Studies on Syngas Production and Conversion
合成ガスの製造および転換に関する研究

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Preface

Syngas, a gas mixture consisting of H₂ and CO, is an important chemical raw material. It is used for producing a lot of downstream products through famous technical processes, like methanol synthesis, Fischer–Tropsch synthesis (FTS) and ammonia syngas etc. Syngas can be produced industrially from coal, petroleum, biomass gasification or the reforming of natural gas. In recent years, as coal and petroleum are excessively exploited, syngas is mostly produced by CH₄ steam reforming, during which CH₄ reacts with steam to generate CO and H₂ in high temperature. Nowadays, with the rapid development in industry, large amounts of CO₂ are unavoidably emitted into the air, consequently leading to serious greenhouse effect. Therefore, environmental pollution, especially in the greenhouse gas emission, has become a hot topic. At present, CO₂ reforming of methane has been receiving considerable attention, since the reaction converts two greenhouse gases (CH₄ and CO₂) to valuable syngas simultaneously. In addition, due to the potential reserves of shale gas and flammable ice, the more substitution of natural gas into coal and petroleum for producing downstream chemicals become more meaningful. Therefore, designing effective catalyst for syngas production from CO₂ reforming of methane is of great significance.

Dimethyl ether (DME) is widely used as basic chemical feedstock for producing many downstream substances such as methyl acetate, acetaldehyde, acetic acid, etc. Moreover, DME is known as one of the promising substitutes of petroleum-based fuels. Burning DME can effectively reduce the emission of environmental-unfriendly harmful matters, like soot, SOₓ and NOₓ. DME has high cetane number, which can replace the
diesel fuel or act as liquefied petroleum gas (LPG) for cooking or power generation. Generally, DME is produced through two ways: one is methanol dehydration on a single acidic catalyst and another is a tandem catalysis process including the initial syngas to methanol synthesis and the followed methanol dehydration to form DME over mixture catalysts. Therefore, developing effective catalyst for the production or conversion of DME has gradually attracted more attentions.

In chapter (1-2), syngas was first produced from CO$_2$ reforming of methane by Ni-based catalyst. For this reaction, carbon deposition on catalyst becomes the biggest challenge during the reaction, which can lead to catalyst deactivation. Here, Ni-based catalysts that exhibited strong ability for inhibiting carbon deposition and excellent catalytic performance were designed and prepared.

In chapter (3), DME synthesis was accomplished from syngas by a physically mixing catalyst consisting of Cu/ZnO/Al$_2$O$_3$ (CuZnAl) core and Silicoaluminophosphate-11 (SAPO-11) zeolite shell, in which syngas is converted to methanol on CuZnAl core catalyst and then methanol is hydrated to DME on SAPO-11 zeolite. The one-step synthesis of DME from syngas by CuZnAl/SAPO-11 catalyst with core-shell structure is very promising.
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Chapter 1

An in-situ synthesis of low-cost mesostructured nickel nanoparticles embedded carbon/silica composite via a solid–liquid grinding route and its application for the carbon dioxide reforming of methane

Ni-based mesoporous carbon/silica composite catalyst for effectively producing syngas was successfully synthesized via one-step solid–liquid grinding method without further reduction.
Abstract

A facile synthesis route for direct preparation of Ni-based mesoporous carbon/silica composite catalysts without further reduction was established successfully. The synthesis procedure was achieved by using the one-step solid–liquid grinding method with a mixture of SiO₂, soybean oil, and nickel acetyl acetonate. Calcination was then performed at different temperatures to obtain the Ni-based mesoporous carbon/silica composite catalyst. All experimental steps were conducted without solvent addition. In this catalyst preparation, soybean oil was used as the carbon source and provided a large surface area within the silica skeleton; Ni⁰ was used as the active metal. The active component Ni⁰ was formed directly during the soybean oil carbonization process. A series of Ni/SiO₂–C–X catalysts (X = 400–1100, X stands for the carbonization temperature) were applied for the CO₂ reforming of CH₄ reaction. The unreduced Ni-based catalyst showed a better catalytic activity than that of the reduced catalyst under hydrogen atmosphere because the NiO phase was in-situ reduced by the carbonized soybean oil under nitrogen. The Ni/SiO₂–C–500 catalyst showed high catalytic activity and stability in the continuous CO₂ reforming reaction of CH₄ at atmospheric pressure.

Keywords: Solid–liquid grinding, In-situ reduction, Mesostructure, Carbon/silica composite, Reforming
1.1. Introduction

With the increasing depletion of crude oil and liquid fuels and global environmental concerns, the development and utilization of greenhouse gases (including methane and carbon dioxide) into useful chemicals have received considerable attention all over the world. The CO$_2$ reforming of methane to produce syngas (\(\text{CO}_2 + \text{CH}_4 \rightarrow 2\text{CO} + 2\text{H}_2, \Delta H (298 \text{ K}) = 247 \text{ kJ} \cdot \text{mol}^{-1}\)) as a direct reaction of CO$_2$ and CH$_4$ has received widespread attention from both economic and environmental viewpoints in recent years. The generated syngas with an appropriate H$_2$/CO ratio of 1:1 is suitable for Fischer–Tropsch synthesis on Fe-based catalysts and oxosynthesis [1]. However, the main disadvantage preventing the large-scale industrial practice of CO$_2$ reforming CH$_4$ reaction is the rapid deactivation of catalysts because of the sintering of active metals and coke deposition [2–4]. Therefore, achieving high catalytic activity and catalyst stability remains a key task.

Noble metal catalysts have been studied for the CO$_2$ reforming of CH$_4$ reaction, whereas the high catalyst cost is a concern for industrial applications [5]. Nickel-based catalysts can exhibit excellent catalytic activity and are used in industrial applications because of its availability and low cost compared with noble-metal-based catalysts [6–8]. In recent decades, numerous Ni-based catalysts have been investigated by various methods. Impregnation method is widely used for preparing heterogeneous catalyst. Wang et al. [9] reported a CH$_4$/CO$_2$ reforming reaction over Ni/Al$_2$O$_3$ catalyst with the conventional impregnation method; this reaction generally results in catalyst deactivation because of carbon deposition. To resist carbon deposition and improve catalyst stability, considerable attention has been paid to the addition of promoters or noble metals by the co-impregnation method in the reforming reaction.
Yang et al. [10] found that Ni/γ-Al₂O₃ catalysts with the La₂O₃–CeO₂ dual promoters not only decreased the amount of carbon deposition but also improved the activity because of the alkaline function and electronic interactions between promoters and nickel. Tomishige et al. [11] reported that noble metal promoter Pt-doped Ni/Al₂O₃ catalyst showed excellent catalytic performance for CH₄/CO₂ reforming reaction.

The reported Ni-based catalysts were also prepared by various conventional methods such as co-precipitation, sol-gel method, and combined impregnation/sol-gel [12]. Djaidja et al. [13] investigated two series of Ni/MgO catalysts prepared by co-precipitation and then compared them with catalysts by the conventional impregnation method to decrease the strong interaction between the reduced metal and support. The sol-gel technique has been applied widely for the preparation of reforming catalysts. Ji et al. [14] studied that the sol-gel catalyst with small metallic particles exhibited catalytic activity and excellent coking resistivity. However, these methods of catalyst preparation use common solvents, which cause pollution and environmental damage. Therefore, the recovery and recycling of solvents as necessary measures are important [15].

The solid–solid grinding route has been widely applied in the field of catalytic chemistry as a green and promising technique for the fabrication of various catalysts with the simple heating of mixed solid powder containing desired metal salts [16–18]. Wang et al. [19] used the solid–solid grinding route to synthesize Cu/ZnO catalyst for ethanol synthesis from dimethyl ether (DME) and syngas. The catalyst with the ratio of Cu/ZnO = 4:6 was more active than that prepared by the conventional co-precipitation technique. This technique was also used to synthesize magnetite catalysts by a simple one-step process [18]. However, solid–solid grinding leads to a relatively small specific
surface area because of the absence of pores. Therefore, the development of simple and effective solid grinding methods for the large surface area of catalysts is required. Furthermore, the prepared catalysts are generally reduced prior to the reaction to obtain the active metal phase. Nevertheless, researchers have attempted to find a facile and green method of catalyst preparation and a method without reduction for catalytic reaction [20–22].

Herein, we report a facile synthesis route for the direct preparation of Ni-based mesoporous carbon/silica composite catalyst without further reduction process for the CO₂ reforming of CH₄ reaction. The synthesis procedure shown in Fig. 1.1 was achieved by using the one-step solid–liquid grinding method with a mixture of SiO₂, soybean oil, and nickel acetyl acetonate. Calcination was then performed at different temperatures to obtain the Ni-based mesoporous carbon/silica composite catalyst. In this catalyst structure, soybean oil was used as the carbon source and provided a large surface area within the silica skeleton. The active component of Ni⁰ particles was prepared directly during the soybean oil carbonization process. As-prepared Ni-based catalysts were employed for the CO₂ reforming of CH₄ reaction.

1.2. Experimental

1.2.1 Catalyst preparation

The commercially available silica pellet (Cariact Q50, Fuji Silysia Co., pellet size in diameter: 75–500 μm) is used as catalyst support. The soybean oil and nickel acetyl acetonate was purchased from Albis Supermarket and Kanto Chem.Co., respectively; these materials were used without further purification. A typical synthesis route of the
mesoporous Ni-based carbon/silica composite catalyst (Ni/SiO₂–C) via one-step synthesis route was performed to grind a mixture of SiO₂, soybean oil, and nickel acetylacetonate. The obtained wet solid was dried in vacuum for 1 h and then carbonized in the temperature range of 400–1100 °C for 5 h at a rate of 2 °C/min under N₂ atmosphere. The carbonized Ni/SiO₂–C–X series catalysts (X = 400–1100, X stands for the carbonization temperature) were applied for the CO₂ reforming of CH₄ reaction with or without further reduction (reduction conditions: pure H₂, flow rate = 40 mL/min, 1 bar pressure). The final Ni content in the Ni/SiO₂–C catalyst was 5 wt%.

1.2.2 Characterization

X-ray powder diffraction (XRD) patterns were measured with a Rigaku RINT 2400 diffractometer using Cu Kα radiation.

The N₂ sorption isotherms at liquid nitrogen temperature were measured by using a 3Flex analyzer (Micromeritics Instrument Co.).

The morphology of Ni-based catalyst was observed by using a JEOL JSM–6360LV scanning electron microscope (SEM) and JED–2300 energy dispersive spectrometer (EDS) for catalyst surface and mapping-section analysis.

The carbon deposition was performed on a NETZSCH STA 449F3 system thermogravimetric analyzer in flowing air in a temperature range from 50 °C to 900 °C with a heating rate of 10 °C/min.

1.2.3 Activity test

Catalytic performances for the CO₂ reforming of CH₄ reaction were investigated in a fixed-bed quartz reactor under atmospheric pressure. The Ni-based catalyst of 0.2 g was located by quartz wool in the center of a quartz tube and was reduced/not reduced at various temperatures in a pure H₂ flow for 1 h. The reaction gas with a mixture of
CH₄, CO₂, and Ar (CH₄/CO₂/Ar = 5:5:1) was introduced into the reactor bed at a heating rate of 10 °C/min. The gaseous products after the removal of water were analyzed by two online gas chromatographs (GCs) equipped with a thermal conductivity detector.

The conversion of CH₄ and CO₂ as well as the total carbon conversion (C_total) are calculated as follows: (Ar was regarded as the internal standard.)

1. The calculation of methane conversion:

\[
\text{CH}_4 \text{ conv.} (\%) = \frac{\text{CH}_4\text{before}/\text{Ar}_{\text{before}} - \text{CH}_4\text{after}/\text{Ar}_{\text{after}}}{\text{CH}_4\text{before}/\text{Ar}_{\text{before}}} \times 100\%
\]

2. The calculation of carbon dioxide conversion:

\[
\text{CO}_2 \text{ conv.} (\%) = \frac{\text{CO}_2\text{before}/\text{Ar}_{\text{before}} - \text{CO}_2\text{after}/\text{Ar}_{\text{after}}}{\text{CO}_2\text{before}/\text{Ar}_{\text{before}}} \times 100\%
\]

3. The calculation of total carbon conversion:

\[
\text{C}_{\text{total conv.}} (\%) = \frac{(\text{CH}_4\text{before} + \text{CO}_2\text{before})/\text{Ar}_{\text{before}} - (\text{CH}_4\text{after} + \text{CO}_2\text{after})/\text{Ar}_{\text{after}}}{(\text{CH}_4\text{before} + \text{CO}_2\text{before})/\text{Ar}_{\text{before}}} \times 100\%
\]

1.3. Results and discussion

1.3.1 Catalyst characterization

1.3.1.1 XRD analysis

The XRD patterns of Ni-based catalysts with different carbonization temperature are presented in Fig. 1.2. For carbonization temperature at 300 °C, no obvious diffraction peaks of Ni-based species were observed, except for a broad peak of silica support (Q50) at 21.0° [23]. The peaks at 37.2, 43.3, and 62.9° in the XRD patterns were attributed to NiO phase at calcination temperature at 400 °C [24, 25]. Simultaneously, the peaks of metallic Ni with low intensity at the diffraction angle appeared at 44.5°, 51.8°, and 76.6° in the XRD patterns when calcination temperature
increased from 300° to 400°, indicating that a small number of metallic Ni formed even under low carbonization temperature [5, 26, 27]. With the further increase in calcination temperature to 500 °C, the NiO peaks disappeared and the diffraction intensity of metallic Ni increased, thus implying that NiO particles were reduced completely during soybean oil carbonization. When the carbonization temperature ranged from 500–900 °C, the diffraction peaks of Ni⁰ became stronger because the metallic particles were sintered during higher calcination temperature than that during 300 °C or 400 °C. However, compared with those of Ni-based catalysts, the diffraction peaks of Ni⁰ became smaller and almost negligible for the Ni/SiO₂–C–1100 sample. The peaks at the diffraction angle 39.4°, 45.5°, and 48.7° for this sample were the Ni₂Si phase caused by the high carbonization temperature.

1.3.1.2 Textural property

The N₂ adsorption-desorption isotherms of Ni/SiO₂-C-X catalysts are shown in Fig. 1.3. All the samples exhibited typical type-IV adsorption isotherms with clear H3 hysteresis loops at higher relative pressure, suggesting the existence of mesopores. The pore size of mesopore was estimated at around 45 nm based on the curves of pore size distribution, which was important for improving catalytic activity. The textural characteristics of the calcined Ni-based catalysts and Q50 support were summarized in Table 1.1. However, we could not obtain the BET data for the carbonization temperature at 300 °C or 400 °C, thus subsequently leading to the incomplete carbonization of soybean because of the low carbonization temperature. The surface area and volume of Q50 support were 66.1 and 1.41 m³/g, respectively, which implied the absence of micropores for this support. Compared with Q50, the BET presented an enhanced surface area, particularly in a microporous surface area of Ni/SiO₂–C–500 and Ni/SiO₂–C–600,
indicating that the microporous structure was generated from the solid–liquid grinding route with the carbonized mixture of SiO₂, soybean oil, and nickel acetyl acetonate. Their mesoporous surface areas also increased as pore volume decreased. This result could be derived from the intergranular pores of aggregative carbon. With a further increase in carbonization temperature above 700 °C, both the surface area and micropore volume increase, suggesting more micropores were created readily under higher carbonization temperature than under 500 or 600 °C. Furthermore, the BET surface area decreased with increasing carbonization temperature above 700 °C because of the collapse of some micropores and the aggregation of carbon deposition; this result was in good agreement with previous reports [28].

1.3.1.3 H₂-TPR

The reducibility of the catalysts is a crucial factor influencing its catalytic performance. H₂-TPR patterns of Ni/SiO₂-C-x catalyst are shown in Fig. 1.4. A lower H₂ reduction peak of NiO at 320 °C appeared only in Ni/SiO₂-C-400 catalyst indicated that catalyst could be reduced completely when the carbonization temperature was higher than 400 °C. The reduction peak at about 430 °C should be attributed to the decomposition of residual soybean oil based on the previous research [1]. The strong reduction peak around 510 °C was associated with a reduction of strong interaction between Ni and C.

1.3.1.4 SEM–EDS

The morphology and elemental mapping of Ni/SiO₂–C–900 were characterized by SEM–EDS. As demonstrated in Fig. 1.5 (a), the spherical structure of SiO₂ support was presented after the carbonizing mixture of SiO₂, soybean oil, and nickel acetyl acetonate. A number of mesopores are observed clearly in Fig. 1.5 (b), thus suggesting that the
mesoporous channels were well maintained after carbonization. This result was in agreement with the BET results. Further elemental analysis was conducted by using EDS mapping images to observe the metal nanoparticles. Fig. 1.5 (d) displayed the chemical distribution of the Ni/SiO$_2$–C–900 catalyst. The elemental mappings of Ni, C, and Si exhibited homogeneous distributions in the Q50 skeletal structure, thus indicating that Ni atoms were uniformly dispersed in the catalyst particles.

1.3.1.5 TG–DTA

Carbon deposition over the spent catalyst was quantified by TG–DTA. Furthermore, the fresh carbon support prepared by the soybean oil carbonization process was also compared. Fig. 1.6 (a) and 1.6 (b) showed the TG and DTG results respectively under an air atmosphere of as-prepared catalysts with different carbonization temperature. As demonstrated in Fig. 1.6 (a), no obvious mass loss peak was observed below 200 °C. Therefore, the prepared catalyst did not adsorb moisture. DTA profiles of the fresh Ni/SiO$_2$–C–X series catalysts were exhibited in Fig. 1.6 (b). The presence of two weight loss peaks suggested that two different types of carbon were deposited with the carbonization temperature between 400 and 1000 °C. The TG weight loss at lower temperatures reflects the oxidation of amorphous carbon (non-graphitic), whereas the further mass loss step at higher temperatures might be ascribed to the combustion of graphitic carbon [29, 30]. As the carbonization temperature increases, the combustion peak of graphitic carbon shifted gradually to a high temperature, thus indicating that the carbon support was stable under high carbonization temperatures. However, Ni/SiO$_2$–C–1100 (Fig. 1.6a) only showed a weight loss peak at 600 °C, which was higher than other catalysts because of the vaporization of amorphous carbon at higher carbonization temperatures.
The TG and DTA profiles of the spent Ni/SiO_2–C–X series catalysts by a heated process with the rate of 10 °C/min in air are depicted in Fig. 1.6 (c) and (d) respectively. Different types of carbon deposition were found over the carbon dioxide reforming of methane reaction, including primarily CH_4 decomposition (CH_4 → 2H_2 + C) and Boudouard reaction (2CO → CO_2 + C) [25, 31, 32]. As seen from Fig 1.6 (d), the Ni/SiO_2–C–X (X = 400–1000) samples had three main weight loss stages in the DTG curve. The first peak was located at 400 °C and was attributed to the oxidation of amorphous carbon, which is derived from the carbon support and formation of carbon deposition after the CO_2 reforming of CH_4 reaction. The second weight loss appeared at 537 °C in the DTA curve, which was the result of combusting graphitic carbon from carbon support in air. The last weight loss peak at around 640 °C presented the combustion of graphitic carbon over the reforming reaction. However, the first oxidation peak disappears over the spent Ni/SiO_2–C–1100 catalyst in Fig 1.6 (d) because the amorphous carbon was vaporized at 1100 °C. These findings reflect that graphitic carbon was more thermally stable than amorphous carbon, which was in agreement with the previous reports [5, 33–35].

1.3.2 Reaction performance
1.3.2.1 Effect of reduction temperature on catalytic performance

The catalytic performances of Ni/SiO_2–C–800 catalyst with varied reduction temperatures or without further reduction are compared in Table 1.2. During the reforming process, catalysts that were reduced under varied temperatures exhibit significant differences in activity and selectivity. According to the XRD results, metallic Ni was generated after 800 °C carbonization, which promoted the CO_2 reforming of CH_4 reaction as an active center. For this reaction, with H_2 reduction at 400 °C, the
conversion of CH\textsubscript{4}, CO\textsubscript{2}, and C\textsubscript{total} was 46.9, 61.8, and 55.2% with H\textsubscript{2}/CO = 0.724, respectively. With increasing reduction temperature, the catalytic activity of Ni/SiO\textsubscript{2}–C–800 decreased because the metal particles were aggregated under a high reduction temperature. Surprisingly, catalyst without reduction exhibited a similar reaction activity than the reduced catalyst. Therefore, the Ni/SiO\textsubscript{2}–C–800 reduced under H\textsubscript{2} ambience with varied temperatures exhibited poor activity compared with that with catalyst reduction; this result suggested that the BET surface area decreased with increasing reduction temperature [36].

1.3.2.2 Effect of carbonization temperature on catalytic performance

The catalytic performances of Ni/SiO\textsubscript{2}–C–X series catalysts with different carbonization temperature without further reduction are listed in Table 1.3. For the CO\textsubscript{2} reforming of CH\textsubscript{4} reaction with carbonization temperature at 400 °C under N\textsubscript{2} atmosphere, the conversion of CH\textsubscript{4}, CO\textsubscript{2}, and C\textsubscript{total} was 51.3%, 62.8%, and 57.8 %, respectively, as well as H\textsubscript{2}/CO = 0.698. With increasing carbonization temperature, the catalytic activity of other catalyst decreased except Ni/SiO\textsubscript{2}–C–500. Furthermore, Ni/SiO\textsubscript{2}–C–500 gave the best catalytic activity and highest H\textsubscript{2}/CO all the samples. As shown in Table 1.3, when the carbonization temperature was more than 1000 °C, the reaction activity of Ni/SiO\textsubscript{2}–C–1000 and Ni/SiO\textsubscript{2}–C–1100 catalysts decreased significantly because the metal particles were sintered under high temperatures. According to the XRD results, metallic Ni was generated with a carbonization temperature above 400 °C, which promoted the CO\textsubscript{2} reforming CH\textsubscript{4} of reaction as an active center. Nevertheless, as the carbonization temperature increased, the metal particles aggregated easily. In addition, high temperature led to the collapse of SiO\textsubscript{2} skeleton pores and the increase in Ni crystalline size. According to these findings, the
carbonization temperature at 500 °C could be considered as an optimal reaction condition for the CO₂ reforming of CH₄ reaction. The H₂/CO ratio in the reaction over Ni/SiO₂–C–X series catalysts with varied carbonization temperature was presented in Table 1.3. The results of H₂/CO ratio during reaction were less than one which was the theoretical H₂/CO ratio, due to carbon deposition via the elimination reaction (C + CO₂ → 2CO) [37, 38]. The Ni/SiO₂–C–500 showed the highest H₂/CO ratio. For other catalysts with increasing carbonization temperature above 500 °C, the ratio decreased gradually during the reaction.

1.3.2.3 Stability test

The CO₂ and CH₄ conversions of Ni/SiO₂-500 catalyst without further reduction during the reforming reaction at 700 °C for 33 h are shown in Fig. 1.7. CH₄ conversion of 59.3 % and CO₂ conversion of 69.0 % were observed at the beginning of the carbon dioxide reforming of methane reaction, and the catalytic activity decreased slightly during the 33 h test. A superior catalytic performance with H₂/CO ratio of 0.75 was achieved. It was speculated that the promising result was related to advantages of solid–liquid grinding treatment mentioned in this chapter. The longer catalytic life of Ni/SiO₂-500 catalyst without further reduction should be attributed to small particles of active sites and good dispersion of active species over the support.

The TG/DTA profile of the spent Ni/SiO₂–C-500 catalyst by a heated process with the rate of 10 °C/min in air is depicted in Fig 1.8. The catalyst weight loss amount before reaction decreased with carbonization temperature increasing because of the vaporization of amorphous carbon. The weight loss of the Ni/SiO₂–C-500 catalyst was 9.65 % by TG analysis. This number increased to 14.87 % after 8 h activity test. After 33 h activity test, the catalyst weight loss continued increasing to 32.5 %. It was obviously that the carbon
deposition increased gradually with reaction time increasing, in spite of this, the catalytic activity of Ni/SiO$_2$–C-500 catalyst still remained in a stable condition.

1.4. Conclusions

The Ni-based mesoporous carbon/silica composite catalyst was prepared by a facile one–step solid–liquid grinding route. The obtained reforming catalysts with different carbonization temperature were investigated systematically and performed directly in the CO$_2$ reforming of CH$_4$ reaction. The unreduced Ni-based catalyst showed better catalytic activity than the reduced catalyst under hydrogen atmosphere because the NiO phase was in-situ reduced by the carbonized soybean oil under nitrogen and further heat treatment adversely affected catalysis activity. As the reduction temperature increases, the catalytic activity of Ni/SiO$_2$–C–800 decreases because the metal particles are aggregated. A series of Ni/SiO$_2$–C–X catalysts without further reduction process were applied in the CO$_2$ reforming of CH$_4$ reaction. Ni/SiO$_2$–C–500 provides the best catalytic activity and highest H$_2$/CO in all samples. However, when the carbonization temperature is more than 1000 °C, the reaction activity of Ni/SiO$_2$–C–1000 and Ni/SiO$_2$–C–1100 catalysts decreased appreciably because the metal particles were sintered under high temperatures. On the other hand, the high temperature led to the collapse of SiO$_2$ skeleton pores and the increase in Ni crystalline size. The presented solid–liquid grinding route and its application for catalytic reaction would further develop in the field of green chemistry and environmental engineering.
References


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Table 1.1. Summary of the textural properties of different samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S$(m$^2$/g)$^a$</th>
<th></th>
<th></th>
<th>$V$(cm$^3$/g)</th>
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<th></th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Total</td>
<td>Micro$^b$</td>
<td>Meso$^c$</td>
<td>Total$^d$</td>
<td>Micro$^e$</td>
<td></td>
</tr>
<tr>
<td>Q50</td>
<td>66.1</td>
<td>6.3</td>
<td>59.8</td>
<td>1.41</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Ni/SiO$_2$–C–500</td>
<td>90.9</td>
<td>13.6</td>
<td>77.3</td>
<td>0.71</td>
<td>0.006</td>
<td></td>
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<tr>
<td>Ni/SiO$_2$–C–600</td>
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<td>29.7</td>
<td>61.5</td>
<td>0.73</td>
<td>0.015</td>
<td></td>
</tr>
<tr>
<td>Ni/SiO$_2$–C–700</td>
<td>92.4</td>
<td>30.1</td>
<td>62.0</td>
<td>0.72</td>
<td>0.016</td>
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<tr>
<td>Ni/SiO$_2$–C–800</td>
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<td>31.3</td>
<td>59.2</td>
<td>0.70</td>
<td>0.015</td>
<td></td>
</tr>
<tr>
<td>Ni/SiO$_2$–C–900</td>
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<td>27.1</td>
<td>63.8</td>
<td>0.67</td>
<td>0.014</td>
<td></td>
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<tr>
<td>Ni/SiO$_2$–C–1000</td>
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<td>23.9</td>
<td>61.8</td>
<td>0.69</td>
<td>0.013</td>
<td></td>
</tr>
<tr>
<td>Ni/SiO$_2$–C–1100</td>
<td>77.5</td>
<td>21.4</td>
<td>57.1</td>
<td>0.69</td>
<td>0.011</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ BET surface area.

$^b$ Microporous surface area evaluated by the $t$–plot method.

$^c$ Mesoporous surface area evaluated by the $t$–plot method.

$^d$ Total pore volume calculated by single point method at $P/P_0 = 0.99$.

$^e$ Micropore volume evaluated by the $t$–plot method.
Table 1.2. Catalytic performance of Ni/SiO$_2$–C–800 catalyst with varied reduction temperature$^a$.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Reduction temperature</th>
<th>No reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>400</td>
<td>500</td>
</tr>
<tr>
<td>CH$_4$ Conv. (%)</td>
<td>46.9</td>
<td>44.5</td>
</tr>
<tr>
<td>CO$_2$ Conv. (%)</td>
<td>61.8</td>
<td>59.2</td>
</tr>
<tr>
<td>$C_{\text{total}}$ Conv. (%)$^c$</td>
<td>55.2</td>
<td>52.8</td>
</tr>
<tr>
<td>H$_2$/CO</td>
<td>0.724</td>
<td>0.739</td>
</tr>
</tbody>
</table>

$^a$ Reaction conditions: catalyst, Ni/SiO$_2$–C–800, 0.2 g; temperature 700 °C; pressure 0.1 MPa; F(CH$_4$/CO$_2$/Ar = 5:5:1), 50 mL/min.

$^b$ Reaction conditions: pure H$_2$, F=40 mL/min, pressure 0.1 MPa.

$^c$ Total carbon conversion.
Table 1.3. Catalytic performance of Ni-based catalysts with varied carbonization temperature without reduction.

<table>
<thead>
<tr>
<th>Carbonization temperature (°C)</th>
<th>400</th>
<th>500</th>
<th>600</th>
<th>700</th>
<th>800</th>
<th>900</th>
<th>1000</th>
<th>1100</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄ Conv. (%)</td>
<td>51.3</td>
<td>54.3</td>
<td>46.2</td>
<td>46.7</td>
<td>49.2</td>
<td>48.3</td>
<td>39.9</td>
<td>39.4</td>
</tr>
<tr>
<td>CO₂ Conv. (%)</td>
<td>62.8</td>
<td>65.2</td>
<td>61.8</td>
<td>58.3</td>
<td>61.9</td>
<td>61.0</td>
<td>53.2</td>
<td>49.1</td>
</tr>
<tr>
<td>C&lt;sub&gt;total&lt;/sub&gt; Conv. (%)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>57.8</td>
<td>60.5</td>
<td>55.2</td>
<td>54.5</td>
<td>56.4</td>
<td>56.1</td>
<td>47.9</td>
<td>44.4</td>
</tr>
<tr>
<td>H₂/CO</td>
<td>0.698</td>
<td>0.751</td>
<td>0.743</td>
<td>0.719</td>
<td>0.714</td>
<td>0.710</td>
<td>0.680</td>
<td>0.672</td>
</tr>
</tbody>
</table>

<sup>a</sup> Reaction conditions: catalyst, Ni/SiO₂–C–800, 0.2 g; temperature 700 °C; pressure 0.1 MPa; F(CH₄/CO₂/Ar = 5:5:1), 50 mL/min.

<sup>b</sup> Total carbon conversion.
Fig. 1.1. Schematic depiction of the one-step synthesis route of Ni-based carbon/silicacomposite catalyst without reduced procedure.
Fig. 1.2. XRD patterns of calcined catalysts without reduction: ▼Ni$^{0}$, ◆NiO, ▼Ni$_2$Si.
Fig. 1.3. N$_2$ adsorption-desorption isotherms and pore distribution of Ni/SiO$_2$-C-x catalyst.
Fig. 1.4. \( \text{H}_2\text{-TPR} \) profiles of the Ni/SiO\(_2\)-C-x catalyst with different carbonization temperature.
Fig. 1.5. SEM images (a, b and c) and EDS mapping images (d) of the Ni/SiO$_2$–C–900 catalyst.
Fig. 1.6. TG/DTA profiles of the before reaction catalysts (A, B) and spent catalysts (C, D) with different calcination temperature: a, 400 °C; b, 500 °C; c, 600 °C; d, 700 °C; e, 800 °C; f, 900 °C; g, 1000 °C; h, 1100 °C.
Fig. 1.7. Stability test of Ni/SiO$_2$-500 catalyst in carbon dioxide reforming of methane reaction.
Fig. 1.8. TG/DTA profiles of the Ni/SiO$_2$–C-500 catalyst after 33 h activity test.
Chapter 2

Designing a novel Ni–Al₂O₃–SiC catalyst with a stereo structure for the combined methane conversion process to effectively produce syngas

In this study, honeycomb-like SiC monolith, due to its excellent physicochemical property such as high heat conductivity, strong mechanical hardness and extreme chemical inertness, was used for combined methane conversion process to produce syngas.
Abstract

In this research, a novel Ni–Al₂O₃–SiC catalyst with a stereo structure was prepared through an evaporation-induced self-assembly (EISA) method. This Ni–Al₂O₃–SiC catalyst consisted of a monolithic SiC foam support and a mesoporous Al₂O₃ layer with embedded Ni nanoparticles (Ni–Al₂O₃) coated on the SiC support. It was characterized by X-ray diffraction (XRD), N₂ physisorption (BET), scanning electron microscope (SEM), H₂ temperature-programmed reduction (H₂-TPR), CO₂ temperature-programmed desorption (CO₂-TPD), thermogravimetry (TG) etc. The catalyst texture properties analysis by SEM and BET showed that the Ni–Al₂O₃ mesoporous layer was coated uniformly on the SiC support surface and increased the specific surface area of the pristine SiC foam obviously. A combined reaction of dry reforming of methane (DRM) with CO₂ and partial oxidation of methane (POM) with O₂, for syngas (CO + H₂) production, was developed to test the catalytic performance of this Ni–Al₂O₃–SiC catalyst. In this combined reaction of DRM–POM, the monolithic Ni–Al₂O₃–SiC catalyst, due to its stereo structure and highly dispersed Ni species, showed better catalytic activity and longer life time, better than the reference catalyst prepared by general impregnation method. In addition, H₂/CO molar ratio in the produced syngas was more tunable than other conventional methane reforming methods. By simply adjusting the proportion of O₂ in the feed gas, we could facilely realize the syngas synthesis with desired composition.

Keywords: Dry reforming, partial oxidation, nickel catalyst, mesoporous Al₂O₃, SiC
2.1. Introduction

Syngas (CO + H\textsubscript{2}) is an important raw material. It is widely used to produce liquid hydrocarbons through syngas to liquid (GTL) processes [1], like methanol synthesis, Fischer–Tropsch synthesis (FTS), etc. Syngas can be produced by coal, biomass gasification or the reforming of natural gas [2, 3]. Recently, since the utilization of greenhouse gas such as methane (CH\textsubscript{4}) and carbon dioxide (CO\textsubscript{2}) favors environment protection, increasing interests have been focused on the conversion of methane and carbon dioxide via dry reforming of methane (DRM) to form other value-added chemicals [4, 5], like alcohols.

But, as a highly endothermic reaction similar to the steam reforming of methane (SRM), considerable energies [6, 7] are required for the process of DRM depending on reaction thermodynamics. Meanwhile, H\textsubscript{2}/CO molar ratio produced by DRM is less than 1, which is unsuitable to be directly used for the downstream utilization such as Fischer–Tropsch synthesis (FTS) or methanol synthesis [8, 9]. H\textsubscript{2}/CO ratio of syngas produced by another SRM is greater than 3, exceeding the requirement of FTS and methanol synthesis reactions as well [10]. The syngas with H\textsubscript{2}/CO = 2:1 is substantially required, as it can be directly used without additional steps to regulate the composition. Therefore, it is considerably important to develop a syngas production process through methane conversion to get the syngas that can be used directly for the downstream processes. From the point of view of reducing energy consumption, the exothermic partial oxidation of methane (POM) is an energy-save way to produce syngas. This POM method, as an alternative route, can produce syngas with a H\textsubscript{2}/CO ratio of 2, but it is not easy to operate due to the formation of hot spots [11–13].
Therefore, to overcome the disadvantages of single process, developing some combined processes that consist of more than one of the followed processes: dry reforming of methane (DRM), steam reforming of methane (SRM) and partial oxidation of methane (POM) [14, 15], has attracted more attentions. The combined process of DRM–POM is considered as a promising way due to its energy-saving and efficient feature. It has three major advantages [16, 17]: (i) it can facilitate the heat transfer between the exothermic POM and endothermic DRM, thus performing in a safer way than single POM, (ii) coke deposition can be effectively inhibited because of the oxidation of carbon species, (iii) H$_2$/CO ratio of the produced syngas can be manipulated facilely by using alternative feedstock, whereby realizing on-site syngas production depending on the requirement of the GTL process. The Ni-based catalysts with considerable catalytic activity can be used for the combined process of DRM–POM. However, it is easily subjected to deactivation due to sintering and coke deposition at high reaction temperature [18, 19]. Therefore, until now, it is still in challenge to find a new catalyst support and develop a new Ni-based catalyst. The new catalyst should have special nature that not only enhance the mass and heat transfer, but also be resistant to metal sintering.

Silicon carbide (SiC) exhibits excellent heat conductivity, strong mechanical hardness, high resistance to oxidation, extreme chemical inertness to acid and base, all of which make it more suitable catalyst support than other conventional support materials like SiO$_2$ and Al$_2$O$_3$ [20]. Recently, SiC as catalyst support has been applied for various catalytic reactions [21, 22]. In particular, its utilization as support for methane reforming has been paid more attention. Jesús et al. reported that SiC supported Ni catalysts showed high catalytic activity and lower coke deposition in the methane reforming reaction [23].
Liu et al. presented that SiC supported Ni catalysts presented stable catalytic activity and kept its intrinsic shape without any changes after 100 h reaction [24]. However, the application of SiC as catalyst support is limited severely by its low specific surface area. The active metals loaded directly on its surface will aggregate and grow easily since the weak interaction between bulk SiC and metals. Recently, we reported a new mesoporous–Al₂O₃–layer modified SiC support for Ni-based catalyst preparation [25], and the application of this catalyst exhibited better catalytic activity and excellent stability in methane reforming.

In this study, we employ a new SiC support as the Ni-based catalyst support. This SiC support has a monolithic foam structure and good thermal conductivity, by which we can quickly in-situ transfer the excess heat generated in methane reforming. The Ni-based SiC catalyst, named Ni–Al₂O₃–SiC, is prepared via an evaporation-induced self-assembly (EISA) method and applied in the combined process of DRM–POM reaction. This Ni–Al₂O₃–SiC monolithic foam catalyst has a stereo structure that consists of a Al₂O₃ ordered mesoporous layer with embedded Ni nanoparticles coated on the SiC support. The high porosity of Ni–Al₂O₃–SiC catalyst will enhance the mass and heat transfer, at the same time inhibiting the formation of hot spots and catalyst sintering. In addition, the Al₂O₃ ordered mesoporous layer on the SiC support has highly dispersed Ni metals, which affords excellent catalytic activity, catalyst stability and lower carbon deposition in DRM–POM reaction.

2.2. Experimental

2.2.1 Catalyst preparation
The nickel-aluminum supported monolithic SiC catalyst was prepared via an one-step evaporation-induced self-assembly (EISA) method similar to the previous reports [26, 27]. 1g of triblock copolymer P123 (Sigma-Aldrich, EO$_{20}$PO$_{70}$EO$_{20}$, Mr = 5800) was first dissolved in 20 ml of anhydrous ethanol and stirred for 30 min. After that, a certain amount of nickel nitrate hexahydrate, 1.6 ml of 61 wt% nitric acid and 2.04 g of aluminum isopropoxide were added into the above solution with vigorous stirring. The obtained solution was then stirred for another 4 h. The monolithic foam-like SiC (diameter 15 mm and length 20 mm), as shown in Fig. 2.2 (a), was used as the catalyst support and dipped in the above Ni–Al salts containing solution. After ultrasonic treatment for 15 min, the solvent was evaporated at a 60 °C oven for 48 h, in which both the self-assembly and transformation from sol to gel occurred, and the formed gel uniformly coated on the SiC surface. And then the obtained sample was calcined at 700 °C for 4 h in a muffle furnace to get the final Ni–Al$_2$O$_3$–SiC catalyst. This Ni–Al$_2$O$_3$–SiC catalyst had a composited structure that a Ni loaded Al$_2$O$_3$ mesoporous layer was coated on the monolithic foam-like SiC support. In this preparation, the molar ratio of Ni to Al was adjusted as 1:3.6, and the theoretical nickel loading amount of this Ni–Al$_2$O$_3$–SiC catalyst was 2 wt%.

In order to investigate the catalytic activity of Ni–Al$_2$O$_3$–SiC catalyst, another reference catalyst, noted as Ni/SiC–IMP, was also prepared by the general impregnation method. The SiC was mixed with pre-prepared Ni(NO$_3$)$_2$·6H$_2$O aqueous solution, followed by drying at 120 °C and calcination at 500 °C for 4 h respectively. The Ni loading amount for this Ni/SiC-IMP catalyst was also 2 wt%.

2.2.2 Catalyst characterization

The crystalline phases of catalysts were measured by using a Rigaku RINT2000
diffractometer with a Cu-Kα radiation (λ = 0.154 nm) operated at 40 kV and 20 mA. The specific area, average pore size and total pore volume of catalysts were determined by N₂ adsorption-desorption isotherms with an automated analyzer of Quantachrome Nova 2200e apparatus. The morphologies of catalyst were observed by scanning electron microscope (SEM, JEOL JSM-6360LV). Energy dispersive X-ray spectrometer (EDX, SHIMADZU EDX-70) was also employed to analyze the catalysts element composition. The active metal surface area and dispersion of catalysts were measured by hydrogen chemisorption experiments with Quantachrome Autosorb-1 apparatus. The coke deposition on the surface of spent catalyst was quantified using a thermogravimetric analyzer (Shimadzu DTG-60 apparatus).

H₂ temperature-programmed reduction (H₂-TPR) experiments were performed for analyzing the metal-support interaction, as well as the reduction properties of the catalysts by using a BELCAT-B-TT (BEL, Japan) analyzer. Prior to measurement, the sample was dried and purified at 200 °C for 1 h with a flowing Ar (30 ml/min). After cooling down to 50 °C, the reduction gas of H₂/Ar (10%, 30 ml/min) was introduced into the reactor, at the same time the reactor was heated to 900 °C. The gas product was analyzed online by a thermal conductivity detector (TCD). In addition, CO₂ temperature-programmed desorption (CO₂-TPD) was also conducted to measure the catalyst basicity. The catalyst was pretreated at 200 °C for 1 h in Ar gas flow (30 ml/min) and then cooled down to 50 °C. After that, CO₂ was introduced at this temperature for 1 h, followed by purging with Ar gas flow for another 30 min to remove the physically adsorbed CO₂. And then the CO₂-TPD was performed by heating the reactor from 50 °C to 900 °C with a ramp rate of 10 °C/min. Temperature-programmed hydrogenation (TPH) was also used to analyze the surface carbon species of the spent catalyst. The active metal
surface area and dispersion on catalysts were measured by hydrogen chemisorption with a Quantacharome Autosorb-1 apparatus. The sample was first pretreated at 200 °C for 2 h under He atmosphere and reduced at 750 °C for 2 h on-line with pure H2. The sample was purged with He for 30 min at the same temperature and cooled down to 30 °C for hydrogen chemisorption. The sample was first purged at 200 °C for 1 h in Ar gas flow (30 ml/min) and then cooled down to 50 °C. After that, TPH analysis was carried out by increasing the reactor temperature to 900 °C with a ramp rate of 10 °C/min in 10% H2/Ar gas flow.

2.2.3 Catalytic reaction on the Ni–Al2O3–SiC catalyst

The catalyst activity evaluation was carried out in a fixed-bed quartz reactor (24 mm i.d.) under ambient pressure. The monolithic foam catalyst of 2 wt% Ni–Al2O3–SiC or reference catalyst of Ni/SiC–IMP was loaded in the middle of reactor, as shown in Scheme 1. Before reaction, the sample was first reduced at 750 °C for 2 h using 5% H2 in Ar with 100 ml/min flow rate. After that, a reactant gas stream consisting of CH4, CO2, O2 and Ar with certain molar ratio was introduced into the reactor for reaction, in which the used Ar acted as internal standard. An online gas chromatograph of GC-8A with a thermal conductivity detector (TCD) and a Porapak Q column was employed to analyze CH4, CO2 and CO; another gas chromatograph of GC-320 with TCD detector and activated carbon column was used to identify H2.

2.3. Result and discussion

2.3.1 Fresh catalyst characterization

2.3.1.1 BET analysis
In this chapter, the new Ni–Al$_2$O$_3$–SiC catalyst consisting of a Ni doped Al$_2$O$_3$ mesoporous layer coated on the monolithic foam SiC support was prepared by an EISA method, and another reference catalyst of Ni/SiC–IMP was obtained by using the traditional impregnation method to load Ni directly on the monolithic foam SiC support. The physical properties of catalysts are shown in Table 2.1. The textural parameters of catalysts prepared by varied methods were clearly different. For the specific surface areas of catalysts, the Ni–Al$_2$O$_3$–SiC catalyst presented the highest value of 18.7 m$^2$/g. Moreover, this Ni–Al$_2$O$_3$–SiC catalyst also had the smallest Ni particle size, highest metal dispersion and the largest metal surface area among the measured samples. All above results indicated that the employed EISA for Ni–Al$_2$O$_3$ coating preparation could afford excellent physical properties on the obtained Ni–Al$_2$O$_3$–SiC catalyst.

2.3.1.2 XRD analysis

XRD analysis was performed to illustrate the crystalline phase of catalysts. The XRD analysis results are given in Fig. 2.1 (a) (the fresh samples of SiC, Ni/SiC–IMP, Ni–Al$_2$O$_3$–SiC and pure Ni–Al$_2$O$_3$ powder) and Fig. 2.1 (b) (the reduced Ni/SiC–IMP, Ni–Al$_2$O$_3$–SiC catalysts and Ni–Al$_2$O$_3$ powder) respectively. For the fresh Ni/SiC–IMP catalyst prepared by general impregnation method, its XRD pattern in Fig. 2.1 (a) exhibited obvious NiO diffraction peaks at 37.1$^\circ$ and 62.8$^\circ$ [28]. Because of the poor microporous structure of SiC supports, the general impregnation method for Ni/SiC–IMP preparation would lead to lower dispersion and large size of Ni particles on its body.

The Ni–Al$_2$O$_3$–SiC catalyst, with one mesoporous Ni–Al$_2$O$_3$ layer coating on the SiC support, was prepared by using the newly developed EISA method. In order to clarify the crystalline composition of the coating layer of Ni–Al$_2$O$_3$–SiC catalyst, a pure Ni–Al$_2$O$_3$ powder sample, without SiC support, was also prepared through EISA method.
The XRD pattern of pure Ni–Al$_2$O$_3$ powder sample is also given in Fig. 2.1 (a). For this pure Ni–Al$_2$O$_3$ powder, three weak peaks appeared at 37.0$^\circ$, 45.0$^\circ$ and 65.9$^\circ$ should be ascribed to the formed NiAl$_2$O$_4$ spinel species instead of the general NiO species formed on the Ni/SiC–IMP catalyst [29]. It seems that these NiAl$_2$O$_4$ spinel species could be formed by means of the reaction of Al$_2$O$_3$ and NiO through high-temperature calcination [30]. For the fresh Ni–Al$_2$O$_3$–SiC catalyst, however, the related NiAl$_2$O$_4$ diffraction peaks could not be distinguished clearly, which should be attributed to the strong intensity of SiC support and low loading amount of Ni–Al$_2$O$_3$ coating layer. Similar results were also observed in the literature [28]. The developed EISA method used for Ni–Al$_2$O$_3$–SiC catalyst preparation could make Ni species being confined well in the mesoporous Ni–Al$_2$O$_3$ coating layer [31, 32], finally leading to the good dispersion of active Ni species for the studied DRM–POM reaction.

On the reduced catalysts, as shown in Fig. 2.1 (b), the diffraction peaks of metallic Ni were detected for both Ni–Al$_2$O$_3$–SiC and Ni/SiC–IMP catalysts. Stronger Ni diffraction peaks on Ni/SiC–IMP catalyst suggested the large Ni particles. In contrast to that of Ni/SiC–IMP catalyst, the peak intensity of Ni on the Ni–Al$_2$O$_3$–SiC catalyst was weaker, which proved the well dispersion and smaller size of Ni particles. These findings were also consistent with the catalyst characterization in Table 1, on the Ni particle sizes obtained by H$_2$ chemisorption.

2.3.1.3 SEM and EDS analysis

We also employed SEM to directly observe the physical property of the prepared catalysts. The surface morphologies of naked SiC, fresh Ni–Al$_2$O$_3$–SiC and Ni/SiC–IMP samples are displayed in Fig 2.2. Monolith SiC support with honeycomb structure showed a concave-convex matrix, as indicated by Fig. 2.2 (a), (b) and (c). For the
Ni–Al₂O₃–SiC catalyst in Fig. 2.2 (d) and (e), it is clear that the Ni–Al₂O₃ active layer was successfully coated on the surface of SiC support by using EISA method. The formed Ni–Al₂O₃ coating could tightly catch the surface of SiC support because of the existence of SiO₂ or SiOₓCy between Ni–Al₂O₃ coating and SiC surface. Another sample of Ni/SiC–IMP prepared by general impregnation method, as a reference, had also been presented. Its SEM image is given in Fig. 2.2 (f), where we could find that a great amount of Ni particles aggregated into larger size on the SiC support. The formed larger Ni particles on Ni/SiC–IMP, in theory, would not afford better catalytic performance in the followed methane conversion reaction compared with the well-designed Ni–Al₂O₃–SiC catalyst.

2.3.1.4 H₂-TPR and CO₂-TPD analysis

In order to investigate the reduction behavior of metallic Ni supported on the SiC support, we performed H₂-TPR on the catalysts, and the analysis results are shown in Fig. 2.3. For Ni/SiC–IMP catalyst, single peak appeared at 360 °C, which could be attributed to the reduction of NiO species to form metallic Ni. However, the Ni–Al₂O₃–SiC catalyst obtained by EISA method displayed three reduction peaks at different temperatures. The first peak at 476 °C was attributed to the reduction of NiO that interacted strongly with SiC support. The other two peaks obtained at 676 and 785 °C should be associated with the reduction of NiAl₂O₄ spinel species and nickel silicate species respectively [33, 34]. During the Ni–Al₂O₃–SiC catalyst preparation, part of Ni²⁺ could directly interact with SiC support by surface SiOₓCy species, therefore leading to the formation of nickel-silicate species in the calcination step. To further identify the reduced substances, the pure Ni–Al₂O₃ powder prepared by EISA method, without SiC support, was also analyzed by H₂-TPR, as shown in Fig. 2.3. Only one broad reduction peak at 699 °C
associated with the NiAl₂O₄ was detected. It seems that the reduction peak of NiAl₂O₄ spinel species over Ni–Al₂O₃–SiC catalyst shifted towards lower temperature in comparison with that of pure Ni–Al₂O₃ powder. The co-existing multiple species, such as NiO, nickel-silicate and SiC support, possibly affected the reduction of NiAl₂O₄ on the Ni–Al₂O₃–SiC catalyst [35].

CO₂-TPD analysis was performed to identify the basic property of Ni–Al₂O₃–SiC, Ni/SiC–IMP and SiC samples, and the results are given in Fig. 2.4. For the Ni–Al₂O₃–SiC catalyst, multiple peaks appeared at different temperatures, indicating various basic sites on this catalyst. The peak at 112 °C was assigned to the physical adsorption of CO₂, the other two peaks at 417 and 493 °C meant the median basic sites derived from the general free NiO species and the NiO species contacted closely with SiC support. The CO₂ desorption peak at 720 °C should be attributed to the strong basic sites afforded by the formed NiAl₂O₄ species. The basic sites are beneficial to CH₄ dry reforming reaction because of their capacity for absorbing CO₂, at the same time inhibiting carbon deposition (2CO ↔ C + CO₂). In contrast to the Ni–Al₂O₃–SiC catalyst, CO₂–TPD profile of Ni/SiC–IMP sample displayed a broad desorption peak around 429 °C. It was also slightly stronger than that of the desorption peak at 417 °C in Ni–Al₂O₃–SiC catalyst. Possibly more free NiO particles were obtained by impregnation method, and there was some weak interaction between the formed NiO particles and SiC support on the Ni/SiC–IMP catalyst. The pure SiC support gave a weak CO₂ desorption peak at 400 °C, which could be explained by the presence of SiOₓCᵧ species on the surface of SiC.

2.3.2 Activity test

The combination of carbon dioxide dry reforming of methane (DRM) and partial
oxidation of methane (POM) is a relatively complicated multi-reaction network process. The mainly involved reaction equations are shown below [36]:

\[
\begin{align*}
\text{CH}_4 + \text{CO}_2 &= 2\text{H}_2 + 2\text{CO} & \Delta H_{298\text{K}} &= 261 \text{ kJ/mol} \\
\text{CH}_4 + 1/2\text{O}_2 &= \text{H}_2 + \text{CO} & \Delta H_{298\text{K}} &= -36 \text{ kJ/mol} \\
\text{CH}_4 + 2\text{O}_2 &= \text{CO}_2 + 2\text{H}_2\text{O} & \Delta H_{298\text{K}} &= -802 \text{ kJ/mol} \\
\text{CO}_2 + \text{H}_2 &= \text{CO} + \text{H}_2\text{O} & \Delta H_{298\text{K}} &= 41 \text{ kJ/mol} \\
\text{CH}_4 + \text{H}_2\text{O} &= 3\text{H}_2 + \text{CO} & \Delta H_{298\text{K}} &= 206 \text{ kJ/mol} \\
2\text{CO} &= \text{C} + \text{CO}_2 & \Delta H_{298\text{K}} &= -173 \text{ kJ/mol} \\
\text{CH}_4 &= \text{C} + 2\text{H}_2 & \Delta H_{298\text{K}} &= 75 \text{ kJ/mol}
\end{align*}
\]

The DRM reaction (eq. 1) is a strongly endothermic reaction, therefore requiring much external heat. The incorporation of exothermic POM reaction (eq. 2) and methane oxidation (eq. 3) will afford their self-produced heat in situ for DRM reaction. The DRM reaction and POM reaction cooperate concertedly and promote mutually. Consequently, as we designed, the combination of DRM and POM reaction can facilely improve CH\textsubscript{4} conversion and regulate H\textsubscript{2}/CO ratio in the produced syngas. Here, it should be noted that O\textsubscript{2} as oxidant shows higher activity than CO\textsubscript{2}, since the latter is more stable, which generally results in the total conversion of O\textsubscript{2} during reaction process [16].

We used the combination reaction of DRM–POM to test the catalytic performance of Ni–Al\textsubscript{2}O\textsubscript{3}–SiC, Ni/SiC–IMP and Ni–Al\textsubscript{2}O\textsubscript{3} catalysts. Fig. 2.5 exhibited CH\textsubscript{4} and CO\textsubscript{2} conversions, as well as H\textsubscript{2}/CO molar ratio in the produced syngas, by adjusting the O\textsubscript{2} proportion in feed gas. In Fig. 2.5 (a), by introducing O\textsubscript{2} into reaction system, CH\textsubscript{4} conversion increased linearly on all catalysts. But the Ni–Al\textsubscript{2}O\textsubscript{3}–SiC catalyst, prepared by EISA method, presented higher activity than that of Ni/SiC–IMP and Ni–Al\textsubscript{2}O\textsubscript{3} catalysts. Fig. 2.5 (c), (d) and (e) gave CH\textsubscript{4} and CO\textsubscript{2} conversion with increasing the O\textsubscript{2}
content in the feed gas. If there was no O₂ in the reaction system (CH₄:CO₂:O₂=8:8:0), that was the pure DRM reaction, CH₄ conversions on both catalysts were lower than CO₂ conversion, owing to the coexistence of the reversed water-gas-shift reaction (RWGS Eq. 4) that facilitates CO₂ conversion. With the addition of O₂ in feed gas, CH₄ conversion increased dramatically. The introduced O₂ would arise the oxidation reactions of CH₄ (Eq. 2 and 3), therefore resulting in the increase of CH₄ conversion. Here, the exothermic heat from CH₄ oxidation reaction could be in-situ recycled by DRM, which was also beneficial to CH₄ conversion. As mentioned above, the used O₂ not only facilitated CH₄ conversion, but also contributed to the CO₂ formation by CH₄ oxidation (Eq. 3). If excessive O₂ is introduced into system, CH₄ oxidation will dominate the total reaction, finally resulting in the decrease of CO₂ conversion. It is also clear that the gap between CH₄ and CO₂ conversions on this Ni–Al₂O₃–SiC catalyst reached a minimum value when the ratio of CH₄:CO₂:O₂ was 8:4:2. In terms of Ni/SiC–IMP catalyst prepared by general impregnation method, both of CH₄ and CO₂ conversions were lower than those of Ni–Al₂O₃–SiC catalyst due to its poor catalytic activity.

Fig. 2.5 (b) showed the change of H₂/CO ratio in the produced syngas with varied CH₄:CO₂:O₂ in feed gas. This result demonstrated that, for the pure CH₄ dry reforming reaction without oxygen (CH₄:CO₂:O₂ = 8:8:0), H₂/CO molar ratio of Ni–Al₂O₃–SiC catalyst was about 0.7. However, by increasing the O₂ content in feed gas, H₂/CO ratio increased clearly and reached to 1.76. The combined reaction of DRM–POM could facilely make significant effect on adjusting the produced syngas composition, by which we could smoothly get the desired syngas ratio for further application like Fischer–Tropsch synthesis, methanol synthesis or DME synthesis.

Fig. 2.6 (a), (b) and (c) exhibited the effect of reaction temperature on the catalytic
performance over Ni–Al₂O₃–SiC, Ni/SiC–IMP and Ni–Al₂O₃ catalysts. Increasing reaction temperature from 650 °C to 800 °C could promote the CH₄ and CO₂ conversion, and the Ni-Al₂O₃-SiC catalyst always kept higher activity than Ni/SiC–IMP and Ni–Al₂O₃ catalysts at each reaction temperature. H₂/CO molar ratios in the produced syngas decreased with increasing reaction temperature, as shown by Fig. 2.6 (c), but H₂/CO molar ratio obtained on the Ni–Al₂O₃–SiC catalyst was higher compared to that of Ni/SiC–IMP and Ni–Al₂O₃ catalysts. By comparison, the monolithic Ni–Al₂O₃–SiC catalyst showed higher catalytic activity than that of Ni/SiC–IMP and Ni–Al₂O₃ catalysts, implying that the stereo structure of Ni–Al₂O₃–SiC could be beneficial to its higher catalytic activity in the combined reaction of DRM-POM.

For our studied DRM-POM, according to the total \( \Delta H_{298K} \) reactions, Eq. 3-4 will predominate if the reaction temperature is lower than 700 °C, and Eq. 1-2 will proceed intensively if higher reaction temperature of 700~800 °C is employed [16]. Irrespective of reaction temperature, other reactions as side reactions are also inevitable. At low temperature, CH₄ combustion and reverse water-gas shift reaction (Eq. 3-4) were the main reactions basing on reaction enthalpies, being accompanied with POM reaction in part. A large number of CO₂ was generated, therefore leading to the negative CO₂ conversion. The over-produced H₂O by Eq. 3-4 will favor SRM reaction (Eq. 5), by which to enhance H₂/CO ratio in the syngas [37]. When higher reaction temperature (>700 °C) is adopted, DRM and POM predominate the total process and promote mutually, whereby we can realize the desired reaction model.

The effect of gas hourly space velocity (GHSV) on the CH₄ and CO₂ conversions of Ni–Al₂O₃–SiC catalyst was also investigated, and the results are shown in Fig. 2.6 (d). CH₄ conversion was stable, and CO₂ conversion decreased slightly as the increase of
GHSV, suggesting that the Ni–Al$_2$O$_3$–SiC catalyst had excellent catalytic activity under varied GHSV.

Catalyst stability is one of the most important factors for CH$_4$ reforming reaction. In order to investigate the catalytic stabilities of Ni–Al$_2$O$_3$–SiC and Ni/SiC-IMP catalysts, lifetime tests were performed at 750 °C with the feed gas of CH$_4$:CO$_2$:O$_2$ = 8:2:3, and the reaction results are shown in Fig. 2.7. CH$_4$ and CO$_2$ conversions of Ni–Al$_2$O$_3$–SiC catalyst were stable, and the catalyst deactivation was not observed during the total reaction process of 50 h. However, the Ni/SiC-IMP catalyst showed lower catalytic performance and shorter lifetime. This could be ascribed to low dispersion and large nanoparticle size of Ni species. The excellent catalytic performance and life time of Ni–Al$_2$O$_3$–SiC catalyst possibly benefited from its highly dispersed Ni active species with smaller size embedded by Al$_2$O$_3$ mesoporous layer, as well as the interaction between active Ni and SiC support indicated by H$_2$-TPR. Here, the smaller metal particles could effectively inhibited carbon deposition and improved reactants conversion [38]. On the other hand, the employed SiC support with distinguished thermal conductivity would also contribute to the catalyst stability. With this SiC support for the combined reactions of DRM–POM, the generated heat from POM reaction could be in-situ transferred quickly to the DRM reaction as required, by which to promote two reactions concertedely.

2.3.3 Spent catalyst characterization

The spent Ni–Al$_2$O$_3$–SiC and Ni/SiC-IMP catalysts had also been characterized to identify its change after lifetime test. TG profiles of spent Ni–Al$_2$O$_3$–SiC and Ni/SiC-IMP catalysts are shown in Fig. 2.8 (a). TG curve was used to calculate the deposited carbon on the surface of catalyst, from which we could find that there was only 2% weight loss on spent Ni–Al$_2$O$_3$–SiC catalyst, significantly lower than catalysts
prepared by general methods [39]. However, the weight loss of 12.5% was detected on the spent Ni/SiC-IMP catalyst, indicating more carbon deposition. It could be also responsible for low catalytic performance. Therefore, the Ni–Al₂O₃–SiC catalyst prepared by EISA method was an efficient catalyst for CH₄ and CO₂ conversions to produce syngas. It not only improved the overall reaction rate, but also diminished the carbon deposition on catalyst surface. The mechanism of carbon deposition on CH₄ reforming catalysts had been widely investigated. It seems that the carbon deposition was mainly caused by two reactions: one was the disproportionation reaction of CO (Eq. 6) and another was CH₄ decomposition (Eq. 7). For the Ni–Al₂O₃–SiC catalyst, because of the utilization of monolith SiC foam support, the mass-transfer efficiency of reactant gas on this catalyst was better than on other traditional powder catalysts, thus suppressing the formation of carbon species in the CO₂-rich atmosphere. In addition, the addition of O₂ in reaction system could further depress the carbon formation. SEM analysis was also employed to observe the morphologies of the spent Ni–Al₂O₃–SiC catalyst. The analysis result is given in Fig. 2.8 (b). There were only a small number of filamentous carbons formed on the catalyst surface. This result also proved that all of active sites on the Ni–Al₂O₃–SiC catalyst were still exposed to reactants even undergoing 50 h lifetime test.

TPH analysis on the spent Ni–Al₂O₃–SiC catalyst was also performed to identify the carbon species deposited on the catalyst surface after reaction, as shown in Fig. 2.9 (a). Generally, the carbon species formed on the catalyst in methane reforming reaction comprised of three types: Cₐ, Cₜ and Cₜ‴. Among these three carbons species, Cₜ‴ was well recognized as the major factor that would deactivate catalyst activity in methane reforming reaction. For the Ni–Al₂O₃–SiC catalyst, two types of carbon species, Cₐ and Cₜ, were observed at 362 °C and 614 °C respectively [40]. The formed Cₐ should be the
amorphous carbon, and another $C_\beta$ was whisker carbon that could effectively depress the catalyst deactivation to some extent. More importantly, there was no $C_\gamma$ (graphitic carbon) species [41] on the spent catalyst. These findings were in consistent with the stable catalytic activity of Ni–Al$_2$O$_3$–SiC catalyst in life time test.

In addition to the deposited carbon type, the catalyst deactivation was also closely related with the sintering of active Ni nanoparticles. Therefore we also used XRD to analyze the spent catalyst. The XRD pattern of the spent Ni–Al$_2$O$_3$–SiC catalyst is presented in Fig. 2.9 (b). There were no diffraction peaks of graphite carbon in the XRD pattern, implying that the monolithic foam catalyst had strong resistance to carbon deposition. The mean size of the Ni nanoparticles of the spent Ni–Al$_2$O$_3$–SiC catalyst was calculated by Scherrer Equation, as given in Table 2.2. The diffraction peak of metallic nickel was still detected after 50 h life time test, and the diffraction intensity of nickel became slightly larger (18.4 nm by XRD) than that of fresh sample (10.7 nm) since the sintering of Ni nanoparticles in reaction. But the growth rate of Ni nanoparticles on this Ni–Al$_2$O$_3$–SiC catalyst was inhibited effectively compared with previously reported catalysts [42]. The lower growth rate, here, should be first attributed to the superior heat conductivity of SiC foam support that conducted the reaction heat homogeneously and quickly. In addition, the mesoporous Al$_2$O$_3$ layer coated on the SiC support should be also considered. The Ni nanoparticles dispersed well in the mesoporous Al$_2$O$_3$ coating layer, and this Al$_2$O$_3$ coating layer could also fix the well dispersed Ni nanoparticles tightly to inhibit their sintering. The Ni nanoparticles, mesoporous Al$_2$O$_3$ coating layer and SiC foam support cooperated concertedly and promoted mutually, performing a synergetic function on the combined reaction of carbon dioxide dry reforming of methane (DRM) and partial oxidation of methane (POM).
2.4. Conclusions

A monolithic Ni–Al$_2$O$_3$–SiC foam catalyst with stereo structure was facilely prepared via developed evaporation-induced self-assembly (EISA) method. This Ni–Al$_2$O$_3$–SiC foam catalyst comprised of mesoporous Ni–Al$_2$O$_3$ layer on the surface of SiC support. The specific surface area of SiC support was increased obviously due to the formation of mesoporous Ni–Al$_2$O$_3$ layer. The obtained monolithic Ni–Al$_2$O$_3$–SiC catalyst was employed for the combined reaction of DRM–POM to produce syngas (CO + H$_2$) and showed excellent catalytic performances, compared with the reference catalyst Ni/SiC–IMP prepared by general impregnation method. Characterization by SEM, XRD and H$_2$-chemisorption on the Ni–Al$_2$O$_3$–SiC foam catalyst indicated that the Ni nanoparticles dispersed well in the mesoporous Ni–Al$_2$O$_3$ layer coated on the surface of SiC support. CO$_2$-TPD and H$_2$-TPR confirmed that more basic sites were obtained on this Ni–Al$_2$O$_3$–SiC catalyst. TG-DTA and TPH analysis illustrated that there was no graphitic carbon formed on the spent catalyst. For the combined reaction of DRM–POM to produce syngas, the stereo structure of Ni–Al$_2$O$_3$–SiC catalyst was crucial to depressing the sintering of Ni nanoparticles, as well as realizing the excellent catalyst performance such as adjusting H$_2$/CO ratio, saving external heating by coexisting O$_2$. 
References

Scheme 1. Schematic illustration of fixed bed reactor for combined DRM–POM reaction to produce syngas on the monolithic foam SiC-supported catalyst.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Specific surface area (m²/g)</th>
<th>Pore volumea (cm³/g·10⁻²)</th>
<th>Metal particle sizeb (nm)</th>
<th>Dispersionc (%)</th>
<th>Metal surface area (m²/g)</th>
<th>Ni amountd (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiC</td>
<td>3.39</td>
<td>0.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ni/SiC–IMP</td>
<td>6.59</td>
<td>1.1</td>
<td>39.8</td>
<td>42.6</td>
<td>0.31</td>
<td>2.6</td>
</tr>
<tr>
<td>Ni–Al₂O₃–SiC</td>
<td>18.70</td>
<td>2.3</td>
<td>10.7</td>
<td>12.8</td>
<td>1.04</td>
<td>1.66</td>
</tr>
</tbody>
</table>

a Pore volumes were calculated by BJH model.

b The Ni particle size were estimated from XRD (D₁) and H₂ chemisorption (D₂) respectively.

c Dispersion was measured basing on H/Ni = 1.

d The exposed metal surface areas were obtained from H₂ chemisorption.

e The Ni content was quantified by EDX analysis.
Table 2.2. The Ni nanoparticle size and rate of carbon deposition over spent Ni–Al$_2$O$_3$–SiC sample

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reaction time (h)</th>
<th>Ni nanoparticle size $^a$ (nm)</th>
<th>Growth rate of metallic Ni (nm/h)</th>
<th>Weight loss (%)</th>
<th>Carbon deposition rate (mg/h·g$_{\text{cat}}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni–Al$_2$O$_3$–SiC</td>
<td>50</td>
<td>10.7</td>
<td>18.4</td>
<td>0.15</td>
<td>2</td>
</tr>
</tbody>
</table>

$^a$Ni nanoparticle size was calculated from Scherrer Equation.
Fig. 2.1. (a) XRD patterns of Ni–Al₂O₃–SiC, Ni/SiC–IMP, SiC and pure Ni–Al₂O₃ samples before reduction, (b) XRD patterns of Ni–Al₂O₃–SiC, Ni/SiC–IMP and pure Ni–Al₂O₃ samples after reduction.
Fig. 2.2. Surface morphologies of different samples: (a, b and c) SiC foam support, (d and e) Ni–Al₂O₃–SiC catalyst prepared by EISA method, (f) Ni/SiC–IMP obtained via impregnation method.
Fig. 2.3. H$_2$-TPR profiles of as-prepared Ni–Al$_2$O$_3$–SiC, Ni/SiC–IMP catalysts and calcined Ni–Al$_2$O$_3$ powder.
Fig. 2.4. CO$_2$-TPD profiles of Ni–Al$_2$O$_3$–SiC, Ni/SiC–IMP catalysts and SiC support.
Fig. 2.5. The reaction results obtained on Ni–Al₂O₃–SiC, Ni/SiC–IMP and Ni-Al₂O₃ catalysts respectively: (a) CH₄ conversion, (b) H₂/CO molar ratio, (c, d and e) The contrast of CH₄ and CO₂ conversions over Ni–Al₂O₃–SiC, Ni/SiC–IMP and Ni-Al₂O₃ catalysts. (Reaction conditions: GHSV = 15000 ml/(h·gcat), T = 750 °C, Atmosphere pressure).
Fig. 2.6. The effect of reaction temperature on catalysts performance with reaction conditions of CH$_4$:CO$_2$:O$_2$ = 8:2:3 and GHSV = 15000 ml/(h·g$_{\text{cat}}$): (a) CH$_4$ conversion, (b) CO$_2$ conversion and (c) H$_2$/CO ratio. (d) The effect of GHSV on CH$_4$ and CO$_2$ conversions over Ni–Al$_2$O$_3$–SiC catalyst at reaction temperature of 750 °C and feed gas ratio of CH$_4$:CO$_2$:O$_2$ = 8:2:3.
Fig. 2.7. The stability tests of Ni–Al₂O₃–SiC catalyst for 50 h and Ni/SiC-IMP catalyst for 8 h: (a) and (b) CH₄ and CO₂ conversions, (c) and (d) H₂/CO molar ratios. Reaction conditions: 750 °C, CH₄:CO₂:O₂ = 8:2:3, GHSV = 15000 ml/(h·gcat), atmosphere pressure.
Fig. 2.8. (a) TG profiles of the spent Ni–Al$_2$O$_3$–SiC and Ni/SiC-IMP catalysts after life time reactions and (b) SEM image of spent Ni–Al$_2$O$_3$–SiC catalyst.
Fig. 2.9. (a) TPH profile and (b) XRD pattern of the spent Ni–Al₂O₃–SiC catalyst after 50 h life time reaction.
Chapter 3

Designing core (Cu/ZnO/Al₂O₃)–shell (SAPO-11) zeolite capsule catalyst with a facile physical way for dimethyl ether direct synthesis from syngas

Zeolite capsule catalyst CuZnAl/SAPO11 prepared by physical mixing method was used for one-step dimethyl ether (DME) synthesis from syngas. The well-organized core-shell structure of CuZnAl/SAPO11 capsule catalyst can facilely fulfill direct DME synthesis by performing sequential reaction, in which syngas firstly was catalyzed by core CuZnAl catalyst to synthesize methanol and then methanol was hydrated by SAPO11 zeolite shell to generate DME.
Abstract

Core–shell like zeolite capsule catalyst can effectively realize tandem catalysis process, like syngas → methanol → dimethyl ether (DME), but the general zeolite shell preparation requires high temperature and alkaline conditions, which severely limits the design, industrial production and application of zeolite capsule catalyst. In this chapter, we present a simple and scalable method, named physical coating (PhyC), to prepare zeolite shell without employing hydrothermal synthesis process. The demonstrated zeolite capsule catalyst, named CuZnAl/SAPO11-PhyC, has a Cu/ZnO/Al2O3 (CuZnAl) core catalyst and a PhyC-prepared silicoaluminophosphate-11 (SAPO-11) shell. This zeolite capsule catalyst CuZnAl/SAPO11-PhyC is characterized by XRD, SEM, EDS, N2 adsorption and NH3-TPD respectively. Tandem catalysis process of syngas to DME (STD) is carried out on this CuZnAl/SAPO11-PhyC zeolite capsule catalyst, comparing its catalytic performance with other general mixture catalyst of CuZnAl/SAPO11-M. The reaction results indicate that the zeolite capsule catalyst of CuZnAl/SAPO11-PhyC prepared by PhyC method can increase not only the syngas conversion, but also the selectivity of the desired DME, considerably better than the mixture catalyst of CuZnAl/SAPO11-M. The excellent catalytic performance of zeolite capsule catalyst CuZnAl/SAPO11-PhyC should be attributed to its special core–shell-like structure that provides a confined reaction field to the studied STD reaction, accelerating the syngas conversion to DME, at the same time suppressing the over-dehydration of DME to form other by-products.

Keywords: Zeolite capsule catalyst, SAPO-11, Cu/ZnO/Al2O3, Syngas, Dimethyl ether
3.1. Introduction

Dimethyl ether (DME) is widely used as basic chemical feed stock for producing many downstream substances such as methyl acetate, acetaldehyde, acetic acid, etc. [1, 2]. Moreover, DME is also known as one of the promising substitute of petroleum-based fuels [3]. Burning DME can effectively reduce the exhaust of environmental-unfriendly particular matters, like soot, SOx and NOx [4]. DME has high cetane number, which can help it to replace the general diesel fuel or act as liquefied petroleum gas (LPG) for cooking or power generation [5, 6]. Therefore, designing more effective catalyst for the production or conversion of DME has gradually attracted more attentions.

Generally, DME is produced through two ways: one is methanol dehydration on a single acidic catalyst and another is a tandem catalysis process including the initial syngas to methanol synthesis and the followed methanol dehydration to form DME over mixture catalysts [7]. The latter one-step process from syngas to DME, also named STD reaction, is more thermodynamically favorable than the first way of methanol to DME, due to the combination of two sequential reactions of methanol synthesis and methanol dehydration. The mixture catalysts for STD reaction usually comprise of a methanol synthesis catalyst (like Cu/ZnO, Cr/ZnO or Pd) and an acid catalyst (such as Al₂O₃ or H-ZSM-5 zeolite) [8–11]. Recently, some silicoaluminophosphate (SAPO) series zeolite, owing to their proper milder acidity property, also arose more research interests for DME production, starting from methanol or even CO₂-containing syngas [11–13].

The assembly style of the used mixture catalysts for STD reaction is physical mixing, that is, two types of different catalysts are simply mixed [14]. In STD reaction, methanol synthesis and methanol dehydration take place consequently on the mixture catalyst. However, although the preparation is simple, the obtained mixture catalysts in fact cannot
facilely realize the precise control on the two sequential reactions: methanol synthesis from syngas and methanol dehydration to from DME. It is difficult for mixture catalyst to define the assigned reaction happening on a fixed position or a required catalyst, as well as suppressing the formation of undesired byproducts through side reactions.

In order to overcome these disadvantages of mixture catalyst, a novel concept of designing catalyst with a core–shell-like structure, named capsule catalyst, was presented, and the prepared zeolite capsule catalyst has proved its premier ability for lots of tandem catalysis processes, including STD reaction [15–19]. The zeolite capsule catalyst is capable of increasing the desired products selectivity by giving severe space confinement to the intermediates and final products in tandem catalysis process [20]. Core–shell like zeolite capsule catalyst, in comparison with the general mixture catalyst, can realize tandem catalysis process more effectively and protect core catalyst from the harsh reaction environments [21–23], but the hydrothermal synthesis process usually used for zeolite shell preparation is rather complex and must be operated carefully, which severely limits the industrially scalable preparation and application of zeolite capsule catalysts. Therefore, in this cheaper, we develop a simple and scalable method, named physical coating (PhyC), to overcome this obstacle. This PhyC method is a considerably simple method to prepare the zeolite capsule catalyst without special equipment. With the assistance of PhyC method, without using direct hydrothermal synthesis process, we can facilely construct a well-organized zeolite shell enwrapping core catalyst to get a core–shell-like capsule catalyst.

The demonstrated zeolite capsule catalyst, named CuZnAl/SAPO11-PhyC in this report, is a core–shell-like silicoaluminophosphate-11 (SAPO-11) zeolite shell encapsulated Cu/ZnO/Al₂O₃ (CuZnAl) catalyst. It is characterized by XRD, SEM, EDS,
N$_2$ adsorption and NH$_3$-TPD. The tandem catalysis process of one-step syngas to dimethyl ether (STD) is investigated on this CuZnAl/SAPO11-PhyC zeolite capsule catalyst, comparing its catalytic performance with another general mixture catalyst.

3.2. Experimental

3.2.1 Catalyst preparation

3.2.1.1 Silicoaluminophosphate-11 synthesis

Silicoaluminophosphate-11 (SAPO-11) was synthesized by hydrothermal synthesis method. The SAPO-11 was prepared with the recipe of 1.2Al$_2$O$_3$:3.0H$_3$PO$_4$:0.6SiO$_2$:2.0 Di-n-propylamine (DPA): 100H$_2$O. Firstly, the aqueous H$_3$PO$_4$ (85%, Chemerion Reagent) was slowly added into the solid aluminium isopropoxide (99%, Sigma–Aldrich). The mixture was stirred for 2 h until a homogenous white solution was obtained. Then certain amount of DPA was added slowly into this mixture under vigorous stirring for 3 h. Finally, the silica sol (LUDOX 40 wt% suspension, Aldrich) was mixed with the above mixture and was further stirred for another 6 h. The final sample was transferred into a Teflon container capped with a stainless steel autoclave and then placed into the hydrothermal unit (DRM-420DA, Hiro Company, Japan). The zeolite crystallization process was performed at 180C for 48h. After crystallization, the product was separated from the mother liquid by centrifuge, dried at 120 °C overnight, followed by calcination in a muffle oven at 500 °C for 2 h to eliminate the organic template in zeolite.

3.2.1.2. Cu/ZnO/Al$_2$O$_3$ (CuZnAl) catalyst preparation

The Cu/ZnO/Al$_2$O$_3$ (CuZnAl) catalyst, a tri-component catalyst consisting of Cu, Zn and Al (Cu/Zn/Al=6:3:1mol ratio), was prepared by a conventional oxalate co-precipitation method [17, 24, 25]. The nitrates of copper, zinc and aluminum were
dissolved in ethanol to get solution (A), and the oxalic acid was dissolved by ethanol independently to get another solution (B). Two solutions of (A) and (B) were mixed rapidly at room temperature under vigorous stirring. And then the formed gel-like precipitate performed ageing treatment at room temperature for 24 h. After ageing step, the precipitate was separated by centrifuge, dried at 120 °C for 6 h, followed by calcination in muffle oven at 370 °C for 1 h. Finally, the obtained sample was compressed and granulated into the fixed pellet size in 0.85–1.70 mm. The prepared catalyst was named CuZnAl catalyst and used as core catalyst for zeolite capsule catalyst preparation.

3.2.1.3. Zeolite capsule catalyst preparation by physical coating (PhyC) method

We developed a new physical coating (PhyC) method to prepare zeolite capsule catalyst without employing hydrothermal synthesis, as illustrated by Fig.3.1. A certain amount of silica sol (Ludox: 40wt%, Aldrich) was diluted by 1.5 times deionized water and then used as adhesive. The CuZnAl core catalyst was immersed in the diluted silica sol for a while, and then it was mixed with the as-prepared SAPO-11 zeolite powder in a round bottomed flask, followed by vigorously shaking until the formation of an integrated zeolite shell on the external surface of CuZnAl core catalyst. This procedure could be repeated for several times to realize the desired zeolite shell thickness. The obtained sample was finally calcined at 500 °C for 2 h to strengthen the zeolite shell. The obtained zeolite capsule catalyst, named CuZnAl/SAPO11-PhyC, had a core–shell structure in which the CuZnAl core catalyst was encapsulated by a well-prepared SAPO-11 zeolite shell. The weight ratio of zeolite shell to core catalyst in capsule catalyst was about 1:5. The contact intensity between core and shell was considerably higher. Even after several gas-phase STD reactions with the prepared capsule catalyst, we still got the unbroken capsule catalyst particles.
3.2.1.4. General mixture catalyst preparation

So far, the general catalyst for STD reaction is mixture catalyst that consists of one methanol synthesis catalyst and another acidic catalyst. Herein, we also prepared a mixture catalyst, as reference catalyst of capsule catalyst, by simply mixing SAPO-11 zeolite with CuZnAl catalyst. The mixture catalyst, named CuZnAl/SAPO11-M in the followed discussion, was prepared by mechanically blending 2g SAPO-11 zeolite with 10g CuZnAl catalyst. The obtained mixture powder was compressed by 60MPa and granulated into the pellet size of 0.85–1.70mm same to that of zeolite capsule catalyst.

3.2.2. Catalysts characterization

The X-ray diffraction (XRD) analysis of catalysts was performed at 40kV and 40mA with a Rigaku RINT 2400 diffractometer equipped with CuKα radiation source. For the prepared SAPO-11 zeolite powder, the energy dispersive X-ray spectroscopy (EDX, Shimadzu Rayny EDX-700) was adopted to determine its elemental composition. The morphology and element composition of CuZnAl core catalyst as well as CuZnAl/SAPO11-PhyC capsule catalyst was also determined by a scanning electron microscop (SEM, JEOL JSM-6360LV) equipped with an energy dispersive X-ray spectrometer (EDS, JEOL JED-2300). The specific surface area, pore volume, and average pore diameter of catalysts were determined by nitrogen adsorption (Quantachrome Autosorb, Japan). The samples were degassed at 200°C before analysis. The temperature programmed desorption of NH$_3$ (NH$_3$-TPD) on catalyst was performed in an automatic adsorption system (BELCAT-B-TT, BEL Japan) equipped with an online thermal conductivity detector (TCD) and a mass spectrometer (MS).

3.2.3. Catalytic activity test

The STD reaction was carried out in a fixed bed reactor under the reaction
temperature of 250 °C and pressure of 5.0 MPa. The STD reaction on each catalyst was performed for 5 h. The syngas composition was 58.10% H₂: 33.80% CO: 5.10% CO₂: 3.09% Ar. The effluent gaseous products were analyzed online by Shimadzu GC-8A with a TCD detector (column: Porapak N) for detecting CO, CO₂ and CH₄. The hydrocarbon products were analyzed online by another Shimadzu GC-8A with a FID detector (column: Gaskuropack + Porapak Q). Before reaction, the catalyst was reduced first in situ by 5% H₂ in Ar at 220 °C for 10 h. The catalytic activity of catalysts given below was the average value of two repeated experiments in order to make the reaction data more credible. The total conversion shown in Table 3.3 was calculated as follow:
Total conv. = (a × CO conv. + b × CO₂ conv.)/(a+b) where “a” and “b” were the contents of CO and CO₂ in the syngas respectively.

3.3. Results and discussion

3.3.1. Catalyst characterization

In this chapter, the Silicoaluminophosphate-11 (SAPO-11) zeolite was firstly synthesized, and then the prepared SAPO-11 zeolite, acting as blending composition or shell block was used to prepare mixture catalyst of CuZnAl/SAPO11-M and zeolite capsule catalyst of CuZnAl/SAPO11-PhyC. The elemental composition of the as-synthesized SAPO-11 zeolite was analyzed by EDX, and the analysis result is shown in Table 3.1, from which we could deduce that the Si/Al ratio of this SAPO-11 zeolite was 0.16. The CuZnAl catalyst used here was widely known because of its excellent ability on methanol synthesis from syngas. The surface SEM and EDS analysis of the bare CuZnAl core catalyst in Fig. 3.2 gave its surface morphology and elemental composition. The EDS analysis result indicated that the CuZnAl catalyst had the molar composition of
Cu:Zn:Al=66.6:29.3:4.1. The obtained molar ratio of Cu to Zn to Al by EDS was only slightly different from the adopted ratio in catalyst preparation recipe. The core–shell-like zeolite capsule catalyst was an optimized design obtained by investigating the relationship between the assembly style of varied catalysts and their catalytic performance in tandem catalysis process [26–28].

In this chapter, we developed a new physical coating (PhyC) method, without employing the general hydrothermal synthesis way [27, 9, 30], for preparing a new zeolite capsule catalyst consisting of a SAPO-11 zeolite shell and a CuZnAl core catalyst. For the conventional zeolite capsule catalysts preparation, the hydrothermal synthesis process was necessary, to synthesize various zeolite shell, such as H-Beta, H-ZSM-5 or Silicalite-1, to encapsulate different core catalysts [18, 31, 32]. The high crystallization temperature and alkaline solution required by hydrothermal synthesis process, however, might cause some serious problems on the active metals on core catalyst. In order to overcome these negative problems of general hydrothermal synthesis process on zeolite capsule catalyst preparation, as well as to accelerate the industrial production of zeolite capsule catalyst, we developed the PhyC method to prepare the SAPO-11 zeolite shell encapsulated CuZnAl capsule catalyst. The surface SEM image and EDS analysis was employed to identify the zeolite shell of the CuZnAl/SAPO11-PhyC capsule catalyst prepared by the PhyC method. The bare CuZnAl core catalyst, as a reference of the capsule catalyst, was first presented in Fig. 3a. The SEM image of the CuZnAl/SAPO11-PhyC capsule catalyst was shown in the followed Fig. 3.3 (b) and (c). The PhyC method was a simple way to construct SAPO-11 shell on the surface of the bare CuZnAl core catalyst by employing the diluted silica sol as a binder. After this shell preparation, the surface of CuZnAl became rough, as shown in Fig. 3.3 (b), compared
with that of the bare CuZnAl core catalyst in Fig. 3.3 (a). The particle size of SAPO-11 zeolite crystal was about 5 µm. The SAPO-11 zeolite shell was considerably uniform and homogeneous, covering the CuZnAl core catalyst completely, without any uncovered surface of the CuZnAl core catalyst. Moreover, EDS analysis was employed to determine the surface elemental composition of zeolite capsule catalysts. The analysis results on CuZnAl/SAPO11-PhyC are showed in Fig. 3.3 (d). The Si/Al ratio obtained by EDS on the zeolite shell was 0.45, slightly higher than that of the original SAPO-11 powder showed in Table 3.1. The adopted silica sol, as binder for zeolite shell preparation, was responsible for this increased Si content of zeolite shell, but it had not active sites for the STD reaction in this work. Moreover, the absence of Cu and Zn signals obtained on this SAPO-11 zeolite shell could help us to further prove that the well-prepared SAPO-11 shell by PhyC method was uniform and compact, indicating the success of this new PhyC method for core–shell-like zeolite capsule catalyst preparation.

XRD was used to identify the crystalline type of pure SAPO-11 zeolite, CuZnAl core catalyst and the formed SAPO-11 zeolite shell of CuZnAl/SAPO11-PhyC capsule catalyst. The XRD diffraction peaks of pure SAPO-11 zeolite, mixture catalyst and capsule catalyst are presented in Fig. 3.4. The classic zeolite peaks found in capsule catalyst CuZnAl/SAPO11-PhyC were in agreement with the pure SAPO-11 zeolite, indicating the existence and unchanged state of SAPO-11 after zeolite shell preparation process. Furthermore, to this zeolite capsule catalyst, three typical peaks among 30–40h attributed to Cu/ZnO/Al₂O₃ had no obvious change, they were same to that of the pure Cu/ZnO/Al₂O₃ catalyst, which further prove that the developed PhyC method for zeolite shell preparation would not affect the properties of Cu/ZnO/Al₂O₃ core catalyst. The weak intensity of SAPO-11 zeolite shell on capsule catalyst CuZnAl/SAPO11-PhyC
Nitrogen adsorption was used to determine the specific surface area and total pore volume of different catalysts. The analysis results are showed in Table 3.2. Both of the zeolite capsule catalyst CuZnAl/SAPO11-PhyC and mixture catalyst CuZnAl/SAPO11-M shows lightly higher specific surface area than the pure CuZnAl catalyst, due to the introduction of SAPO-11 zeolite. The employed zeolite SAPO-11, here, was one of microporous zeolite, hence it had higher specific surface area, which in theory would enhance the final catalyst’s specific surface area. The temperature program desorption of ammonia (NH\textsubscript{3}-TPD) was performed on all catalysts respectively to investigate the catalyst acidic sites amounts. The analysis results are showed in Table 3.2, and the associated ammonia desorption profiles are given in Fig. 3.5. There was only one broad desorption peak between 200 and 300 °C for all catalysts. Pure SAPO-11 zeolite had a large number of milder acid sites [12]. These milder acid sites would significantly contribute to the catalytic performance of the prepared mixture catalyst CuZnAl/SAPO11-M and zeolite capsule catalyst CuZnAl/SAPO11-PhyC, facilitating methanol dehydration to form DME in STD reaction.

3.3.2. Catalytic performance of catalysts in STD reaction

The STD reaction mainly consisted of two sequential reactions: one was syngas to methanol and another was the dehydration of methanol to form DME. We use this STD reaction process to test the catalytic performance of the prepared zeolite capsule catalyst CuZnAl/SAPO11-PhyC. The naked CuZnAl catalyst and mixture catalyst of CuZnAl/SAPO11-M, as reference catalysts, had been tested under the same reaction conditions. All the reaction results obtained on the tested catalysts were compared in Table 3.3. As the prepared CuZnAl catalyst was one of the most used methanol synthesis
catalyst, the reaction results on this CuZnAl catalyst showed higher methanol selectivity of 96.8%, which was in complete agreement with previous reports on its performance. The DME selectivity, however, on this CuZnAl catalyst was zero, because there was no available dehydration catalyst whereby to convert methanol to DME. Another reference catalyst CuZnAl/SAPO11-M was prepared by simply mixing CuZnAl catalyst with SAPO-11 zeolite catalyst. Two components, CuZnAl and SAPO-11, in this mixture catalyst cooperated randomly to convert syngas to DME. Syngas and CO\textsubscript{2} would be first converted to methanol on the CuZnAl catalyst, part of the formed methanol had some chances to contact SAPO-11 zeolite to be converted into DME. But it should also be noted that considerable methanol diffused from CuZnAl catalyst would escape from this mixture catalyst directly without further conversion. As shown in Table 3.3, the CO conversion obtained on CuZnAl/SAPO11-M was 64.9%, higher than that of pure CuZnAl catalyst. The enhanced catalytic activity for this mixture catalyst should be attributed to the parallel methanol dehydration reaction on SAPO-11 catalyst that could accelerate CO conversion on CuZnAl catalyst by removing the formed methanol. The CO\textsubscript{2} conversion was 77.3%, which means the formation of CO\textsubscript{2} from CO by Water–Gas-Shift (WGS) reaction. The methanol selectivity decreased to 51.4% from the highest value of 96.8% on the bare CuZnAl catalyst, along with the increase of DME selectivity reaching up to 46.6%. Therefore, this mixture catalyst CuZnAl/SAPO11-M showed the ability on DME direct synthesis from syngas, but the selectivity of DME was not so satisfactory. For zeolite capsule catalyst CuZnAl/SAPO11-PhyC, it had a special core–shell-like structure that was entirely different with that of mixture catalyst CuZnAl/SAPO11-M. The zeolite capsule catalyst CuZnAl/SAPO11-PhyC contained two parts: CuZnAl core and SAPO-11 zeolite shell, as demonstrated in Fig. 3.1. In STD reaction on this zeolite capsule catalyst,
syngas entered the core section of capsule catalyst, where methanol synthesis reaction occurred. The formed methanol must diffuse passing through SAPO-11 zeolite shell to escape capsule catalyst, thus there were enough chances for methanol to contact the active acidic sites of zeolite shell to be converted into DME. The reaction results of STD reaction on zeolite capsule catalyst are also listed in Table 3.3. This CuZnAl/SAPO11-PhyC zeolite capsule catalyst gave the highest CO conversion of 92.0 % among the tested three catalysts. The DME selectivity reaches up to 90.3 %, and methanol as tiny byproducts accounts for only 9.2 % in total products. The product distribution of all catalysts is showed in Fig. 3.6. It was clear that methanol was the main product on pure CuZnAl, both of methanol and DME accounted for about half of the total products on mixture catalyst CuZnAl/SAPO11-M, but the selectivity of the desired DME obtained on zeolite capsule catalyst CuZnAl/SAPO11-PhyC was much higher than those of the above two reference catalysts. The usually used hydrothermal synthesis method for zeolite shell preparation could partly affect zeolite capsule catalysts activity, as proved by previous reports [28, 32–34]. Here, for zeolite capsule catalyst of CuZnAl/SAPO11-PhyC, the developed new PhyC method could effectively reduce the possible disadvantage caused by shell preparation process. The porous structure and active sites of CuZnAl core catalyst would be safe from the zeolite shell preparation, without undergoing higher hydrothermal synthesis temperature, deactivation by alkaline solution or impregnation of zeolite synthesis solution. Therefore, the core catalyst could hold its original activity for catalytic performance. Furthermore, the STD reaction for DME synthesis consisted of two sequential reactions: methanol synthesis from syngas and methanol dehydration to form DME. The combination of these two reactions on core–shell shaped catalyst was more thermodynamically favorable. To the
CuZnAl/SAPO11-PhyC zeolite capsule catalyst, two sequential reactions, syngas to methanol and methanol dehydration to DME, proceeded smoothly and cooperated more concertedly, especially in comparison with the mixture catalyst of CuZnAl/SAPO11-M. The confinement effect of core–shell-like structure of zeolite capsule catalyst CuZnAl/SAPO11-PhyC should contribute to its highest DME yield. The zeolite shell enwrapped CuZnAl core catalyst uniformly and completely, which created an inevitable way for the formed methanol on CuZnAl core catalyst to contact zeolite. However, for the mixture catalyst CuZnAl/SAPO11-M prepared by simply blending two types of catalysts, it was a random diffusion route for the formed methanol, that was, lots of methanol molecules will escape from mixture catalyst without contact with the acid sites of SAPO-11, as proved by the higher residual methanol content and lower DME selectivity obtained by mixture catalyst CuZnAl/SAPO11-M.

3.4. Conclusions

In this chapter we presented a new physical coating method (PhyC), without employing hydrothermal synthesis way, to successfully prepare a new core–shell-like zeolite capsule catalyst CuZnAl/SAPO11-PhyC. The SEM and EDS analysis results on this zeolite capsule catalyst indicated that the obtained zeolite shell was defect-free, uniform and compact. This zeolite capsule catalyst was used to synthesize dimethyl ether directly from syngas via a tandem catalysis process. The reaction results indicated that the catalyst assembly style of CuZnAl core catalyst encapsulated by SAPO-11 shell by our PhyC method could increase not only the CO conversion, but also the DME selectivity, significantly better than that of the reference mixture catalyst of CuZnAl/SAPO11-M prepared by a general mixing way. The CO conversion and DME selectivity obtained by
this zeolite capsule catalyst reached up to 92 % and 90 %, respectively, accompanied by very low selectivity of by-products. The excellent catalytic performance of zeolite capsule catalyst CuZnAl/SAPO11-PhyC derived from its special core-shell-like structure that provided a confined reaction field to STD reaction and at the same time suppressed the further deep dehydration of DME to form other hydrocarbon by-products. The presented methodology and application, in this report, would give new insight to preparing other zeolite capsule catalysts with a cost-saving and highly flexible manner. Furthermore, from a generalization point of view, the simple replication of such PhyC method into another tandem catalysis process that required more than two different catalysts would also generate fully novel innovation.
References


Yeung, Preparation of core (Ni base)–shell (Silicalite-1) catalysts and their application for alkali resistance in direct internal reforming molten carbonate fuel cell, J. Power Sources 198 (2012) 14–22.


Table 3.1. the elemental composition of SAPO-11 EDX.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elemental analysis(^a) (mol%)</th>
<th>Si/Al</th>
<th>Si/(Al + P + Si)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al</td>
<td>P</td>
<td>Si</td>
</tr>
<tr>
<td>SAPO-11</td>
<td>59.7</td>
<td>31.0</td>
<td>9.3</td>
</tr>
</tbody>
</table>

\(^a\) Elemental composition obtained from EDX analysis.
Table 3.2. The N$_2$ adsorption properties of the different catalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m$^2$/g)</th>
<th>Total pore volume (cc/g)</th>
<th>NH$_3$-TPD (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuZnAl</td>
<td>85</td>
<td>0.207</td>
<td>0.428</td>
</tr>
<tr>
<td>CuZnAl/SAPO11-PhyC</td>
<td>90</td>
<td>0.311</td>
<td>0.505</td>
</tr>
<tr>
<td>CuZnAl/SAPO11-M</td>
<td>91</td>
<td>0.243</td>
<td>0.510</td>
</tr>
<tr>
<td>SAPO-11</td>
<td>154</td>
<td>0.622</td>
<td>0.577</td>
</tr>
</tbody>
</table>
### Table 3.3. The catalytic performance of different catalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conversion(^a) (%)</th>
<th>Selectivity (C-mol%)</th>
<th>DME yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CO</td>
<td>CO(_2)</td>
<td>Total</td>
</tr>
<tr>
<td>CuZnAl</td>
<td>51.0</td>
<td>−16.7</td>
<td>42.1</td>
</tr>
<tr>
<td>CuZnAl/SAPO 92-M</td>
<td>92.0</td>
<td>−163.7</td>
<td>58.5</td>
</tr>
<tr>
<td>CuZnAl/SAPO 11-M</td>
<td>64.9</td>
<td>−77.3</td>
<td>46.2</td>
</tr>
</tbody>
</table>

\(^a\) Reactions conditions: 250 °C, 5.0MPa, W\(_{Cu/ZnO}/F_{SynGas}\) =10 g mol/h, 5th hour data.
Fig. 3.1. Illustration for the CuZnAl/SAPO11-PhyC zeolite capsule catalyst preparation by PhyC method.
Fig. 3.2. Surface SEM image and EDS analysis of the bare CuZnAl catalyst.
Fig. 3.3. SEM images of (a) the CuZnAl core catalyst, (b) the zeolite capsule catalyst CuZnAl/SAPO11-PhyC, (c) the magnified surface and (d) the related surface EDS analysis of zeolite capsule catalyst CuZnAl/SAPO11-PhyC.
Fig. 3.4. XRD diffraction lines of pure SAPO-11, zeolite capsule catalyst CuZnAl, SAPO11-PhyC, mixture catalyst CuZnAl/SAPO11-M and naked CuZnAl core catalyst. (a) The magnified characteristic peaks of SAPO-11 on both capsule catalyst CuZnAl/SAPO11-PhyC and mixture catalyst CuZnAl/SAPO11-M.
Fig. 3.5. NH3-TPD profiles of the SAPO-11 zeolite, CuZnAl, CuZnAl/SAPO11-M and CuZnAl/SAPO11-PhyC catalysts.
Fig. 3.6. Product distribution of the bare CuZnAl core catalyst, zeolite capsule catalyst CuZnAl/SAPO11-PhyC and mixture catalyst CuZnAl/SAPO-M.
Chapter 4

Summary

Syngas, a gas mixture consisting of H$_2$ and CO, is considered as an important chemical raw material. It is used for producing a lot of downstream products through famous technical process, like methanol synthesis, Fischer–Tropsch synthesis (FTS) and ammonia syngas etc. Syngas can be produced industrially by coal, petroleum, biomass gasification or the reforming of natural gas. Recently, a large amount of coal and petroleum was used and then emitted enormous amounts of greenhouse gas CO$_2$ into air, hence leading to serious environmental damage. From the point of view of environment protection, reducing CO$_2$ emission has become an urgent need. However, CO$_2$ dry reforming of methane to syngas has been receiving considerable attention, since the reaction converts two greenhouse gases (CH$_4$ and CO$_2$) to valuable syngas simultaneously. In addition, due to the potential reserves of shale gas and flammable ice, the more substitution of natural gas into coal and petroleum for producing downstream chemicals become more meaningful. Therefore, designing effective catalyst for syngas production from CO$_2$ dry reforming of methane is of great significance.

In this work, we designed and prepared Ni-based catalyst for effectively producing syngas from the reaction process of CO$_2$ dry reforming of methane in chapter 1-2.
Firstly, a nickel nanoparticles embedded carbon/silica catalyst was synthesized by one-step solid-liquid grinding method. In this process of preparation, the Ni-based species was directly reduced to metallic Ni due to the generation of reduction species such as H\textsubscript{2}, CO and CH\textsubscript{4} from soybean decomposition over calcination. The prepared catalyst without further reduction was directly employed to produce syngas in the reaction process of CO\textsubscript{2} dry reforming of methane. The result indicated that the catalyst without further reduction exhibited higher catalytic activity compared to that of the catalyst with H\textsubscript{2} reduction. Therefore, using the solid–liquid grinding route for catalyst preparation presented important significance because of its excellent catalysis activity as well as low preparation cost. In order to further enhance the catalysis activity and stability in the process of CO\textsubscript{2} dry reforming of methane, a monolithic foam catalyst Ni–Al\textsubscript{2}O\textsubscript{3}–SiC with a stereo structure was prepared via an one-step evaporation-induced self-assembly (EISA) method and then used for CH\textsubscript{4} reforming process to effectively produce syngas. The monolithic Ni–Al\textsubscript{2}O\textsubscript{3}–SiC catalyst showed higher catalysis activity and stability than Ni/SiC catalyst prepared by impregnation method, which was attributed to the small crystalline size of metallic Ni nanoparticles and high heat conductivity of SiC.

In this chapter 3, syngas was used for directly producing dimethyl ether (DME). As
known, DME was widely used as basic chemical feedstock for producing many downstream substances such as methyl acetate, acetaldehyde, acetic acid, etc. Moreover, DME is one of the promising substitutes of petroleum-based fuels. Burning DME can effectively reduce the emission of environmental-unfriendly harmful matters, like soot, SO$_x$ and NO$_x$. Generally, DME is produced through two-step way: syngas to methanol on Cu-based catalyst and methanol dehydration to DME over acidic catalyst. Here, one-step DME synthesis was accomplished from syngas by a tailor-made shell-core-like capsule catalyst SAPO-11 zeolite encapsulated Cu/ZnO/Al$_2$O$_3$ core. In this reaction process, methanol was firstly synthesized from syngas over core Cu/ZnO/Al$_2$O$_3$, and then methanol dehydrated to DME on SAPO-11 shell catalyst. The reaction result showed that the capsule catalyst Cu/Zn/Al/SAPO-11- PhyC presented higher catalytic activity, better than physical mixture catalyst CuZnAl/SAPO11-M, which was assigned to the special space structure of shell-core. The synthesized Ni-based catalyst and capsule catalyst will play an important role in the field of green chemistry and environmental engineering.
List of publications

Papers
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2. Rungravee Phienluphon, Kitima Pinkaew, Guohui Yang, Jie Li, Qinrong Wei, Yoshiharu Yoneyama, Tharapong Vitidsant, Noritatsu Tsubaki, Designing core (Cu/ZnO/Al2O3)–shell (SAPO-11) zeolite capsule catalyst with a facile physical way for dimethyl ether direct synthesis from syngas, Chemical Engineering Journal, 270 (2015) 605-611.

Conferences
2. Ethanol direct synthesis from dimethyl ether and syngas on the combination of noble metal impregnated zeolite with Cu/ZnO catalyst, The international chemical congress of pacific basin societies, Honolulu, Hawaii, United States, December 15-20, 2015.
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