM-41 support. In contrast, the TEM image of the Ni_{out}/MCM-41 catalyst (Fig. S4) showed that Ni NPs were mostly distributed on the outer surface of MCM-41, with the statistical Ni particle size being about 7.8 nm. Since the mesopores were blocked by the templates during Ni incorporation, we could not find confined Ni NPs within the mesopores based on the TEM images (Fig. 3). The EDX mapping image of Ni_{out}/MCM-41 (Fig. S5) showed that the Ni element was randomly distributed on the outer surface of the MCM-41 support, which agreed with the N₂ sorption and TEM results. The Ni_{in&out}/MCM-41 sample was prepared by impregnation with a water-ethanol solvent having weaker capillary action. The TEM images (Fig. S6) showed that some of the smaller Ni NPs were in the mesopores of the MCM-41, while much larger Ni NPs were unconfined and dispersed on the outer surface of MCM-41. Therefore, the Ni NPs seemed to be unevenly dispersed on the internal and external pores of MCM-41 having a large size deviance of 0.5 nm for a mean particle size of 3.0 nm.

In agreement with the TEM images, XRD patterns of the reduced Ni/MCM-41 samples showed a similar structural trend. The XRD pattern of the reduced Ni_{in}/MCM-41 catalyst (Fig. 4) did not show any diffraction peak for Ni, suggesting the small size of the Ni NPs. In contrast, peaks due to Ni(111) and Ni(200) facets were observed at 44.5° and 51.8° (PDF, No.

Fig. 3. (a,b) TEM images of Ni_{in}/MCM-41; (c-f) EDX mapping profiles.

04-0850), respectively, in the XRD pattern of the $\text{Ni}_{\text{out}}/\text{MCM-41}$ sample. The particle size of $\text{Ni}(111)$ was calculated to be 6.7 nm using the Scherrer equation (shape factor, $K = 0.89$). In the case of the $\text{Ni}_{\text{in\&out}}/\text{MCM-41}$ catalyst having both internal and external Ni NPs, the diffraction peak due to the $\text{Ni}(111)$ crystal facet was observed, while the $\text{Ni}(200)$ diffraction peak was diminished. The XRD patterns of the calcined $\text{Ni}/\text{MCM-41}$ catalysts (Fig. S7) showed the same trend for the reduced samples, implying that the Ni NPs located at the internal or external pores of MCM-41 may exhibit different catalytic properties for the methane dry reforming reaction.

Finally, H_2 -TPR profiles were obtained to reveal the reduction of calcined $\text{NiO}/\text{MCM-41}$ samples with different oxide-support interactions. As shown in Fig. 5, the high-temperature (595 °C) reduction peak of the $\text{Ni}_{\text{in}}/\text{MCM-41}$ catalyst was attributed to the reduction of the NiO species confined in the mesopores, while the small reduction peak at 335 °C was assigned to the trace amount of NiO on the outer surface of MCM-41. The high reduction temperature of the former indicated strong metal-support interaction for $\text{Ni}_{\text{in}}/\text{MCM-41}$. This H_2 -TPR profile again confirmed that Ni NPs were predominantly (about 97%) located in the internal channels of MCM-41, consistent with the N_2 sorption, TEM, mapping images, and XRD pattern results. In comparison, the reduction of the NiO species of $\text{Ni}_{\text{out}}/\text{MCM-41}$ majorly occurred at 382 °C (external surface, ~60%), with a small degree of NiO reduction occurring at 544 °C. This lower reduction temperature indicated weak interaction between the abundant external NiO species and the support. The $\text{Ni}_{\text{in\&out}}/\text{MCM-41}$ catalyst showed reduction peaks at 335 °C (external surface, ~10.3%) and 617 °C (internal channel, ~89.7%), indicating that the NiO NPs were distributed both inside and outside the pores of MCM-41.

3.2. Methane dry reforming reactions over the three $\text{Ni}/\text{MCM-41}$ catalysts

The three $\text{Ni}/\text{MCM-41}$ samples were tested in methane dry reforming reactions at varying temperatures and 1 atm. The equilibrium compositions of species, at diverse reaction temperatures, were calculated by HSC Chemistry software (Fig. 6(a)) based on the minimum Gibbs free energy calculation. The

Fig. 4. XRD patterns of the $\text{Ni}_{\text{in}}/\text{MCM-41}$, $\text{Ni}_{\text{in\&out}}/\text{MCM-41}$ and $\text{Ni}_{\text{out}}/\text{MCM-41}$.

Fig. 5. H_2 -TPR profiles of $\text{Ni}_{\text{in}}/\text{MCM-41}$, $\text{Ni}_{\text{in\&out}}/\text{MCM-41}$ and $\text{Ni}_{\text{out}}/\text{MCM-41}$.

equilibrium conversion values at temperatures from 0–1000 °C can be obtained from this graph, as shown by the dotted line in Fig. 6(b). It was noted that methane conversion over $\text{Ni}_{\text{in}}/\text{MCM-41}$ nearly reached the equilibrium value, having a gas hourly space velocity (GHSV) of 45000 $\text{mL}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$. This was 10%–20% higher than the conversion over $\text{Ni}_{\text{out}}/\text{MCM-41}$, suggesting that the confined smaller Ni NPs (~3 nm) in the limited mesopores have high activities. Additionally, the initial conversion of methane and carbon dioxide in the DRM reaction, at different temperatures ranging from 450–800 °C, is displayed in Fig. 6(b). Due to the high endothermicity of the dry reforming reactions ($\Delta H = 247 \text{ kJ}\cdot\text{mol}^{-1}$), the conversion of methane and carbon dioxide increased gradually with temperature over two of the $\text{Ni}/\text{MCM-41}$ catalysts. However, the conversion of methane was always lower than that of carbon dioxide at specific reaction temperatures, due to the occurrence of the reverse water-gas shift reaction (RWGS , $\text{CO}_2 + \text{H}_2 = \text{CO} + \text{H}_2\text{O}$) over the selected catalyst.

The stabilities of the three catalysts were compared at 700 °C (Fig. 7(a)). For the $\text{Ni}_{\text{in}}/\text{MCM-41}$ catalyst, the initial conversions of methane and carbon dioxide were 72% and 82%, respectively, with an initial TOF_{CH_4} of 667 h^{-1} . After a long reaction time (200 h), only slight activity loss (0.7%) was observed, with a nearly constant TOF of 662 h^{-1} and Ni dispersion of 29% (Table 2). This implies that the $\text{Ni}_{\text{in}}/\text{MCM-41}$ catalyst was quite stable on-stream, as compared to the reported activity performance of Ni/SiO_2 or Ni/SBA catalysts (Table S2). In contrast, the $\text{Ni}_{\text{out}}/\text{MCM-41}$ catalyst showed initial conversions of methane and carbon dioxide at 65% and 73%, respectively. However, this catalyst rapidly deactivated within 12 h, and the conversions of methane and carbon dioxide reduced to 39% and 50%, respectively. After the initial rapid decrease in activity at 12 h, the deactivation rate decreased, with the conversions of methane and carbon dioxide being 32% and 44%, respectively, after 60 h. The activity decreased by 17.9% after 60 h and the Ni dispersion changed from 13.8% to 9.6% over the $\text{Ni}_{\text{out}}/\text{MCM-41}$. The $\text{Ni}_{\text{in\&out}}/\text{MCM-41}$ sample also showed an obvious activity loss of 14% after 60 h, with the TOF dropping from 656 to 563 h^{-1} (Table 2).

Fig. 6. (a) Thermodynamic equilibrium plots for DRM at 1 atm, from 0–1000 °C; (b) Conversion of CH₄ and CO₂ for DRM at different temperatures (450–800 °C). Conditions: $P = 1$ atm, inlet feed ratio of CH₄:CO₂ = 1:1, GHSV = 45000 ml·g⁻¹·h⁻¹.

Fig. 7. Stability tests over 200 h with conversion of CH₄ (a), and molar ratio of H₂/CO (b). Conditions: $P = 1$ atm, $T = 700$ °C, catalyst = 0.1 g, inlet feed ratio of CH₄:CO₂ = 1:1, GHSV = 45000 ml·g⁻¹·h⁻¹.

Table 2

The steady state TOF_{CH₄} of various Ni/MCM-41 catalysts during dry reforming of methane at 700 °C and their variation of activity and dispersion.

Sample	Ni loading ^a (wt%)	Ni dispersion ^b (%)		TOF ^c (h ⁻¹)		Activity loss (%)
		$t = 10$ min	$t = 60$ h	$t = 10$ min	$t = 60$ h	
Ni _{in} /MCM-41	10.1	29.1	28.5 ^d	667	662 ^d	0.7
Ni _{in&out} /MCM-41	9.7	27.5	20.1	656	563	14
Ni _{out} /MCM-41	9.8	13.8	9.6	1260	1034	17.9

^a Determined by ICP.

^b Determined by CO chemisorption.

^c in mol_{CH₄}·mol⁻¹_{surf. Ni}·h⁻¹

^d Calculated at the reaction time of $t = 200$ h.

Furthermore, changes in the molar ratio H₂/CO were recorded as a function of the reaction time, as shown in Fig. 7(b). It was found that the H₂/CO value was always slightly lower than 1.0 due to the RWGS reaction. For the Ni_{in}/MCM-41 sample, the H₂/CO value remained at around 0.86 during the 200 h test. The H₂/CO ratio dropped to 0.80 and 0.83, respectively, on the Ni_{out}/MCM-41 and Ni_{in&out}/MCM-41 samples, suggesting the disparity of the Ni NP properties in the internal or external pores of the MCM-41 changed the RWGS side reaction. It can generally be concluded that the confined Ni_{in}/MCM-41 catalyst showed significantly higher activity and stability, although a slight loss in activity was still observed after a long reaction time.

3.3. Characterization of the spent Ni/MCM-41 catalyst after the

methane dry reforming reaction

Aiming to explore the superior performance of Ni_{in}/MCM-41, we characterized the three Ni/MCM-41 catalysts after the reaction by TEM, XRD, Raman, TPO, and TGA. The XRD spectra for the three spent Ni/MCM-41 samples are displayed in Fig. 8. The much sharper diffraction peaks of Ni(111) at $2\theta = 44.5^\circ$ and Ni(200) at $2\theta = 51.8^\circ$ as compared to the case of the fresh samples indicated that the Ni NPs were sintered on all three Ni/MCM-41 samples. The high-temperature reaction led to an increase in the Ni(111) particle size, 4.0, 9.2, and 18 nm for Ni_{in}/MCM-41, Ni_{out}/MCM-41, and Ni_{in&out}/MCM-41, respectively, as calculated using the Scherrer equation. It should be noted that both Ni_{out}/MCM-41 and Ni_{in&out}/MCM-41 gave a new diffraction peak at $2\theta = 25.8^\circ$, which was assigned to the (002)

Fig. 8. XRD patterns of the spent $\text{Ni}_{\text{in}}/\text{MCM-41}$ for 200 h, the spent $\text{Ni}_{\text{in\&out}}/\text{MCM-41}$ and $\text{Ni}_{\text{out}}/\text{MCM-41}$ for 60 h after reaction at 700 °C.

peak of graphitized carbon (Graphite-2H; PDF No. 41-1487). This peak indicated that a large amount of graphitized carbon was deposited on the two Ni samples, which may be responsible for the fast catalyst deactivation.

TEM was used to observe carbon deposition and Ni particle evolution on the spent catalysts. As shown in Figs. 9(a) and 9(b), the Ni NPs of the $\text{Ni}_{\text{in}}/\text{MCM-41}$ catalyst grew slightly, to 4 nm, after 200 h, although graphitized carbon nanotubes were not formed on the surface. However, for the $\text{Ni}_{\text{out}}/\text{MCM-41}$ catalyst, many whisker-like carbon nanotubes were formed after 60 h, and the particle was sintered to 16.7 nm, as shown in Fig. 9(c). These results were in accordance with the XRD patterns, as indicated in Fig. 8. With further magnification, we could clearly see that the surface of the metal Ni was coated with multiple layers of carbon sheets (Fig. 9(d)). This may prevent contact of the Ni metal with the reactants, resulting in deactivation of the catalyst. Interestingly, as shown in Fig. S8, in the case

Fig. 9. (a, b) TEM images of $\text{Ni}_{\text{in}}/\text{MCM-41}$ after reaction at 700 °C for 200 h; (c, d) TEM images of $\text{Ni}_{\text{out}}/\text{MCM-41}$ after reaction at 700 °C for 60 h.

of $\text{Ni}_{\text{in\&out}}/\text{MCM-41}$, some of the Ni NPs confined in the mesopores after the reaction had similar properties to those of the $\text{Ni}_{\text{in}}/\text{MCM-41}$ catalyst, with the average particle size increasing slightly to 3.8 nm. However, the Ni NPs distributed on the outer surface of the MCM-41 were drastically sintered, and the outer surfaces of these particles were coated with multiple layers of graphitized carbon, because of which the catalytic properties were similar to those of $\text{Ni}_{\text{out}}/\text{MCM-41}$ after the reaction. The TEM results were consistent with the XRD patterns, indicating that the confined Ni NPs impede the sintering of Ni particles, and more importantly, inhibit the formation of graphitized carbon on the catalyst surface. This enables the $\text{Ni}_{\text{in}}/\text{MCM-41}$ catalyst to maintain highly stable activity over a long reaction time.

Raman spectroscopy was used to characterize the carbon deposition of the spent catalysts, as shown in Fig. 10. The peak at 1320 cm^{-1} (D band) was assigned to sp^3 hybridized amorphous carbon, while that at 1580 cm^{-1} (G band) indicated the presence of graphitized carbon. The peak intensity ratio $I_{\text{D}}/I_{\text{G}}$ represents the degree of graphitization of the carbon. The $I_{\text{D}}/I_{\text{G}}$ value of $\text{Ni}_{\text{out}}/\text{MCM-41}$ (2.0) was lower than that for the $\text{Ni}_{\text{in\&out}}/\text{MCM-41}$ catalyst (4.0). Significantly, the G band for the $\text{Ni}_{\text{in}}/\text{MCM-41}$ catalyst at 1580 cm^{-1} was almost unobservable, indicating that amorphous carbon was the dominant carbon species on the surface, consistent with the XRD and TEM results.

TGA was performed on the spent catalysts to determine the amount of carbon deposited on the catalysts. As shown in Fig. 11(a), the weight loss below 100 °C was due to the removal of adsorbed water, while that above 100 °C was caused by the removal of deposited carbon. TGA (air atmosphere) measurements on the used Ni catalysts showed that oxidation of the three $\text{Ni}/\text{MCM-41}$ catalysts occurred at 350–400 °C. The weight increases were comparable, 1.1%, 1.2%, and 0.9% for $\text{Ni}_{\text{in}}/\text{MCM-41}$, $\text{Ni}_{\text{in\&out}}/\text{MCM-41}$, and $\text{Ni}_{\text{out}}/\text{MCM-41}$, respectively (Fig. 11(a)). When calculating the carbon deposition from the TGA measurements, we subtracted the increase due to Ni metal oxidation. After deducting this value at 300–400 °C, the weight loss of carbon deposition was 5.1% (200 h), 13.8% (60 h), and 19% (60 h) for $\text{Ni}_{\text{in}}/\text{MCM-41}$, $\text{Ni}_{\text{in\&out}}/\text{MCM-41}$, and $\text{Ni}_{\text{out}}/\text{MCM-41}$, respectively. Accordingly, the average carbon

Fig. 10. Raman spectra of the spent $\text{Ni}_{\text{in}}/\text{MCM-41}$ for 200 h, the spent $\text{Ni}_{\text{in\&out}}/\text{MCM-41}$ and $\text{Ni}_{\text{out}}/\text{MCM-41}$ for 60 h after reaction at 700 °C.

Fig. 11. TGA curves (a) and TPO profiles (b) the spent $\text{Ni}_{\text{in}}/\text{MCM-41}$ for 200 h, the spent $\text{Ni}_{\text{in\&out}}/\text{MCM-41}$ and $\text{Ni}_{\text{out}}/\text{MCM-41}$ for 60 h after reaction at 700 °C

deposition rates were calculated to be 0.26, 2.3, and 3.2 $\text{mg}\cdot\text{g}_{\text{cat}}^{-1}\cdot\text{h}^{-1}$, respectively, with the carbon formation rates of the latter two Ni samples being 8.9 and 12.2 times higher than that of the $\text{Ni}_{\text{in}}/\text{MCM-41}$ catalyst. The heavier carbon deposition on the unconfined $\text{Ni}/\text{MCM-41}$ sample was also evidenced by the TEM, XRD, and Raman results.

The different types of carbon on the Ni surface were further confirmed by TPO measurements, as illustrated in Fig. 11(a). The oxidation temperature of $\text{Ni}_{\text{in}}/\text{MCM-41}$ was 542 °C, while $\text{Ni}_{\text{in\&out}}/\text{MCM-41}$ and $\text{Ni}_{\text{out}}/\text{MCM-41}$ showed much higher carbon oxidation temperatures of 623–643 °C. After calibration of the TPO profile peaks (Fig. 10(b)), the quantitative ratios of the carbon deposition weight were approximately 1:2.8:3.5 for $\text{Ni}_{\text{in}}/\text{MCM-41}$, $\text{Ni}_{\text{in\&out}}/\text{MCM-41}$, and $\text{Ni}_{\text{out}}/\text{MCM-41}$, consistent with the TGA weight gains of 5.1% (200 h), 13.8% (60 h), and 19% (60 h). These results also suggested that the amorphous carbon accumulated on the $\text{Ni}_{\text{in}}/\text{MCM-41}$ surface may vaporize to form CO at a lower oxidation temperature (542 °C) and lead to much higher reactivity in the DRM, without deactivating the catalyst by carbon coverage. However, the thick carbon nanotubes covering the sintered large Ni NPs ($\text{Ni}_{\text{in\&out}}/\text{MCM-41}$ and $\text{Ni}_{\text{out}}/\text{MCM-41}$) were difficult to vaporize, and they gradually coating the Ni particles, causing rapid deactivation of the catalyst.

To understand the formation of different types of carbon in the confined channels and outside the mesoporous MCM-41, we previously used computer modelling for representing different carbon clusters (i.e., C_1 , C_{12} , C_{20} , C_{40} , and C_{60}) on a confined structure (Ni_{55} cluster) and an unconfined $\text{Ni}(111)$ surface [21]. The results suggested that on a confined small-sized Ni_{55} cluster, the C_1 atoms preferred to be adsorbed separately instead of aggregating into larger sp^2 clusters or caps of nanotubes, thus preventing carbon formation. However, on the unconfined $\text{Ni}(111)$ surface, C_1 atoms tended to rapidly aggregate into larger-sized C_{12} – C_{60} , with sp^2 carbon clusters having much lower formation energies, leading to formation of substantial carbon nanotubes. This can partly explain the disparity in carbon formation on the confined and unconfined Ni surfaces from the viewpoint of molecular modelling.

4. Conclusions

In this work, we developed a simple method for encapsulating uniform Ni NPs into the straight channels of MCM-41 via ethanol-induced capillary action. The confined catalyst showed 10 wt% Ni loading, with a Ni particle size around 2 nm, and strong metal-support interactions between NiO and silicon oxide. Under the test conditions (700 °C, 1 atm, GHSV = 45000 $\text{mL}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$), the encapsulated $\text{Ni}/\text{MCM-41}$ catalyst maintained high methane conversion for 200 h (72%, close to the equilibrium conversion) and a high TOF of 667 $\text{mol}_{\text{CH}_4}\cdot\text{mol}_{\text{surfNi}}^{-1}\cdot\text{h}^{-1}$. Additionally, no obvious Ni NP agglomeration was observed after the reaction time of 200 h, as shown by TEM images ($d = 3\text{--}4$ nm). TGA experiments revealed an average carbon formation rate of 0.26 $\text{mg}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$. In comparison, the unconfined $\text{Ni}/\text{MCM-41}$ rapidly deactivated within 12 h. After 60 h, the Ni particle size increased to 16.7 nm, and the surface of the catalyst was covered by carbon nanotubes, resulting in a high average carbon deposition rate of 3.2 $\text{mg}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$. This impeded further contact of the metal center and the gas feedstock, leading to rapid deactivation. This work provides a facile and effective approach for the synthesis of anti-sintering, carbon-resistant confined Ni catalysts operating at high temperatures.

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Graphical Abstract

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Facile immobilization of Ni nanoparticles into mesoporous MCM-41 channels for efficient methane dry reforming

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The developed encapsulated Ni/MCM-41 catalyst highly rendered metal sintering and carbon deposition at 700 °C and exhibited long-term (200 h) high activity for DRM.

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限域Ni/MCM-41催化抗积碳和金属烧结的甲烷干重整反应

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摘要: 干重整反应为同时转化两种主要的温室气体甲烷和二氧化碳为合成气(CO和H₂)。发展干重整高温反应是转化工业废气(如焦炉煤气、煤制油尾气等)为合成气平台分子的有效手段。由于廉价的金属镍具有良好的甲烷解离能力, 因此干重整反应中二氧化碳的解离很关键, 可添加如MgO, BaO, CaO等碱土氧化物来加强二氧化碳的吸附, 或添加具有氧空位的CeO₂, ZrO₂, La₂O₃的氧化物来捕集二氧化碳。双金属NiFe催化剂中, Fe通过将CO₂还原为CO和FeO来激活CO₂, 然后FeO可通过氧化还原反应将解离的C*转化为CO和Fe, 从而实现高温下活化CO₂和表面C去除的完美结合。

干重整反应面临高温下催化剂金属中心烧结和催化剂表面积碳严重的问题, 而将活性金属粒子限域是一种有效阻止金属高温烧结的方法。本文利用乙醇诱导的毛细管作用力, 发展了均匀负载Ni纳米粒子于MCM-41直型孔道结构内的简易方法。该限域结构催化剂的Ni金属负载量为10 wt%, X射线粉末衍射(XRD)测试显示无明显的Ni衍射峰, 表明Ni颗粒高度分散, 透射电子显微镜(TEM)表征结果表明Ni颗粒大小为2 nm左右, Ni颗粒主要分布在MCM-41的孔道内。程序升温还原

(TPR)表明该限域结构催化剂具有较高的还原温度,说明NiO与硅氧化物之间有较强的相互作用.在反应条件下(700 °C,常压,空速为45000 mL/g/h),催化剂具有高的甲烷转化率(72%,接近该温度下的平衡转化率),TOF达到667 mol_{CH₄}/mol_{surf. Ni}/h.经过200 h反应后,甲烷转化率未见明显下降,H₂/CO摩尔比维持在0.87左右.反应后TEM结果显示,Ni颗粒未见明显团聚(其平均粒径为3–4 nm左右),没有观察到Ni颗粒被碳包覆的现象.同时,反应后催化剂的拉曼光谱测试结果表明,催化剂上积碳为无定型碳,程序升温氧化(TPO)测试说明这种无定型碳更容易被气化,不会导致催化剂失活,热重分析(TGA)表明其平均积碳速率为0.26 mg/g/h.对比Ni纳米粒子负载于MCM-41外表面的催化剂,其甲烷初始转化率为65%,并且在反应开始后的12 h内快速失活.反应60 h后催化剂的XRD测试结果表明,Ni的衍射峰变强,Ni晶粒尺寸增大,并且出现了明显的石墨化碳的衍射峰.进一步TEM结果显示,平均Ni颗粒尺寸增大到16.7 nm,且催化剂表面布满积碳生成的碳纳米管,从高分辨TEM结果可以看出,大颗粒的Ni表面被多层石墨化碳覆盖.TPO测试结果显示,这种碳更难被气化,TGA分析得出平均积碳速率达到3.2 mg/g/h,是限域结构催化剂的12倍.这种石墨化碳阻断了金属中心和反应物分子间的接触,导致催化剂失活.

关键词: 甲烷干气重整; 限域结构; CO₂利用; 抗积碳; 高温稳定催化剂

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