A Comparison Study on Carbon Dioxide Reforming of Methane Over Ni Catalysts Supported on Mesoporous SBA-15, MCM-41, KIT-6 and γ-Al₂O₃

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Abstract—The activity of Ni supported on mesoporous SBA-15, MCM-41, KIT-6, and a sol-gel prepared Ni/γ-Al₂O₃ for catalysing methane dry reforming was investigated. The chemical and physical characteristics of the catalysts before and after catalytic testing were investigated using X-Ray diffraction, X-ray Photoemission Spectroscopy, Transmission Electron Microscopy, Scanning Electron Microscopy / Energy Dispersive X-ray analysis, Thermogravitmetric Analysis, Temperature Programmed Reduction techniques and N₂ adsorption-desorption isotherms. Support type was found to have a significant influence on catalytic activity and stability. Among all the supported catalysts tested, the Ni/SBA-15 exhibited excellent catalytic performance in terms of conversion and long-term stability. The activity for the silica framework catalysts correlated strongly with the surface area and pore diameter of these materials with the degree of CH₄ and CO₂ conversions observed increasing with decreasing surface area and increasing pore diameter.

Keywords: CO₂ reforming of methane; Ni/SBA-15; Ni/γ-Al₂O₃; Ni/KIT-6; Ni/MCM-41.

I. INTRODUCTION

Catalytic reforming of methane with carbon dioxide, also known as dry reforming (CH₄(g) + CO₂(g) ↔ 2CO(g) + 2H₂(g)), is a promising process for simultaneous chemical transformation of two major greenhouse gases, CO₂ and CH₄, to syngas, which can be used in a variety of downstream processes such as methanol production, Fischer-Tropsch synthesis processes and in carbylation, hydrogenation, and hydroformylation processes [1, 2]. In recent years the main aim of research on CO₂ reforming of methane has been the development of improved materials for catalysing this reaction. Different types of catalysts have been employed for dry reforming but from an industrial standpoint, Ni based catalysts are considered to be the most promising as they exhibit high catalytic activity [4-7], are readily available, and cost effective.

Ni/SiO₂ and Ni/Al₂O₃ have been two of the most often investigated catalysts for dry reforming of methane since 1979 [8] and 1980 [9] respectively. This interest has been mostly due to SiO₂ and γ-Al₂O₃ (with melting points of 1973°C and 2318°C [10] respectively) having high mechanical strength and relatively low cost. Recently, three types of siliceous materials with different structural features have been investigated as support materials for Ni dry reforming catalysts. These materials, MCM-41, SBA-15 and KIT-6 are silica-based mesoporous materials with different pore diameter and surface area. In 1992, C. T. Kresge and coworkers [11] synthesized MCM-41 mesoporous molecular sieves by a liquid-crystal template mechanism. These materials presented an opportunity for the design of catalytically active sites inside uniform channels with controllable nano-size pore diameters. In 2009, Liu et al. employed MCM-41 as support and prepared a Ni/MCM-41 catalyst for dry reforming of methane [12]. They reported that the catalyst had good catalytic activity, high stability and produced syngas with reasonable H₂/CO ratios.

In 1998, B. F. Chmelka and G. D. Stucky et al. [13] reported the use of amphiphilic triblock copolymers to direct the organization of polymerizing silica species resulting in the preparation of well-ordered hexagonal mesoporous silica structures (SBA-15). SBA-15 is a type of ordered mesoporous silica with large pore diameter, thick wall, and good hydrothermal stability. In 2006, JI Shengfu and LI Chengyue et al. [14] investigated dry reforming of methane using a Ni/SBA-15 catalyst and reported that the 12.5% Ni/SBA-15 catalyst showed high activity and good stability at 800°C. In 2012, W. Yang and Z. Liu et al. [19] used a kind of Ni containing mesoporous silica, Ni-KIT-6 as a dry reforming catalyst.

In this work, a comparison study on methane dry reforming with carbon dioxide over Ni supported on mesoporous SBA-15, MCM-41, KIT-6 and sol-gel prepared γ-Al₂O₃ has been investigated. This involved evaluation of CH₄ and CO₂ conversions using a custom built catalysis rig. Activity and stability results were compared and are discussed with regards to the characterisation data obtained.
II. EXPERIMENTALS

A. Catalyst preparation

Ni/γ-Al₂O₃ containing 15wt% Ni was prepared using a sol-gel method as reported earlier [1]. SBA-15 and KIT-6 were prepared using tetraethyloxysilane (TEOS) as silica sources and triblock copolymer P123 (Pluronic P123) as surfactant for both support materials. MCM-41 was prepared using hexadecyl trimethylammonium bromide C₁₆H₃₃(CH₃)₃NBr (CTMABr) as surfactant and sodium silicate solution (27 wt.% SiO₂, Aldrich) as the silicate source. The support materials were collected after calcining at 540 °C for 6 h in flowing air.

The Ni(15 wt%)/silica based catalysts were prepared via wetness impregnation. The SBA-15, MCM-41 and KIT-6 supports were impregnated with aqueous solutions containing appropriate amount of nickel nitrate at room temperature overnight, followed by drying at 110°C for 12 h and calcination at 550°C for 5 h.

B. Characterization

Materials were characterised using the following techniques / instruments – surface area Micromeritics ASAP 2010 surface area analyser and thermogravimetric Analysis (TGA). The temperature-programmed reduction (TPR) of the calcined catalysts was undertaken in a quartz reactor (I.D. 4.5 mm), packed with 50 mg catalyst in a flow (20 mL min⁻¹) of H₂-Ar mixture (4.14 mol% H₂) from 250 °C to 880 °C at a linear heating rate of 10°C.min⁻¹. The H₂ consumed in the TPR study was measured quantitatively by TCD. Before the TPR study, the catalyst was pretreated at 500 °C for 1h under a flow (20 cm³ min⁻¹) of argon.

C. Catalytic activity testing

Catalytic CO₂-reforming of methane was carried out in a fixed-bed continuous flow quartz reactor at atmospheric pressure at a gas hourly space velocity (GHSV) of 52,000 mL g⁻¹ h⁻¹. In the current study, the activity and stability runs were performed at 700 °C. All the catalysts were pre-reduced in situ in a mixed flow of H₂ and He (10:40 mL min⁻¹) at 700°C for 2h. Then the reactant gases (CO₂ and CH₄) were fed (CO₂: CH₄: He = 1: 1: 2) into the reactor. The effluent mixed gases were cooled in an ice-water trap to remove gaseous water generated via the reverse water gas shift (RWGS) reaction. The product gas mixture was analysed by on-line gas chromatography (Shimadzu GC, 17A) equipped with a silica packed column and a TCD. The time-on-stream activity and durability of the catalysts were carried out at 700 °C for 20 h. The catalytic properties have been evaluated in term of the conversion of CO₂ and CH₄. After the durability test, the catalyst was removed and thermogravimetric Analysis (TGA) (Perkin-Elmer TGA 7) was used to calculate the amount of deposited carbon.

The effects of residence time (feed flow rate (gas film thickness)) and particle size were determined experimentally with a feed mixture composed of CO₂: CH₄: He (=1:1:2 vol. %) at 700 °C. It was found that methane conversion was independent of average particle size, within a particle size range of 500-710 microns. Therefore mass transfer limitations did not occur under the aforementioned conditions. The potential influence of external diffusion limitations was also investigated by measuring the activity as a function of the catalyst loading at constant W/F ratio (W= catalyst mass, F = total flow of feed gas). It was found that conversion was not affected by varying catalyst load and the flow, i.e., at constant contact time. Thus, external mass transfer limitations do not occur under the conditions applied.

III. RESULTS AND DISCUSSIONS

A. Characterization

The textural characteristics of the prepared mesoporous materials are summarized in Table 1. All samples exhibited type IV nitrogen adsorption-desorption isotherms with H1 shaped hysteresis loops (not shown), which are characteristic of materials having uniform “cylindrical shaped” pores in the framework [20]. Three distinct regions can be discerned in the isotherms for these mesoporous materials: (1) monolayer–multilayer adsorption of nitrogen on the pore walls at low pressures, (2) a sudden steep increase of the adsorbed nitrogen at intermediate pressures due to capillary condensation, and (3) multilayer adsorption on the external surface of the particles. The existence of capillary condensation at higher relative pressures in SBA-15 relative to KIT-6 and MCM-41 samples is consistent with the larger pore diameters of the SBA-15. The broad hysteresis loop observed for the SBA-15 was most likely caused by the presence of long mesopores connected by smaller micropores, thus hampering the filling and emptying of the accessible volume [15]. After introducing Ni, an obvious decrease in the BET surface area, pore volume and pore diameter is observed. The introduction of Ni causes local blockage of pore channels by depositing Ni species at the pore entrance and/or partial structural degradation [15].

The reducibility of the nickel in the prepared catalysts was studied using temperature-programmed reduction (TPR). Figure 1 shows the TPR profiles of the catalysts and a non-supported NiO for comparison.
## Table 1. Textural properties of different samples

<table>
<thead>
<tr>
<th>Support</th>
<th>Nickel content (wt.%)</th>
<th>Surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ-Al₂O₃</td>
<td>0</td>
<td>142</td>
<td>0.25</td>
<td>7.81</td>
</tr>
<tr>
<td>SBA-15</td>
<td>0</td>
<td>165</td>
<td>0.53</td>
<td>13.95</td>
</tr>
<tr>
<td>KIT-6</td>
<td>0</td>
<td>900</td>
<td>1.22</td>
<td>6.05</td>
</tr>
<tr>
<td>MCM-41</td>
<td>0</td>
<td>1355</td>
<td>1.14</td>
<td>4.16</td>
</tr>
<tr>
<td>γ-Al₂O₃</td>
<td>15</td>
<td>124</td>
<td>0.24</td>
<td>8.17</td>
</tr>
<tr>
<td>SBA-15</td>
<td>15</td>
<td>161</td>
<td>0.40</td>
<td>10.5</td>
</tr>
<tr>
<td>KIT-6</td>
<td>15</td>
<td>463</td>
<td>0.38</td>
<td>4.04</td>
</tr>
<tr>
<td>MCM-41</td>
<td>15</td>
<td>1392</td>
<td>0.64</td>
<td>2.96</td>
</tr>
</tbody>
</table>

**Figure 1.** TPR profile of 15 wt.% Ni catalysts on different support.
The TPR profile for NiO shows that reduction of the Ni(II) started at \(-240^\circ\text{C}\) and reached a maximum rate at \(-400^\circ\text{C}\). The TPR profile of the Ni\(\gamma\)-Al\(\text{II}_2\)O\(_3\) catalyst consisted of two clear reduction temperature zones. The low temperature zone (\(-370 – 570^\circ\text{C}\)) and a high temperature zone (\(600 – 900^\circ\text{C}\)) represent the reduction of NiO and non-stoichiometric nickel aluminate in Ni\(\gamma\)-Al\(\text{II}_2\)O\(_3\) respectively [1]. Based on the amount of H\(_2\) consumed in the two temperature zones the majority of the oxidised Ni in Ni\(\gamma\)-Al\(\text{II}_2\)O\(_3\) catalyst presents in the form of a non-stoichiometric nickel aluminate. All the SiO\(_2\) based catalysts exhibit similar hydrogen reduction profiles showing a reduction peak at the low temperature zone which implies the presence of NiO particles. However, the reduction of Ni(II) in the Ni/KIT-6 and Ni/MCM-41 catalysts was slightly higher than that observed for the Ni/SBA-15 catalyst. This is most likely due to the arrangement of Si–OH on the inner surface is relatively regular for Ni/KIT-6 and Ni/MCM-41 while the pore surface of Ni/SBA-15 is rough with a substantial amount of Si(OH)\(_2\) groups associated with surface defects [15].

B. Catalytic activity for dry reforming of methane
The ability of the supported nickel materials to catalyse the dry reforming of methane was investigated at 700 \(^\circ\text{C}\) using a GHSV of 5.2 x 10\(^3\) mLg\(^-1\) h\(^-1\) for a period of 20 h. The results, in terms of CH\(_4\) and CO\(_2\) conversion, from the aforementioned tests are presented in Figures 2a and b. From the results presented in Figures 2a and b it can seen that the Ni/SBA-15 catalyst was clearly more active in terms of CH\(_4\) and CO\(_2\) conversion than all of the other materials tested. This catalyst was able to catalyse CH\(_4\) conversions between 84.5 and 85.1 % and a CO\(_2\) conversion of \(-92.4\%\) throughout the entire testing period studied. The CH\(_4\) conversion approached the conversion expected for the system at thermodynamic equilibrium which is 91.5% [17] (CH\(_4\)/CO\(_2\)=1, atmospheric pressure and 700\(^\circ\text{C}\)). The CO\(_2\) conversion was higher than that expected if the system was at thermodynamic equilibrium (66.3%) [21], due to the influence of the reverse water gas shift (RWGS) reaction, which has been reported to occur under the experimental conditions used in this study [22].

$$\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O} \quad \text{(RWGS)}$$

Of the other catalysts tested (Ni\(\gamma\)-Al\(\text{II}_2\)O\(_3\), NiKIT-6 and Ni/SBA-15) the Ni/MCM-41 was clearly the least active material. After 20 h time on stream, the activity sequence in terms of CH\(_4\) conversion was as following: Ni/SBA-15 (84%) > Ni/KIT-6 (77%) > Ni\(\gamma\)-Al\(\text{II}_2\)O\(_3\) (67%) > Ni/MCM-41 (51%). The trends observed in activity for the SiO\(_2\) based catalysts correlated strongly with the surface area and pore diameter of these materials (Figure 3a and b) with the degree of CH\(_4\) and CO\(_2\) conversions observed increasing with decreasing surface area and increasing pore diameter. Similar behavior was observed for PdNi/MCM-41 [23], Ni(5wt%)/SBA-15 and Ni(5wt%)/MCM-41 catalysts [24] where catalysts exhibiting higher surface area were less active. Based on these results it can be concluded that catalyst activity in these materials is also strongly influence by other factors, such as pore diameter active metal environment and / or morphology [23-27].

The H\(_2\)/CO ratios obtained at 20h are shown in Table 2. From the data given in Table 2 it can be seen that the H\(_2\)/CO ratio did not equal one (as predicted based on the stoichiometry of the overall dry reforming reaction). This however was expected as thermodynamics predicts a H\(_2\)/CO ratio of unity only at temperatures above 800\(^\circ\text{C}\) [28]. The H\(_2\)/CO ratios that were obtained have a similar pattern to the activity trends observed for the different supports. The Ni/MCM-41 catalyst produced a product gas with a low H\(_2\)/CO ratio (0.83) which suggests that the reverse water gas shift (RWGS) easily occurs on this catalyst, which results from the presence of more unreacted CO\(_2\) under low catalytic activity [15], whilst the Ni/SBA-15 catalyst produced synthesis gas with the highest H\(_2\)/CO ratios of 0.97. This high H\(_2\)/CO ratio in the Ni/SBA-15 catalyst was most likely due to reduced water gas shift reaction occurring which may have been due to more rapid conversion of CO\(_2\) on Ni/SBA-15. In terms of stability all of the catalysts were relatively stable over the time frame tested (20 h) except for the Ni/KIT-6 catalyst which had a gradually reduced activity during the reaction.

The amount of carbon deposited on the spent catalysts (which is expressed in Table 2 in terms of carbon deposition rate) was determined using TGA. Carbon deposition over the spent catalysts after 20 h time on stream was quantified by TG analysis. As shown in Table 2, the rate of carbon deposition on the catalyst was as follows: Ni/KIT-6 (0.0002) < Ni/MCM-41 (0.0003) < Ni/SBA-15 (0.0005) < Ni\(\gamma\)-Al\(\text{II}_2\)O\(_3\) (0.0011). It is evident that the carbon deposition rate was lowest when using the Ni/KIT-6 catalyst and highest when using the Ni\(\gamma\)-Al\(\text{II}_2\)O\(_3\) catalyst. No clear trend in carbon deposition rate was observed for the materials tested. Interestingly the amount of carbon deposited on the Ni/KIT-6 catalyst, which underwent a gradual loss in activity in terms of CH\(_4\) and CO\(_2\) conversion, was lower than the amount deposited on the other catalysts which displayed stable activity up to 20 h of testing. This result indicates that the amount of carbon deposited was either most likely not solely responsible for the significant loss of activity observed and that it may have been due to the type(s) of carbon deposited and / or the location of the carbon deposition [1].

<table>
<thead>
<tr>
<th>Support</th>
<th>(\gamma)-Al(\text{II}_2)O(_3)</th>
<th>SBA-15</th>
<th>KIT-6</th>
<th>MCM-41</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon deposition rate (g(_c) g(^{-1}) cat. h(^{-1}))</td>
<td>0.0011</td>
<td>0.0005</td>
<td>0.0002</td>
<td>0.0003</td>
</tr>
<tr>
<td>H(_2)/CO ratios</td>
<td>0.90</td>
<td>0.97</td>
<td>0.93</td>
<td>0.83</td>
</tr>
</tbody>
</table>
**CONCLUSIONS**

Three different mesoporous molecular sieves SBA-15, KIT-6, MCM-41 and \( \gamma \)-Al\( _2 \)O\( _3 \) were used to support Ni and catalyse CO\(_2\) reforming of CH\(_4\). Based on the results obtained the catalytic conversion of CH\(_4\) using supported Ni is highly dependent on the nature of support. Among all the supported catalysts tested, Ni/SBA-15 exhibited excellent catalytic
performance in terms of catalytic conversion and long-term stability. The activity for the SiO$_2$ based catalysts correlated strongly with the surface area and pore diameter of these materials with the degree of CH$_4$ and CO$_2$ conversions observed increasing with decreasing surface area and increasing pore diameter. In summary, the advantages of good structural stability and the unique pore structural properties of SBA-15 make this a promising catalytic support material for Ni for use in the dry reforming of methane.

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