Assembly of ordered mesoporous alumina-supported nickel nanoparticles with high temperature stability for CO methanation

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The high-temperature methanation of CO is an important reaction in the processes used to produce substitute natural gas, while the Ni-based catalysts prepared using the conventional impregnation method tend to deactivate under high-temperature reaction conditions. This paper describes the design and assembly of ordered mesoporous alumina (OMA) using highly disperse ~5 nm nickel nanoparticles (Ni NPs), via a one-pot, evaporation-induced self-assembly (EISA) method. Small-angle X-ray diffraction (XRD), transmission electron microscope (TEM), and N₂ adsorption and desorption results revealed that this catalytic material had highly ordered mesopores, which were retained even after long-term stability tests. The catalyst exhibited excellent sintering-resistant and anti-coking properties in high-temperature CO methanation reactions (60% CO conversion after 50 hours of accelerated deactivation at 700°C). The improved catalytic performance was attributed to the matrix of the OMA, which effectively improved the dispersion of the nickel particles, and prevented the Ni NPs from sintering, via a particle migration and coalescence mechanism. The Ni-OMA catalyst demonstrated here shows promise for high-temperature methanation.

The production of substitute natural gas (SNG) from coal and biomass is significant in areas such as China and India where the available quantity of domestic natural gas cannot meet the enormous demand [1]. SNG is typically produced via the gasification of feedstock and CO methanation reaction. In industry, the CO methanation is typically performed in an adiabatic fixed-bed reactor. However, the reaction is highly exothermic ($\Delta H_{298\text{ K}} = 206.1 \text{ kJ mol}^{-1}$), and the hotspot tend to form in the catalyst bed; the methanation catalyst can be deactivated at such high reaction temperature (typically above 550°C) [2]. Industrial high-temperature methanation processes favor more energy-efficient designs. For example, in Topsøe's recycle energy-efficient methanation process (TREMP), the exit temperature at the point after the first methanation reactor is approximately 650–700°C [3]. Practical methanation

catalysts therefore need to be resistant to both sintering and coking at high temperature [4].

As a result of their low cost and relatively high activity, Ni-based catalysts have been widely applied in large-scale industrial methanation processes [3,4]. The size of the Ni nanoparticles (NPs) is intimately related to the performance of the catalysts. Ni NPs, which have a small crystal size, not only have a high surface-to-volume ratio, but also show an improved resistance to coke formation [5,6]. However, Ni NPs tend to grow larger through particle migration and coalescence as a result of their low Tammann temperature (590°C), especially under the long-term application of extreme reaction conditions (e.g., temperature > 600°C) [7]. The suppression of the sintering of Ni NPs via rational design is critical to the improvement of the performance of Ni-based catalysts. Much effort has been dedicated to tackling this matter, and materials with well-defined, ordered mesopores can confine metal NPs to maintain a relatively high degree of dispersion, and increase the high-temperature stability of the NPs [8–10].

Nanoscale metal particles of traditional, supported catalyst materials, which were prepared via conventional impregnation, were dispersed on the surface of a bulk matrix composite consisting of substrate oxide particles (Scheme 1a). The metal particles grew, and sintered gradually, under the high-temperature conditions. It was shown previously that Ni/Al₂O₃ catalysts prepared via the conventional impregnation method lost catalytic activity for methanation under industrial, high-temperature operating conditions [11]. Here, ordered mesoporous alumina (OMA)-supported nickel oxide was obtained using a modified one-pot method. Upon reduction, the Ni NPs were highly dispersed and stabilized in the pore channels of the OMA (Scheme 1b) [12–14]. We applied a Ni-OMA catalyst in a CO methanation reaction, and tested the stability of the catalysts in long-term high-temperature stability tests.

Two catalysts were synthesized with the nickel loading

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Scheme 1 Schematic illustration of (a) supported metal catalyst prepared using a conventional impregnation method, and (b) ordered mesoporous material-supported metal catalyst.

fixed at ca. 10 wt%. The Ni-OMA catalyst was prepared via a modified one-pot evaporation-induced self-assembly (EISA) method [15,16]. In a typical synthesis procedure, ~2.0 g of $(\text{EO})_{20}(\text{PO})_{70}(\text{EO})_{20}$ triblock copolymer (Pluronic P123, average $M_n = 5,800$) and 0.255 g of nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was dissolved in 10.0 mL of anhydrous ethanol under vigorous stirring. At the same time, 1.6 mL of 67 wt% nitric acid and 1.860 g of aluminum isopropoxide ($\text{Al}(\text{i-PrO})_3$) was dissolved in another 10.0 mL of anhydrous ethanol under vigorous stirring. Subsequently, the two solutions were mixed, and stirred for at least 6 h. Finally, the solution was placed in a drying oven, and subjected to the EISA process at 60°C for at least 48 h. A green solid xerogel was obtained after the EISA process. The removal of the organic template contained within the pores is an important step in the synthesis of ordered mesoporous materials. Calcination in air is the most popular and versatile technique used to achieve this. However, significant lattice shrinkage often takes place in ordered mesoporous materials at high temperatures [17]. Here, a thermogravimetric analysis (TGA) of the as-prepared catalysts was carried out in air, after the EISA process; three peaks (at 150, 210, and 320°C) were present in the differential thermal gravity (DTG) curve. Following a consideration of the TGA results, we used a four-stage calcination method: first, the gel was calcined using a 2°C min^{-1} ramping rate, until the temperature reached 150°C ; the temperature was then maintained for 2 h; then the temperature was increased to 210°C using a ramping rate of 2°C min^{-1} , and the temperature was maintained at 210°C for 4 h; next, the temperature was increased to 320°C using a ramping rate of 2°C min^{-1} , and the temperature was maintained at 320°C for 2 h; finally, the temperature was increased to 700°C using a ramping rate of 1°C min^{-1} , and the temperature was maintained at

700°C for 4 h, to enhance the high-temperature stability of the material. It was anticipated that, as a result of this treatment method, the Ni-OMA catalysts would maintain their ordered mesoporous structure under the long-term application of high reaction temperature. To provide a comparison, a supported Ni/ Al_2O_3 catalyst was synthesized using the conventional impregnation method. Both catalysts were reduced *in situ* in a mixed flow of H_2 and N_2 (H_2 : 10 mL min^{-1} , N_2 : 20 mL min^{-1}) at 700°C for 2 h. Prior to the catalytic activity tests, the catalysts were purged with N_2 (100 mL min^{-1}) for half an hour, to remove the adsorbed hydrogen.

The morphological properties of the as-synthesized Ni-based catalysts were obtained by measuring the N_2 adsorption/desorption at -196°C (Fig. 1a and Table 1). The isotherms for the as-prepared Ni-OMA materials showed a type IV curve with an H1-shaped hysteresis loop, indicating that the catalysts had a cylindrical channel. As a result of the high-temperature calcination, the Brunauer-Emmett-Teller (BET) surface areas of the Ni-OMA and Ni/ Al_2O_3 were less than $200 \text{ m}^2 \text{ g}^{-1}$. The pore size distributions for the Ni-OMA and OMA were similar, and the peaks in the curves were located in the range of 5–7 nm (Fig. 1b). As shown in Fig. 2a, the small-angle X-ray diffraction (XRD) patterns for the Ni-OMA showed strong (100) and (110) peaks associated with the P6mm symmetry; this provided evidence of the hexagonally ordered nature of the mesoporous structure. Fig. 2b shows the wide-angle XRD patterns for the as-prepared and reduced catalysts. The wide-angle XRD patterns for the as-prepared catalysts showed no apparent NiO diffraction peaks, demonstrating the high level of dispersion of the NiO in the OMA framework. For the reduced catalysts, the metallic Ni (200) peak for the Ni-OMA was broader than that for the Ni/ Al_2O_3 , in-

Figure 1 (a) Isotherms for the samples, before and after stability tests (P/P_0 : relative pressure); (b) pore size distributions for the Ni-OMA and Ni/Al₂O₃, before and after stability tests.

dicating that the Ni-OMA had a smaller average Ni particle size. The sizes of the metallic Ni particles in the Ni-OMA and Ni/Al₂O₃ (which was calculated for each material from the broadening of the Ni (200) peak, using the Scherrer equation) were approximately 5.7 and 9.3 nm, respectively.

The transmission electron microscope (TEM) images illustrate the morphologies of the reduced Ni-OMA (Fig. 3a), and Ni/Al₂O₃ (Fig. 3d). For Ni-OMA, the Ni NPs were uniformly dispersed inside the ordered mesoporous chan-

Figure 2 (a) Small-angle XRD patterns for the Ni-OMA; (b) wide-angle XRD patterns for various samples.

nels. In addition, the Ni NPs were isolated from each other, and the active sites of the metallic Ni NPs were fully exposed. The particle size distribution histogram shows that the Ni-OMA had a narrow size distribution, from 2.6 to 7.1 nm. The average Ni particle sizes were 5.1 and 10.8 nm for the Ni-OMA and Ni/Al₂O₃, respectively, which was in line with the XRD results. To allow a quantitative analysis of the metal dispersion, H₂-TPD (temperature programmed desorption) experiments were also performed

Table 1 Morphological properties for the samples, before and after stability tests

Sample	S_{BET}^a (m² g⁻¹)	V_{pore}^b (cm³ g⁻¹)	D_{pore}^c (nm)	Dispersion ^d (m² g _{Ni} ⁻¹)
OMA	216	0.54	6.7	N.A.
Al₂O₃	182	0.54	8.5	N.A.
Ni-OMA	196	0.40	5.0	10.5
Ni/Al₂O₃	160	0.41	7.6	4.5
The used Ni-OMA	120	0.31	5.6	18.0
The used Ni/Al₂O₃	79	0.20	17.5	3.1

a) BET surface area (S_{BET}) at $P/P_0 = 0.05-0.20$. b) Total pore volumes (V_{pore}) were obtained at $P/P_0 = 0.97$. c) Average pore diameters (D_{pore}) were calculated using the Barrett-Joyner-Halenda (BJH) desorption method. d) Metal surface areas were calculated from the H₂ pulse chemisorption.

Figure 3 (a) TEM image of the reduced Ni-OMA; (b) and (c) TEM and HRTEM images of the Ni-OMA after stability tests; (d) TEM image of the reduced Ni/Al₂O₃; (e) TEM image of the Ni/Al₂O₃ after stability tests.

over the nickel catalysts. The results showed a metal surface area of $10.5 \text{ m}^2 \text{ g}_{\text{Ni}}^{-1}$ for the Ni-OMA catalyst, more than two times larger than the value measured for the Ni/Al₂O₃ (Table 1). These results showed that the Ni-OMA catalyst had a smaller Ni particle size and a larger exposed Ni surface area, which were likely responsible for the higher activity in the CO methanation. The surface interaction between the NiO and Al₂O₃ in the catalysts was evaluated in H₂-TPR (temperature programmed reduction) experiments. No reduction peak was observed around 400°C for either Ni-OMA or Ni/Al₂O₃, implying the absence of dissociated bulk NiO species. Only one reduction peak was observed, at approximately 650°C; this peak was assigned to the reduction of NiO which was interacted strongly with the support [18]. The real nickel loadings of the catalysts were determined using inductively coupled plasma optical emission spectroscopy (ICP-OES). The nickel loadings for Ni-OMA and Ni/Al₂O₃ were 10.0 wt% and 9.8 wt%, respectively. The results indicated that the nickel loading values for these two catalysts were very similar.

Both catalysts were tested in methanation reaction performed from 300 to 500°C (N₂:H₂:CO = 6:3:1, 1 bar, GHSV = 60,000 mL g⁻¹ h⁻¹). As a reference, the CO thermodynamic equilibrium conversion in this temperature range was also given in Fig. 4a [19]. As expected, the Ni-OMA catalysts showed higher CO conversion and CH₄ yield values in the range of 300–500°C (Fig. 4a). The superior catalytic activity of the Ni-OMA was attributed to the smaller and more uniformly dispersed Ni NPs, which had a higher number of active sites exposed to the reactant gases. To avoid extremely lengthy stability tests, the stability tests on the nickel catalysts were performed using an accelerated deactivation process under high temperature [20]. The methanation reaction was first conducted at 400°C for 2 h, and then at 700°C for 50 h, and then at 400°C for another 2 h. The rate and composition of the feed gas were kept constant during the test. As shown in Fig. 4b, the CO conversion values for the two catalysts were close to the equilibrium limit at 700°C. However, there was an obvious difference in the second run at 400°C. The Ni/Al₂O₃ catalyst lost almost 30% of its initial activity (the activity dropped to 40%), clearly indicating that the catalyst was deactivated under the harsh reaction conditions. In contrast, the CO conversion performance of the Ni-OMA showed no drastic change after 50 h of accelerated deactivation; the activity decreased only slightly to 60%, illustrating the superior durability of the Ni-OMA catalyst under high temperature.

To explain the superior stability of the Ni-OMA, the spent catalysts (after the stability tests) were characterized using N₂ physisorption, XRD, TEM, and TGA. The isotherms for the spent Ni-OMA (Fig. 1a) retained a type IV curve, with H1-shaped hysteresis loop. The pore size distri-

Figure 4 (a) CO conversions and CH₄ yields at different temperatures for the Ni-OMA and Ni/Al₂O₃ catalysts; (b) CO conversions for the two catalysts, before and after 50 h of accelerated deactivation in the stability tests.

bution for the spent Ni-OMA (Fig. 1b) was also similar to that for the as-prepared Ni-OMA. The low-angle XRD patterns (Fig. 2a) showed diffraction peaks attributed to (100) and (110) plane reflections, which provided evidence of the ordered mesoporous structure. The ordered mesoporous structure could also be seen clearly in the TEM images of the spent Ni-OMA (Fig. 3b). These results demonstrated that the Ni-OMA retained its ordered mesoporous structure after the long-term stability tests performed under harsh conditions.

The Ni particle size for the spent Ni-OMA (calculated from the wide-angle XRD patterns) was approximately 6.1 nm, slightly larger than the particle size for the reduced Ni-OMA (Fig. 2b). The nickel particle size was 12.1 nm for the Ni/Al₂O₃, according to the wide-angle XRD patterns. TEM images of the spent Ni-OMA (Fig. 3b) showed that the good dispersion of the Ni NPs was maintained, with an average Ni particle size of 5.6 nm after the stability tests. The average Ni particle size for the spent Ni-OMA was only slightly larger than that for the reduced Ni-OMA, in accordance with the results calculated from the XRD patterns. For comparison, the Ni particle size for the Ni/Al₂O₃

increased from 10.8 to 12.3 nm, according to the TEM images (Figs 3d and e). Some sintered Ni particles were observed in the TEM images for the spent Ni/Al₂O₃. The growth of the Ni particles resulted in a reduction in the Ni surface area, and hence a decrease in the catalytic activity. An HRTEM image of the Ni-OMA taken after the stability tests (Fig. 3c) showed an Ni particle that was confined by a wall of OMA, and that had retained a size of approximately 5 nm, even after 50 h of the high-temperature reaction. As a result of the confinement imposed by the OMA, the Ni NPs retained their small size and high surface-to-volume ratio during the long-term, high-temperature stability tests, and showed improved catalytic activity after the accelerated deactivation process.

Graphitic carbon is a hard-oxidizing carbon species, and has a strong negative effect on catalytic activity [21]. Graphitic carbon peaks were clearly observed in the wide-angle XRD patterns for the spent Ni/Al₂O₃ (Fig. 2b). The intensity of the graphitic carbon peaks for the spent Ni-OMA was much lower. The results from the XRD patterns were in accordance with those from the TG curves (Fig. 5). The total weight loss from the Ni/Al₂O₃ was approximately 5%, and the weight loss above 500 °C, which corresponded to the graphitic carbon, was almost 2%. In comparison, the total weight loss from the spent Ni-OMA was not significant, and the weight loss above 400 °C was less than 1%. The anti-coking properties of the Ni-OMA were attributed to its smaller Ni NPs, which were stabilized by the OMA matrix, and had a better resistance to the formation of deposited carbon [12].

In summary, we synthesized Ni-OMA catalysts with an ordered mesoporous structure using a modified EISA method, and the catalysts exhibited high stability for the methanation of CO. As a result of the confinement imposed by the catalyst, the introduction of the Ni NPs into the ordered alumina mesopores effectively improved the dispersion of the nickel metal, and prevented the Ni NPs from

Figure 5 TGA profiles for the spent Ni-OMA and Ni/Al₂O₃.

sintering via a particle migration and coalescence mechanism. The Ni-OMA showed higher activity and superior stability in the high-temperature methanation reaction. It was also verified that the ordered mesoporous structure and the size distribution of the nickel particles were maintained after the long-term, high-temperature methanation reaction. The OMA was also effective in helping to resist the formation of carbon. This Ni-OMA methanation catalyst could be further improved via the addition of additives, or the introduction of a different kind of active metal.

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information The Experimental section is available in the online version of the paper.

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中文摘要 CO高温甲烷化反应是工业上生产合成天然气的重要反应, 采用传统的浸渍方法合成的镍基催化剂在高温的反应条件下容易发生烧结和积碳现象而导致失活。本文以蒸发引导的自组装方法为原理, 通过“一锅法”设计并合成了有序介孔氧化铝负载高分散镍纳米颗粒(粒径在5 nm左右)的催化剂。通过小角XRD、TEM和N₂物理吸附等表征验证了有序介孔结构的存在, 并且这种结构在长时间的高温稳定性测试后仍能保持。该催化剂在CO高温甲烷化反应中表现出良好的抗烧结、抗积碳性能。载体氧化铝的有序介孔结构是这种催化剂性能提升的关键, 因为有序介孔结构有利于改善活性组分镍颗粒的分散情况, 同时纳米级的介孔孔道可以限制镍颗粒在高温下通过颗粒迁移和聚集而烧结长大。