CATALYTIC PERFORMANCE OF COMPOSITE OXIDE SUPPORTED Ni-BASED CATALYSTS FOR CO₂ METHANATION

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Abstract
Composite oxide supported Ni-based catalysts were prepared by wet impregnation technique and applied for the methanation of carbon dioxide. The composite oxide supports were prepared by an impregnation-precipitation method using commercial γ-Al₂O₃ powder loaded with different percentages of ZrO₂, TiO₂ and CeO₂ promoters. The as prepared catalysts were characterized by BET specific surface area, AAS, XRD, H₂-TPR and CO chemisorption. Catalytic activity of the synthesized catalysts was investigated towards hydrogenation of CO₂ at atmospheric pressure by varying reaction temperature between 250 and 400 °C. Experimental results revealed that the composite oxide supported Ni-based catalysts showed superior performance than the γ-Al₂O₃ only supported Ni-based catalyst. Among the investigated catalysts, the catalyst with the highest amount of promoter oxides showed the best activity: 81.4% conversion of CO₂ to CH₄ at 300°C. The better performance of the composite oxide supported Ni-based catalysts was achieved due to the improvements in reducibility nature of the catalysts (investigated using H₂-TPR).

Introduction
Significant reductions in carbon dioxide (CO₂) emissions and the development of non-fossil fuel energy sources are critical to minimize the effects of CO₂ as a greenhouse gas in the atmosphere and reduce our dependence on non-renewable energy sources, most notably crude oil [1]. The penetration increase of renewable energy sources (RES) and their integration with electric grid and related infrastructure is not straight-forward and poses new challenges, especially due to the intermittent nature of renewable sources as wind and solar power, so power production does not necessarily coincide with demand of end-users. Energy storage solutions need to be implemented or energy consumption patterns need to be adapted to compensate for the fluctuations in intermittent energy production from renewable sources. Chemical conversion in synthetic fuels might represent one of the most convenient ways in order to store large amounts of surplus electricity for long periods.
The Power-to-Gas (PtG) technology is a promising option in this context, enabling a combined temporal and spatial balancing solution for a time when renewable energy will supply the major part of the electrical demand. The storage concept links power and gas networks by the conversion of power into gas by two major steps: hydrogen (H₂) production by water electrolysis and the following conversion of H₂ and carbon dioxide (CO₂) into methane (CH₄) in the Sabatier reaction. In this way, renewable electricity can be stored in the already existing infrastructure (the natural gas distribution grid), and be used in many sectors through a mature technology.

The methanation (Sabatier reaction) is an exothermic reaction where H₂ and CO₂ reacts to form CH₄ and H₂O. The reaction is favoured at lower temperatures, but due to kinetic limitations, a catalyst needs to be utilized [2]. The catalysts investigated for CO₂ methanation are generally made up of Group 8, 9, 10 and 11 transition metals. Nickel based catalysts are the most common studied for CO₂ methanation because of their high activity and low price. However, conventional Ni catalysts supported on γ-alumina are easily deactivated as a result of sintering of Ni particles and coke deposition during the exothermic methanation reaction. Also, to increase their catalytic activity, Ni/Al₂O₃ catalysts usually need to have a high Ni content, which may cause faster deactivation of the catalyst during long-term operation [3].

The support plays a vital role on the active site dispersion, activity and stability. For the improvement of the Ni/γ-Al₂O₃ catalysts, it is frequently reported in the literature by γ-Al₂O₃ modification with addition of alkali metal oxides, rare earths oxides and other basic oxides, which can improve the reducibility, enhance the oxygen mobility, improve the metal dispersion, prevent the sintering of the metal sites and modify the interaction between Ni and Al₂O₃, inhibiting the formation of NiAl₂O₄ spinel phase. Therefore, the addition of metal oxide promoters can improve reducibility and chemisorption capacity due to a better dispersion of the nickel species on the composite metal oxide supports. Among the most employed modifiers, ZrO₂, SiO₂, MgO, La₂O₃, CeO₂ and TiO₂ have been introduced in the supports for the methanation catalysts [4,5].

In this work, we focused our attention on the synthesis by an impregnation-precipitation method of quaternary system supports (i.e. composite oxide of γ-Al₂O₃, ZrO₂, TiO₂ and CeO₂) and their application for Ni-based catalysts with relatively low Ni content, in order to study the promotional effect of all the three metal oxide promoters on performance of Ni/γ-Al₂O₃ catalysts for methanation of CO₂.

**Experimental procedures**

The composite oxide supported Ni-based catalysts were synthesized using a method described by Cai et al. [4] except increasing the number of loaded metal oxide promoters. Briefly, commercial γ-Al₂O₃ (Sasol-Puralox SCCa-20/200) was impregnated with aqueous solutions of Zirconyl nitrate, Titanium (IV)
isopropoxide and Cerium (III) nitrate hexahydrate salts of different ratios to get the desired percentages of composite oxide supports. Subsequently, the suspension was stirred for 2 h using a magnetic stirrer, and then NH₄OH aqueous solution was added until pH reached 10, at which precipitation occurred. The precipitate was filtered, washed with deionized water repeatedly and dried overnight at 120 °C and then calcined at 550 °C for 4 h. Each composite support was impregnated with suitable amount of Ni(NO₃)₂·6H₂O aqueous solution for getting a final loading of 20 wt% of Ni on the composite supports. The impregnated samples were dried at 120 °C for 16 h and calcined at 450 °C for 5 h. For comparison, commercial γ-Al₂O₃ was impregnated with 20 wt% of Ni employing the same procedure. The as synthesized catalysts were designed as 20%Ni/100% γ-Al₂O₃ = Ni/A; 20%Ni/85%γ-Al₂O₃-5%ZrO₂-5%TiO₂-5%CeO₂ = Ni/C5; 20%Ni/70%γ-Al₂O₃-10%ZrO₂-10%TiO₂ 10%CeO₂ = Ni/C10 and 20%Ni/55%γ-Al₂O₃-15%ZrO₂-15%TiO₂-15%CeO₂ = Ni/C15.

The as-synthesized catalysts were characterized using Atomic Absorption Spectroscopy (AAS), X-ray diffraction (XRD), BET specific surface area (SSA), temperature programmed reduction by H₂ (H₂-TPR) and CO chemisorption. The catalytic activity was measured by placing 600 mg catalyst (previously pelletized) in a fixed bed quartz reactor placed in an oven with temperature varied from 250 to 400 °C with steps of 25 °C. Before catalytic tests, all the samples were reduced at a temperature of 500 °C for 3 h by flowing 10 vol% H₂ in N₂. For the catalytic tests, a stoichiometric mixture (H₂/CO₂ = 4) highly diluted with N₂ was fed to the fixed bed. The overall inlet flow was varied, resulting in a GHSV from 20,000 to 30,000 h⁻¹. For the gas analysis, a multi-channel analyser (Emerson X-Stream) was used, equipped with NDIR sensors for CO, CO₂ and CH₄ measurement, a TCD detector for H₂ and a paramagnetic sensor for O₂.

Results and discussion
XRD patterns (not illustrated) of the composite oxide supports showed the presence of γ-Al₂O₃ and CeO₂. No clear characteristic diffraction peaks of ZrO₂ and TiO₂ phases were detected, since most of them were included in the peaks attributed to the Al₂O₃ and/or the CeO₂ phases. The Ni-based catalysts exhibited small reflections belonging to NiO. The crystalline size of NiO, calculated by the Scherrer equation, are reported in Table 1. The NiO crystallite size increased by increasing the percentage of the promoter oxides. This is in agreement with Takenaka et al. [6], showing that the nickel crystallites with relatively large sizes are suitable for methanation reactions.

Physicochemical properties of both the supports and catalysts are summarized in Table 1. From the BET measurements, the values of specific surface area for all composite oxides were higher with respect to the only γ-Al₂O₃ support. Moreover, a slight decreases of the surface area by increasing the percentage of promoter oxides was observed. The nickel content of the catalysts, reported in Table 1 as determined by AAS analysis, were in good agreement with the designed values.
CO chemisorption results of all the catalysts are summarized in Table 1. As a result, the nickel surface area in the reduced catalysts decreased in the order of Ni/C5 > Ni/C15 > Ni/C10 > Ni/A. Among the catalysts investigated, Ni/C5 showed the highest metallic surface area. This might be due to the highest BET surface area of the Ni/C5 catalyst. On the other hand, the Ni dispersion slight increased by increasing the percentage of composite oxides.

**Table 1.** Physicochemical properties of both the supports and catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface area (m²/g)</th>
<th>Ni (wt%)</th>
<th>Crystalline size of NiO (nm)</th>
<th>Nickel dispersion (%)</th>
<th>Nickel surface area (m²/g-Ni)</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ-Al₂O₃</td>
<td>186</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C5</td>
<td>188</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C10</td>
<td>182</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C15</td>
<td>183</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ni/A</td>
<td>149</td>
<td>15.42</td>
<td>15</td>
<td>2.33</td>
<td>16</td>
</tr>
<tr>
<td>Ni/C5</td>
<td>166</td>
<td>16.55</td>
<td>12</td>
<td>2.67</td>
<td>18</td>
</tr>
<tr>
<td>Ni/C10</td>
<td>165</td>
<td>17.20</td>
<td>16</td>
<td>3.17</td>
<td>15</td>
</tr>
<tr>
<td>Ni/C15</td>
<td>151</td>
<td>16.45</td>
<td>17</td>
<td>3.38</td>
<td>16</td>
</tr>
</tbody>
</table>

Three elementary species of reducible NiO were identified in the TPR profiles: α-type (surface amorphous NiO or bulk NiO), β-type (weakly interacted with Al₂O₃ or called Ni-rich phase) and γ-type (strongly interacted with Al₂O₃ or called Al-rich phase). For the composite oxide supported Ni-based catalysts, the β-peak and γ-peak temperatures shifts downwards, suggesting a weaker interaction between NiO and the composite support. Quantitative results of the TPR profiles (Table 2) showed that all the composite oxide supported catalysts possessed a higher fraction of β-type NiO. Moreover, the amount of H₂ consumed increased on the composite oxides support, confirming the weaker metal support interaction.

**Table 2.** Quantitative H₂-TPR data for the as-synthesized catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Fraction of total area (%)</th>
<th>Peak temperature (°C)</th>
<th>H₂ consumed (mmol/g_cat)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>α-type</td>
<td>β-type</td>
<td>γ-type</td>
</tr>
<tr>
<td>Ni/A</td>
<td>22</td>
<td>46</td>
<td>32</td>
</tr>
<tr>
<td>Ni/C5</td>
<td>27</td>
<td>51</td>
<td>22</td>
</tr>
<tr>
<td>Ni/C10</td>
<td>9</td>
<td>52</td>
<td>39</td>
</tr>
<tr>
<td>Ni/C15</td>
<td>12</td>
<td>54</td>
<td>34</td>
</tr>
</tbody>
</table>
Concerning the catalytic activity results, Figure 1A presents a comparison between the oxides-supported nickel catalysts. Above a temperature of ≈ 325 °C, chemical equilibrium is (almost) reached by testing each sample and all the curves are very similar. After an initial yield increase due to the positive impact of the temperature on the catalyst activity, a decrease due to the growing temperature effect on the equilibrium followed, reducing the thermodynamically achievable CH₄ yield.

![Figure 1A](image)

**Figure 1A.** Catalytic performance of the (A) Ni/composite oxide supported catalysts at GHSV=20,000 h⁻¹; (B) Ni/C15 catalyst at different space velocities.

As can be appreciated by the amounts of CO detected, the catalysts showed a very high methane selectivity. As a consequence, CO₂ conversion and CH₄ yield are very similar, especially at low temperature.

Far from equilibrium, the catalytic performance of the samples reflects the following order: Ni/C15 > Ni/C10 > Ni/C5 > Ni/A. All the catalysts with nickel supported on a quaternary system presented higher activity than the reference sample with Ni/γ-Al₂O₃, meaning that the addition of different oxides (TiO₂, CeO₂ and ZrO₂) within the support played a positive role. The amount of the added oxides increased the conversion at low temperature.

The performance order reflects the catalyst reducibility (see Table 2): the higher hydrogen consumed during H₂-TPR results in a major methane yield. The activity increase could be partly related to the amount of β-type NiO. Moreover, nickel dispersion (see Table 1) seems to reflect the activity results: both the Ni dispersion and calculated methane yield increase with a higher amount of TiO₂, CeO₂ and ZrO₂.
Figure 1B shows the impact of the space velocity on CH$_4$ yield, CO$_2$ conversion and CO selectivity for the Ni/C15 catalyst. As expected, the activity lowers by increasing the GHSV especially far from the equilibrium and the curve peak seems to shift towards a higher temperature value. On the other hand, the CO selectivity remained unchanged at low temperature, meaning that the developed catalysts showed very high selectivity to methane irrespective to contact time.

Conclusions
Four nickel-based catalysts for carbon dioxide hydrogenation into methane have been prepared and studied. Three nickel-supported on quaternary metal oxides system (γ-alumina, ceria, zirconia and titania) were compared with a Ni/γ-Al$_2$O$_3$ sample. All the catalysts have been characterized from a physicochemical standpoint. Nickel supported on quaternary system samples showed a higher surface area than the reference Ni/γ-Al$_2$O$_3$. Moreover, higher nickel dispersion resulted by increasing additional metal oxides (TiO$_2$, ZrO$_2$ and CeO$_2$) within the support.

The catalysts reducibility showed three reducible NiO types: ‘α’ (bulk NiO), ‘β’ (NiO weakly interacted with Al$_2$O$_3$), and ‘γ’ (NiO strongly interacted with Al$_2$O$_3$). The β-type and γ-type temperatures decreased for Ni on quaternary system catalysts, suggesting a weaker interaction between NiO and the composite support. The content of β-type NiO increased for Ni-supported composite supports (proportionally with the CeO$_2$, ZrO$_2$ and TiO$_2$ share), favouring the formation of large-sized metal Ni particles active at lower temperature values.

Activity tests showed higher conversion for the samples with a composite support and methane yield values resulted with the following order: Ni/C15 > Ni/C10 > Ni/C5 > Ni/A. Thus, higher fraction of TiO$_2$, ZrO$_2$ and CeO$_2$ within the support seems to imply superior catalytic performance, mainly depending on the reduction properties rather than the physical ones.

References

