Mesoporous nano Ni-Al₂O₃ catalyst for CO₂ methanation in a continuously stirred tank reactor

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ABSTRACT

Mesoporous nano Ni-Al₂O₃ catalysts were prepared by using Pluronic P123 (P123) and fatty alcohol polyoxyethylene ether (AEO-7) as structure directing agents (SDAs), and applied for CO₂ methanation in a continuously stirred tank reactor (CSTR). Compared with NiAl-N prepared by using AEO-7 as SDA and NiAl-P without SDA, NiAl-P prepared by using P123 as SDA possesses ordered mesopores, high Ni dispersion, large metal surface area and amounts of adsorbed CO₂, which benefits CO₂ conversion. Under the conditions of 1.0 MPa, 300 °C and H₂/CO₂ ratio of 4, NiAl-P shows the highest CO₂ conversion of 74.0% and CH₄ yield of 73.6%.

1. Introduction

In the past decades, the industrialization and urbanization across the world has resulted in a significant increase of CO₂ emissions, well known as main greenhouse gas leading to global warming [1,2]. The consequences of this global warming are mostly desertification, rising sea levels, and animal species extinction [2]. Therefore, the CO₂ mitigation and utilization are one of the most important challenges for modern societies [3,4]. The CO₂ capture and utilization technology, which capture the CO₂ and use it as feedstock to produce fuels, can play a significant role in CO₂ reduction, which is due to that the dependence of fossil fuels cannot be relieved in short term. The power-to-gas (PtG) route is regarded as a mature route because it can convert the intermittent renewable energy to synthetic natural gas [5–7]. In this concept, the captured CO₂ reacts with the H₂ originated from the water electrolysis by renewable energy, such as wind, solar or hydropower, to synthesize CH₄. Thus, the fluentant renewable energy can be stored by the form of CH₄ which can be easily transported or injected into the existing gas pipelines [4]. Moreover, compared to other CO₂ conversion reactions like methanol, and dimethyl ether, CO₂ methanation possesses many advantages, such as high activity and selectivity and high energy efficiency [8].

Great efforts have been made to develop metal-based catalysts for CO₂ methanation in a fixed-bed reactor, for example, the Ni [4,9,10], Ru [11] and Rh [12] on various supports Al₂O₃ [9,13], SiO₂ [1,14], ZrO₂ [11], CeO₂ [15,16] and zeolite [4,17]. Among these, Al₂O₃ supported Ni catalysts possess high activity and CH₄ selectivity, and relatively low cost [4,13,18]. However, the thermodynamic analysis shows that CO₂ methanation (CO₂ + 4H₂ ↔ CH₄ + 2H₂O, ΔH₂98K = −164 kJ/mol) is highly exothermic [7,19], for every 1% CO₂ conversion, the temperature rise for a typical methanator gas composition in an ammonia plant is 60 °C [20]. The large amounts of released heat may cause catalyst sintering and carbon deposition, resulting in the decrease of CO₂ equilibrium conversion [1,7]. To solve the local overheating problem, one of the major challenges is to remove the highly exothermic heat in time. The continuously stirred tank reactor (CSTR) can be operated at a uniform temperature in the reaction process by using an inert liquid medium, such as liquid paraffin, to suspend catalyst, thus it is suitable for highly exothermic reactions [19,21,22]. Now, the CSTR has been widely used in many reactions, such as F-T synthesis [21,22] and methanol synthesis [23]. Recently, the studies on CO hydrogenation to CH₄ in a slurry-bed reactor have been reported [24–26].

It is known that physical and chemical properties of Ni-Al₂O₃ catalyst depends on catalyst preparation methods [27,28]. Compared with the conventional impregnation method, the one-pot evaporation induced self-assembly (EISA) method has attracted much attention due to its excellent property for material preparation and high dispersion of active metals [29–31]. Morris et al. [29] found that alumina-supported metal oxides via EISA method possess well-developed mesoporosity, relatively high BET surface area and large pore widths. For CO₂ methanation
reaction, it is well accepted that CO$_2$ is adsorbed on the support, then reacts with H$_2$ on the metal to produce CH$_4$. Thus, the physiochemical properties and Ni dispersion of Ni-Al$_2$O$_3$ are crucial for the reaction; moreover, since the inert liquid medium was adopted to suspend catalyst in CSTR, the catalysts with ordered mesoporous structure would benefit the mass transfer of feed gases and products [30]. Up to date, the reports of CO$_2$ methanation in a CSTR using Ni-Al$_2$O$_3$ catalyst have not been published before, which initiates the current work.

In this work, Ni-Al$_2$O$_3$ catalysts were prepared via EISA method using different structure directing agents (SDAs) to explore their physicochemical properties on CO$_2$ methanation in a CSTR. The catalysts were characterized by N$_2$ adsorption-desorption, X-ray diffraction (XRD), temperature-programmed reduction in H$_2$ (H$_2$-TPR), H$_2$-chemisorption, X-ray photoelectron spectroscopy (XPS), temperature-programmed desorption of CO$_2$ and NH$_3$ (CO$_2$-TPD and NH$_3$-TPD) and transmission electron microscopy (TEM). The effects of reaction conditions, including stirring speed, reaction temperature, pressure, H$_2$/CO$_2$ molar ratio and gas hourly space velocity (GHSV) on CO$_2$ methanation performance were studied. The relationships between the CO$_2$ methanation activity and physicochemical properties of the catalysts were discussed.

2. Experimental

2.1. Catalyst preparation

Ni-Al$_2$O$_3$ catalyst was prepared by the method reported elsewhere [29]. Briefly, Pluronic P123 (P123) was dissolved in ethanol, then Al (C$_6$H$_{12}$O$_7$)$_3$, nitric acid and Ni(NO$_3$)$_2$·6H$_2$O were added in sequence. The mixed solution was stirred for 5 h and dried at 60 °C for 48 h. The obtained solid was calcined in air at 550 °C for 4 h, and denoted as NiAl-P. The sample NiAl-A was prepared by using AEO-7 as SDA. The sample NiAl-N prepared without SDA.

The content of Ni in Ni-Al$_2$O$_3$ was set at 30 wt%. All the calcined samples were crushed and grounded to 140–200 mesh particles before reduction. The reduction was carried out at 550 °C in 25%H$_2$/75%N$_2$ for 6 h. The detailed preparation description was supplied in Electronic Supporting Information (ESI).

2.2. Catalysts characterisation

Ni-Al$_2$O$_3$ catalysts were characterized by powder and in-situ XRD, N$_2$ adsorption-desorption, TEM, H$_2$-TPR, XPS, H$_2$-chemisorption, CO$_2$-TPD and NH$_3$-TPD. The details of these characterizations were given in ESI.

2.3. Catalytic performance evaluation

The performance of CO$_2$ methanation was conducted in a CSTR. The gas products were analyzed by an online Agilent 7890A gas chromatography. CH$_4$ and C$_2$H$_4$ were analyzed by using FID equipped with HP-AL/S column. CO$_2$, N$_2$ and CO were analyzed by using TCD equipped with Porapak-Q column, PLOT/Q column and HP-MOLESIEVE column. The detailed reaction conditions and performance analysis were described in ESI.

3. Results and discussion

3.1. Textural properties

N$_2$ adsorption-desorption isotherms of calcined NiAl-P, NiAl-N and NiAl-A catalysts are displayed in Fig. 1(a). All samples exhibit typical type IV isotherms as defined by IUPAC classification, characteristic of the mesoporous structure. NiAl-P possesses an H1 type hysteresis loop, suggesting a uniform mesopores and a cylindrical mesopore channel among the framework [17]. NiAl-A catalyst, prepared by using AEO-7 as SDA, shows type IV curves with H3 type hysteresis loop, which is probably due to the non-rigid aggregation of plate-like particles. NiAl-N catalyst exhibits an H2 type hysteresis loop, which is the characteristic of mesopore with ink-bottle shaped pores. The pore size distributions of the samples are shown in Fig. S1. Obviously, NiAl-A and NiAl-N exhibit narrow peaks from 2 nm to 5 nm, whereas NiAl-P generates a broad pore size range from 6 nm to 12 nm. The textual properties of NiAl-P, NiAl-N and NiAl-A catalysts are listed in Table 1. NiAl-N sample shows slightly higher BET surface area than NiAl-A and NiAl-P samples. However, NiAl-P sample exhibits larger pore volume and average pore size than the NiAl-A and NiAl-N samples, which is due to the different SDAs in constructing the mesopore structure in the process of catalyst preparation.

3.2. Catalyst structure and morphology

The small-angle XRD patterns were selected to confirm the presence of ordered mesoporous structures of calcined Ni-Al$_2$O$_3$ catalysts. As shown in Fig. 1(b), NiAl-P catalyst presents an intense (100) peak at 0.9° and a weak one (110) around 1.4°, which is associated to the long-range and well-ordered mesoporous structure [32,33]. NiAl-A and NiAl-N catalysts do not display the characteristic peaks for mesoporous structures, the reason is probably due to the calcined SDA does not preserve the well-ordered mesopores.

The wide-angle XRD patterns of reduced Ni-Al$_2$O$_3$ catalysts are shown in Fig. S2. All samples exhibit the diffraction peaks of Ni metal at 2θ angle of 44.5°, 51.8° and 76.3° (JCPDS No. 47–1849). NiAl-N sample
shows much higher diffraction peaks than the other two. The crystallite sizes of metallic Ni listed in Table 1 show that NiAl-P and NiAl-A exhibit much smaller Ni crystallite sizes than NiAl-N. The in-situ XRD patterns of NiAl-P catalyst in a H$_2$ atmosphere at various reduction temperature are shown in Fig. S3. As the reduction temperature lower than 450 °C, there is almost no diffraction peaks. However, increasing the reduction temperature to 500 °C, the peaks at 2θ of 44.5° and 51.8° corresponding to Ni metal appear and gradually intensify as the reduction temperature increases. The results suggest that 550 °C was enough for the catalyst reduction.

TEM images of calcined Ni-Al$_2$O$_3$ catalysts are displayed in Fig. 2. It can be seen that a contrast of NiO and Al$_2$O$_3$, the dark black particles are recognized as NiO particles, whereas the gray colored particles are Al$_2$O$_3$ [34]. All samples exhibit NiO particles, which is due to the high Ni content in Ni-Al$_2$O$_3$ catalysts. Even at this high Ni content, NiAl-P shows small and uniform particles size of NiO around 10 nm, and no obvious aggregation of large particles were observed, indicating the high dispersion of NiO particles. NiAl-A and NiAl-N catalysts exhibit large particles and obvious aggregation of NiO, consistent with the XRD results.

### 3.3. Catalyst surface properties

H$_2$-TPR was performed to determine the reducibility of Ni species and interaction between Ni and support, as shown in Fig. S4. NiAl-N and NiAl-A exhibit the reduction temperature at 516 °C and 585 °C, respectively, while NiAl-P exhibits the main reduction peaks at 627 °C and a shoulder peak appears at 543 °C, which is probably attributed to the reduction of NiO located outside the ordered channels. The TPR results indicate that NiAl-P exhibit a stronger interaction between NiO and Al$_2$O$_3$ than NiAl-N and NiAl-A. The amounts of H$_2$ consumption and NiO reduction degree are summarized in Table 1. It can be found that NiAl-P possesses the highest amount of H$_2$ consumption (4.91 mmol/g) and reduction degree (96%), while NiAl-N shows the lowest values. The H$_2$ pulse chemisorption data listed in Table 1 shows that NiAl-P exhibits the highest Ni metal surface area of 7.31 m$^2$/g$_{cat}$ and highest Ni dispersion of 1.10%. NiAl-N exhibits the lowest values, which is attributed to the low reduction degree of Ni species.

XPS was performed to determine the chemical states of Ni species and interaction between Ni species and Al$_2$O$_3$. Fig. 3(a) shows the Ni 2p$_{3/2}$ spectra of the reduced catalysts. The peaks at binding energies (B. E.s) of ~853.0 eV can be attributed to Ni$^0$ metal, while the peaks located around 856.2 eV indicates the presence of NiAl$_2$O$_4$ spinel (856.2 eV) [5, 34]. It is worth to mention that NiAl-P and NiAl-A exhibit larger peak areas around 853.0 eV than NiAl-N, indicating the presence of larger amounts of NiO$^+$ on catalyst surface, consistent with the TPR analysis.

CO$_2$-TPD was performed to study the adsorption strength of CO$_2$ on Ni-Al$_2$O$_3$ catalysts, the profiles are shown in Fig. 3(b). Two desorption peaks are presented in the range of 50 ~ 200 °C and 200 ~ 350 °C. The peaks at low temperatures are attributed to the physical or weakly chemisorbed CO$_2$ on catalyst surface, while the peaks at high temperatures are ascribed to the strong basic sites on the catalyst surface [35].

**Table 1**

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>BET surface area (m$^2$/g)$^a$</th>
<th>Pore volume (cm$^3$/g)$^b$</th>
<th>Average pore diameter (nm)$^c$</th>
<th>Ni crystallite size (nm)$^d$</th>
<th>H$_2$ uptake (mmol/g)$^e$</th>
<th>Reduction degree (%)$^f$</th>
<th>Metal surface area (m$^2$/g$_{cat}$)$^g$</th>
<th>Dispersion (%)$^h$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiAl-P</td>
<td>298</td>
<td>1.13</td>
<td>6.79</td>
<td>6.2</td>
<td>4.91</td>
<td>96%</td>
<td>7.31</td>
<td>1.10</td>
</tr>
<tr>
<td>NiAl-A</td>
<td>292</td>
<td>0.61</td>
<td>4.95</td>
<td>6.4</td>
<td>3.96</td>
<td>77%</td>
<td>7.08</td>
<td>1.06</td>
</tr>
<tr>
<td>NiAl-N</td>
<td>362</td>
<td>0.58</td>
<td>4.80</td>
<td>10.4</td>
<td>2.75</td>
<td>54%</td>
<td>6.69</td>
<td>1.10</td>
</tr>
</tbody>
</table>

$^a$ Calculated by the BET equation.  
$^b$ BJH desorption volume.  
$^c$ BJH desorption average pore diameter.  
$^d$ obtained from XRD results.  
$^e$ obtained from H$_2$-TPR results.  
$^f$ Determined from H$_2$ chemisorption by assuming that one hydrogen atom occupies one surface metallic Ni atom.

NiAl-P shows a higher peak area and peak intensity at high temperature (~275 °C) than the other two, indicating that NiAl-P adsorbed more amounts of CO$_2$ benefiting the CO$_2$ conversion. NH$_3$-TPD profiles in...
Fig. S5 shows that all samples exhibit two desorption peaks for NH$_3$. As shown in Fig. S6(a), the CO$_2$ reaction conditions do not change the selectivity of CH$_4$. The results agree well with the CO$_2$-TPD analysis.

3.4. Catalyst performance for CO$_2$ methanation

The CO$_2$ methanation performance over Ni-Al$_2$O$_3$ catalyst was carried out in a CSTR. Before the evaluation, the reaction conditions were studied, including the stirring speed, reaction temperature, reaction pressure, H$_2$/CO$_2$ molar ratio and GHSV. The catalytic results are shown in Fig. S6. As shown in Fig. S6(a), the CO$_2$ conversion slightly increased as the stirring speed increased from 500 r/min to 800 r/min. Further increase in the stirring speed, the CO$_2$ conversion does not change. It is suggested that the stirring speed of 800 r/min is enough to exclude the mass diffusion during the reaction.

Table 2

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>CO$_2$ conversion (%)</th>
<th>Selectivity (%)</th>
<th>CH$_4$ yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiAl-P</td>
<td>74.0</td>
<td>99.5</td>
<td>0.3</td>
</tr>
<tr>
<td>NiAl-A</td>
<td>69.6</td>
<td>99.4</td>
<td>0.4</td>
</tr>
<tr>
<td>NiAl-N</td>
<td>57.5</td>
<td>99.1</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Fig. S6(b)–(d) show that CO$_2$ conversion as the reaction temperature changed (220–320 °C), pressure (0.5–3.0 MPa) or H$_2$/CO$_2$ ratio (2–5) increases. The increase of GHSV reduced the CO$_2$ conversion. Moreover, it is interesting to find that the reaction conditions do not change the selectivity of CH$_4$ obviously. Thus, the performance tests of Ni$_2$Al$_2$O$_3$ catalysts were carried out under the reaction conditions of 300 °C, 1.0 MPa, and 800 r/min with a H$_2$/CO$_2$ ratio of 4 and GHSV of 3000 mL/g h. The catalytic activity and stability are displayed in Fig. S7 and Table 2, respectively. It could be found in Fig. S7 that, after the catalyst induction period, all the catalysts exhibit high stability and selectivity for CH$_4$, C$_2$H$_4$ and CO. As shown in Table 2, NiAl-P catalyst exhibits the highest CO$_2$ conversion of 74.0% and CH$_4$ yield of 73.6%, while that of NiAl-N catalyst was only 57.5% and 57.0%, respectively. All the catalysts exhibit high selectivity for CH$_4$, and the selectivity of CO was only 0.2%. The high activity for NiAl-P catalyst was mainly attributed to the well-ordered mesopores, large Ni metal surface area, high Ni dispersion and amounts of adsorbed CO$_2$.

4. Conclusions

Mesoporous nano Ni-Al$_2$O$_3$ catalysts were prepared by using different SDAs. The reaction conditions for CO$_2$ methanation in a CSTR including the stirring speed, reaction temperature, reaction pressure, H$_2$/CO$_2$ molar ratio and GHSV were studied. The catalytic performance shows that NiAl-P prepared by using P123 as SDA exhibits higher CO$_2$ conversion and CH$_4$ yield than those of NiAl-A and NiAl-N, which is due to that NiAl-P catalyst possesses ordered mesopores, high Ni dispersion, large metal surface area and amounts of adsorbed CO$_2$.

CRediT authorship contribution statement

Fanhu Meng: Conceptualization, Methodology, Writing – review & editing, Funding acquisition, Supervision. Lina Wang: Investigation. Xin Li: Investigation, Data curation. Michal Perdjon: Investigation. Zhong Li: Conceptualization, Funding acquisition, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcatcom.2022.106437.

References


