Deactivation of supported nickel catalysts during CO methanation

J. Barrientos*, M. Lualdi, M. Boutonnet, S. Järås

KTH (Royal Institute of Technology), Chemical Technology, Teknikringen 42, S-100 44 Stockholm, Sweden

A R T I C L E   I N F O

Article history:
Received 15 May 2014
Received in revised form 28 July 2014
Accepted 21 August 2014
Available online 28 August 2014

Keywords:
Methanation
Deactivation
Support
Titania
Carbon formation

A B S T R A C T

Deactivation of Ni-based catalysts was investigated during CO methanation over different supported catalysts. X-ray diffraction and temperature-programmed hydrogenation analyses were used to investigate nickel particle sintering and carbon formation during the first 24 h on stream. Titania-supported catalysts presented high resistance towards carbon deposition and nickel particle growth in comparison with the other tested catalysts. Particle size effects on these two deactivation causes were also evaluated. It was shown that carbon formation rates are higher on bigger crystal particles. However, it was found that titania-supported nickel catalysts reduced at high temperatures show the opposite effect. This difference is most probably due to a stronger interaction between nickel and TiO2 (x < 2) species on smaller crystals which changes the CO dissociation properties and, in consequence, carbon formation rates.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Production of synthetic natural gas (SNG) from coal or biomass has recently re-emerged due to the increasing price of natural gas and the will to reduce the dependency from this fossil source, especially in countries where natural gas or shale gas is not available [1–5]. Moreover, the thermo-chemical conversion of biomass into SNG is also an opportunity to minimize anthropogenic greenhouse gas emissions [6–9]. In addition, it has been technically and economically assessed that co-production of diesel and SNG from biomass via Fischer–Tropsch and methanation results in a higher biomass-to-fuel efficiency [10].

Excellent reviews can be found in the literature regarding the activity and selectivity of materials catalyzing the methanation reaction [11], especially the studies done by Vannice et al. [12–17] on the kinetics and selectivity of different metal supported catalysts.

Alumina-supported nickel catalysts have been widely used in the methanation process and have performed satisfactorily as regards life time and activity [1,18]. The loss of activity on Ni/Al2O3 catalysts has been broadly studied. Bartholomew et al. [19] studied the effect of temperature, chemical and physical properties of alumina and water on the activity loss due to sintering. Shen et al. [20] also investigated sintering due to nickel carbonyl formation. Ni/Al2O3 catalysts have also been used to study deactivation due to sulphur poisoning [21–23] and carbon formation [2,5,21,24,25].

However, in the literature, studies comparing the deactivation behavior of different nickel supported catalysts are quite few. Bartholomew et al. [25] reported a study of the support effect on carbon formation. Mirodatos et al. [26] performed a deactivation study with Ni supported on MgO, SiO2 and γ-Al2O3 at low reaction temperatures. In addition, van de Loosdrecht et al. [27] studied the effect of metal loading and reduction temperature on carbon deposition for SiO2 and TiO2 supported nickel catalysts.

In this work four different supported nickel catalysts were prepared and tested under methanation conditions. The aim of this study is to compare their deactivation behavior and their resistance towards carbon formation and nickel sintering. It is important to notice that the preparation of catalysts using supports with different morphology can easily lead to catalysts with different physicochemical properties. For instance, the size of the metal particles is influenced by the pore size of the support [28]. Therefore, this work also gives an insight into the effect of nickel particle size on catalyst deactivation in order to get a better understanding on the impact of different supports.

2. Experimental

2.1. Catalyst preparation

A total of six Ni-based catalysts were prepared by using incipient wetness impregnation (IW). The catalysts were prepared on four different support materials (γ-Al2O3, α-Al2O3, SiO2, and TiO2) with various Ni loadings (10–20 wt%).

The γ-Al2O3 (Puralox SCCa-5/200 from Sasol), SiO2 (Kieselgel 60 from Merck) and TiO2 (Degussa P25) support materials were
dried at 393 K for 6 h and then calcined in flowing air for 10 h at 773 K, 773 K and 973 K (ramp = 1 K/min), respectively. The α-Al2O3 support was prepared from the γ-Al2O3 support by calcining it in flowing air at 1373 K for 10 h.

The support materials were impregnated with aqueous solutions of Ni(NO3)2·6H2O (puriss. p.a.: ≥98.5% (KT), Fluka), dried for 3 h at 393 K and subsequently calcined in air at 723 K for 3 h (heating rate: 2.5 K/min).

For most of these high-loaded nickel catalysts, the volume of aqueous solution required to solve the nickel salt was higher than the pore volume of the support. Therefore, the aqueous solution was deposited batch wise, drying the samples at 393 K for 2 h after every deposition.

2.2. Catalyst characterization techniques

Brunauer–Emmett–Teller ( BET) surface area and porosity measurements for the γ-Al2O3 and SiO2-supported catalysts were performed in a Micromeritics ASAP 2000/2010 unit. The samples were evacuated and dried at 523 K overnight prior to analysis. The BET surface area was estimated by N2 adsorption at liquid nitrogen temperature at relative pressures between 0.06 and 0.2.

A Micromeritics Mercury Porosimeter, AutoPore IV was used to characterize the TiO2 and α-Al2O3-supported catalysts where the macropore contribution to surface area and pore volume is significant.

Hydrogen static chemisorption was performed on the reduced catalysts in order to estimate the nickel dispersion (D, %) and the nickel crystallite size (d(Ni0)H, nm). The chemisorption measurements were conducted on a Micromeritics ASAP 2020C unit at 308 K, after reducing about 0.15 g of the calcined catalyst samples in flowing H2 at 773 K for 4 h (heating rate = 5 K/min). The average particle size of Ni was calculated according to [29]:

\[
d(Ni^{0}_H) = \frac{97}{D} \times DoR
\]

where DoR stands for degree of reduction.

X-ray diffraction (XRD) measurements on the catalyst samples were performed on a Siemens D5000 diffractometer with Cu-Kα radiation (2θ = 10°–90°, step size = 0.02°) equipped with a Ni filter. Average crystallite diameter of Ni (d(Ni0)XRD, nm) and NiO (d(NiO)XRD, nm) were estimated by using the Scherrer formula and assuming spherical particles [30].

The degree of reduction (DOR) was estimated from temperature-programmed reduction (TPR) of the samples after in situ reduction in flowing hydrogen for 4 h at 773 K (heating rate = 5 K/min) and subsequent purging with helium for 1 h at the reduction temperature. The TPR of the samples was performed at a heating rate of 10 K/min up to 1203 K in a flow of 5% H2 in Ar while monitoring the difference on thermal conductivity between the inlet and outlet gas. Calibration of the thermal conductivity detector (TCD) signal was done by the reduction of Ag2O powder. The DOR was calculated assuming that the unreduced nickel was composed of Ni (II) as evidenced from X-ray diffraction. The DOR calculation procedure has been described in [31].

Temperature-programmed hydrogenation (TPH) was performed on the spent samples in order to compare, qualitatively, the amount and the species of carbon formed after reaction. The TPH of the samples was performed in situ at a heating rate of 5 K/min up to 963 K in H2 while monitoring the product gas with a mass spectrometer QMG700. The mass spectrometer monitored the evolution of CH4, resulting from carbon hydrogenation, during the treatment (m/z = 15, instead of 16 to avoid the interference of ionized oxygen from water vapor as in [32]). The H2 space velocity used was 233 Nml/min gcat. The pressure in the MS chamber, the SEM voltage and the signal reading time were set, respectively, at 5 × 10−6 mbar, 2000 kV and 1 s for all the experiments. The carbonaceous species present in this study were determined according to the temperatures of formation and hydrogenation of carbon defined by McCarthy and Wise [33] and later reported in other works [24].

Temperature-programmed oxidation (TPO) was performed on the spent samples in order to measure the amount of carbon left after TPH. The TPO of the samples was performed at a heating rate of 10 K/min up to 1203 K in a flow of 5% O2 in He while monitoring the difference on thermal conductivity between the inlet and outlet gas. After TPO, the samples were exposed to the TPR procedure described previously, and once again, to TPO. This was performed in order to subtract the contribution of nickel oxidation in the TCD signal.

2.3. Methanation synthesis

The methanation synthesis was carried out in a down-flow stainless steel fixed-bed reactor (i.d. 9 mm) with a catalyst loading of 0.1−0.2 g (pellet size: 53–90 μm) diluted with 3.5 g of SiC (average pellet size: 75 μm). The process conditions were: 583 K, 20 bar and inlet H2/CO=3. The small pellet size used for the methanation catalysts ensured the absence of any mass transfer limitations at these operating conditions. Intraparticle temperature differences were also estimated by using the method described by Satterfield [34]. The maximum estimated temperature difference inside these small catalyst pellets was 1 K. The reactor tube was heated by means of an oven and the temperature inside the reactor was regulated by cascade control with one sliding thermocouple in the catalyst bed and another one placed in the oven. This system, together with an aluminum jacket placed between the reactor and the oven, allowed for a quasi-isothermal temperature profile along the catalyst bed (583 ± 2°K) for all the samples tested. A detailed description of the equipment has been given elsewhere [28,35].

Prior to reaction, the catalyst was reduced in situ in pure H2 (450 Nml/min gcat) at atmospheric pressure and 773 K for 4 h (heating rate = 5 K/min). After reduction, the catalyst was cooled to reaction temperature (583 K) and then flushed with He before increasing the pressure to the desired level (20 bar for all the experiments). The syngas gas hourly space velocity (GHSV) used for the experiments was in the range of 75,000−150,000 Nml/hgcat. The syngas feed contained 3% N2 as an internal standard. The reaction was stopped after 24 h on stream in order to compare, by means of TPH and XRD measurements, carbon formation and nickel crystallite growth between the different supported catalysts.

The product gases were analyzed on-line by means of a GC Agilent 6890 equipped with a TCD and a flame ionization detector (FID). H2, N2, CO, CH4 and CO2 were separated by a Carbosieve II packed column and analyzed on the TCD. C1−C6 products were separated by an alumina-plot column and quantified on the FID allowing for determination of the SCL. A detailed description of the product analysis and data treatment is given in [36].

3. Results and discussion

3.1. Characterization of supports and catalysts

Table 1 shows the physical properties of the pure support materials and the catalysts. The γ-Al2O3 and SiO2 are typical microporous supports with high surface areas, while the TiO2 and α-Al2O3 have larger pores and lower surface areas. The number in front of the element (Ni) indicates the loading in wt%.

Table 2 summarizes the physicochemical properties of the studied catalysts. The reduction profiles of the calcined catalysts are presented in Fig. 1. The TPR profiles of the γ-Al2O3 supported
Table 1
Physical properties of the pure support materials and the catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Average pore diameter (nm)(^a)</th>
<th>Surface area (Å(^2)/g(_{\text{cat}}))</th>
<th>Pore volume (V) (cm(^3)/g(_{\text{cat}}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ-Al(_2)O(_3)</td>
<td>10.4</td>
<td>193</td>
<td>0.50(^b)</td>
</tr>
<tr>
<td>10Ni/γ-Al(_2)O(_3)</td>
<td>9.7</td>
<td>175</td>
<td>0.43(^b)</td>
</tr>
<tr>
<td>20Ni/γ-Al(_2)O(_3)</td>
<td>7.0</td>
<td>146</td>
<td>0.34(^b)</td>
</tr>
<tr>
<td>SiO(_2)</td>
<td>5</td>
<td>360</td>
<td>0.64(^b)</td>
</tr>
<tr>
<td>20Ni/SiO(_2)</td>
<td>4.9</td>
<td>264</td>
<td>0.41(^b)</td>
</tr>
<tr>
<td>TiO(_2)</td>
<td>409</td>
<td>14</td>
<td>1.39</td>
</tr>
<tr>
<td>20Ni/TiO(_2) batch 1</td>
<td>279</td>
<td>9</td>
<td>0.63</td>
</tr>
<tr>
<td>20Ni/TiO(_2) batch 2</td>
<td>248</td>
<td>13</td>
<td>0.42</td>
</tr>
<tr>
<td>α-Al(_2)O(_3)</td>
<td>255</td>
<td>7</td>
<td>0.47</td>
</tr>
<tr>
<td>20Ni/α-Al(_2)O(_3)</td>
<td>71</td>
<td>30</td>
<td>0.53</td>
</tr>
</tbody>
</table>

\(\text{a}\) The average pore diameter (d\(_p\)) estimated from surface area (A) and pore volume (V) according to: d\(_p\) = 4V/A.

\(\text{b}\) Determined from a single point of adsorption at p/p\(_0\) = 0.998.

Table 2
Physicochemical properties of the studied catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>DoR(^a) (%)</th>
<th>D(^b) (%)</th>
<th>d(Ni(_0))(^c) (nm)</th>
<th>d(NiO)(_{\text{ex}})(^d) (nm)</th>
<th>d(NiO)(_{\text{aex}})(^e) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10Ni/γ-Al(_2)O(_3)</td>
<td>100</td>
<td>10.1</td>
<td>10</td>
<td>8</td>
<td>-</td>
</tr>
<tr>
<td>20Ni/γ-Al(_2)O(_3)</td>
<td>96</td>
<td>6.7</td>
<td>14</td>
<td>12</td>
<td>10</td>
</tr>
<tr>
<td>20Ni/SiO(_2)</td>
<td>100</td>
<td>3.2</td>
<td>30</td>
<td>14</td>
<td>13</td>
</tr>
<tr>
<td>20Ni/TiO(_2) batch 1</td>
<td>100</td>
<td>1.2</td>
<td>84</td>
<td>23</td>
<td>25</td>
</tr>
<tr>
<td>20Ni/TiO(_2) batch 2</td>
<td>100</td>
<td>0</td>
<td>-</td>
<td>15</td>
<td>13</td>
</tr>
<tr>
<td>20Ni/α-Al(_2)O(_3)</td>
<td>100</td>
<td>3.3</td>
<td>29</td>
<td>19</td>
<td>25</td>
</tr>
</tbody>
</table>

\(\text{a}\) Degree of reduction as estimated by H\(_2\)-TPR after reduction at 773 K for 4 h in H\(_2\).

\(\text{b}\) Metal dispersion estimated by H\(_2\) chemisorption after reduction at 773 K for 4 h in H\(_2\).

\(\text{c}\) Average Ni\(_0\) particle size estimated by H\(_2\) chemisorption after reduction at 773 K for 4 h in H\(_2\).

\(\text{d}\) Average NiO particle size estimated by X-ray diffraction after calcination.

\(\text{e}\) Average NiO particle size estimated by X-ray diffraction after reduction at 773 K for 4 h in H\(_2\).

\(\text{f}\) The peak corresponding to NiO was not visible.

Fig. 1. H\(_2\)-TPR of the calcined catalysts. a 20Ni/α-Al\(_2\)O\(_3\), b 20Ni/TiO\(_2\) batch 1, c 20Ni/TiO\(_2\) batch 2, d 20Ni/SiO\(_2\), e 20Ni/γ-Al\(_2\)O\(_3\), f 10Ni/γ-Al\(_2\)O\(_3\).

catalysts show that complete reduction of nickel oxide occurs at higher temperature in comparison with the other supported-catalysts. This difficulty in the reduction of NiO/γ-Al\(_2\)O\(_3\) can be explained by the presence of spinel phase (NiAl\(_2\)O\(_4\)) formed after catalyst calcination which has also been observed in previous studies [37,38]. It is not surprising to see, from these reduction profiles, that the degree of reduction (DoR) is 100% for all the catalysts, except for the 20Ni/γ-Al\(_2\)O\(_3\) which is almost fully-reduced. The titania-supported catalysts present a second reduction peak at 800 K. This peak most probably formed due to the reduction of nickel titanate species which formed during catalyst calcination. Partial reduction of the TiO\(_2\) support could also have a contribution, in a minor extent, to the TPR profiles. These two phenomena have also been observed in several literature studies [27,39–48].

The average Ni particle diameter was estimated both from hydrogen static chemisorption and X-ray diffraction measurements. As can be seen in Table 2, there is a significant difference between the particle size predicted by these two methods, especially for the TiO\(_2\) and SiO\(_2\) supported catalysts. It has been reported [49] that the H\(_2\) and CO chemisorption properties of titania-supported catalysts can be significantly decreased due to a strong metal support interaction (SMSI). This phenomenon has also been observed in previous research work [17].

The average Ni particle diameter is different for the two batches of 20Ni/TiO\(_2\). As explained in the catalyst preparation section, the deposition of the active phase was performed batch-wise. This difference in Ni crystal size is a result of a different number of impregnations of nickel aqueous solution during the preparation of the catalysts. This difference between these two catalysts allowed the authors for studying the effect of nickel particle size on titania-supported nickel catalysts. In addition, this second batch of 20Ni/TiO\(_2\) with a smaller average nickel particle size could give a more suitable comparison with the Ni/Al\(_2\)O\(_3\) and Ni/γ-Al\(_2\)O\(_3\) catalysts, since it allows for de-coupling particle size effects and so, provided the authors a better understanding of the effect of the support on catalyst deactivation.

The average Ni particle sizes obtained for the 20Ni/γ-Al\(_2\)O\(_3\) and 20Ni/SiO\(_2\) catalysts are larger than the average pore diameters of the supports estimated from the N\(_2\) physisorption measurements. This implies that there could be a significant part of the Ni located outside the pore network. It is stated that the pore size of the support can limit the metal crystal growth during reaction [50], and in consequence, increase the stability of the catalyst. Therefore, the
authors decided to prepare and test a 10Ni/γ-Al2O3 catalyst which should provide a higher amount of Ni located inside the pores due to its lower metal loading. As expected, the average Ni particle size of the 10Ni/γ-Al2O3 catalyst resulted to be smaller than that of the 20Ni/γ-Al2O3. The preparation of these two Ni/γ-Al2O3 catalysts also allowed the authors for an indication of the effect of particle size on carbon formation.

3.2. Catalytic performance in methanation synthesis

The CO conversion as a function of time on stream is presented in Fig. 2 for the different supported catalysts. The deactivation is severe for all the catalysts during the first hours under these operating conditions. As can be clearly seen in Fig. 2, the titania-supported catalysts present the lowest deactivation rates during the first 24 h on stream.

Fig. 3 presents the CO conversion as a function of time for the 20Ni/γ-Al2O3 and 10Ni/γ-Al2O3 catalysts. The 10Ni/γ-Al2O3 catalyst also presented a very high deactivation rate. Apparently, a smaller Ni particle size did not show any significant improvement in what concerns catalyst stability.

3.3. Carbon deposition during methanation synthesis

After 24 h of reaction, the reactor was cooled down to room temperature and brought down to atmospheric pressure in helium. Afterwards, TPH was performed in situ on the catalyst samples. The TPH profiles shown in Fig. 4 were obtained after the experiments presented in Fig. 2. As can be deduced from the figure, there is a clear effect of the nature of the support on carbon formation.

According to the work of Bartholomew et al. [24,25,51], three species of carbon form during methanation at the employed reaction temperature (583 K). These species are atomic carbon (Cα), polymeric carbon (Cβ) and vermicular filaments (Cv) presenting hydrogenation peaks at 473 K, 673 K and 873 K, respectively.

The TPH profiles of γ-Al2O3 and SiO2 supported catalysts present formation of carbon hydrogenating around 800 K. Therefore, this carbon species can be identified as Cv. Nevertheless, it should be noted that this identification of carbon is based only on temperature information from literature. Hence, it is not proven that filamentous carbon formed. Instead, these peaks could result, for instance, from the hydrogenation of other types of polymeric carbon. Previous studies from Bartholomew et al. [25] showed that, most probably, vermicular carbon formed during methanation between 325 °C and 450 °C was not present on the nickel surface and that its amount was not sufficient to plug the micropores of these catalysts. It is, thereby, possible that these amounts of carbon are not responsible for loss of activity. It was also stated that the specific rates of filamentous carbon formation at low H2/CO ratios are larger on Ni/TiO2 than on Ni/γ-Al2O3 and Ni/SiO2 which is in disagreement with the results obtained in the present study. However, the work was performed using different operating conditions (H2/CO = 1 and atmospheric pressure). Moreover, it was concluded that the turnover frequencies of carbon accumulation were very similar for Ni/TiO2 and Ni/γ-Al2O3 if the H2/CO was increased to a value of 2. This, together with the results presented in Fig. 4, suggests that there may be a significant effect of these operating conditions on the amount and nature of carbon formed.

Formation of Cβ species occurs on the γ-Al2O3 and α-Al2O3 supported catalysts whose TPH profiles show a hydrogenation peak close to 673 K. The TPH profile of the 20Ni/SiO2 catalyst also presents a peak around 600 K. In fact, the 20Ni/γ-Al2O3 catalyst also presents another type of carbon hydrogenating slightly above
600 K. This carbon species hydrogenating above the reaction temperature may also result from the polymerization of C₆, and, in consequence, may be responsible for catalyst deactivation.

The TPH profiles of the 20Ni/TiO₂ catalysts only present carbon species hydrogenating below the reaction temperature. This may suggest that the type of carbon observed is C₆, which remained adsorbed on the nickel surface when the reaction was stopped. However, the expected peak temperature for C₆ hydrogenation is 473 K, significantly below the peak temperature observed in the TPH results. Unfortunately, it is not possible to evaluate from these results the degree of hydrogenation of the different types of surface carbon.

In order to confirm the nature of the carbon formed on the 20Ni/TiO₂ catalysts, a TPH was performed on a spent sample which was exposed to methanation under the same reaction conditions for only 2 h. In Fig. 5, the TPH profiles of the 20Ni/TiO₂ batch 2 catalyst after 24 h and on stream are presented. It can be clearly deduced from the TPH signal corresponding to 2 h on stream that two different species of carbon coexist: atomic carbon, reacting at 473 K, and carbon reacting around the reaction temperature, which is possibly another type of polymeric carbon. Moreover these results also show that the proportion between these two carbon species change during reaction.

Furthermore, the amount of carbon formed is larger for the second batch of 20Ni/TiO₂ than for the first batch. In other words, the deposition of carbon is significantly larger for the 20Ni/TiO₂ with initially smaller particle size. In contrast, the amount of carbon formed is larger for the 20Ni/γ-Al₂O₃ catalyst than for the 10Ni/γ-Al₂O₃, which has smaller Ni crystal size. This observation is illustrated in Fig. 6 which presents the TPH profiles of these four spent catalysts. The TPH profiles of the γ-Al₂O₃ supported catalysts correspond to the spent samples of the experiments shown in Fig. 3. The phenomenon observed for the Ni/γ-Al₂O₃ catalysts is in agreement with another recent study performed on SiO₂ supported nickel catalysts [52]. Christensen et al. [53,54] also showed that the rates of carbon formation increase with increasing particle size on α-Al₂O₃ and γ-Al₂O₃ supported catalysts during steam methane reforming. Moreover, it has been shown that hydrogen coverage is larger at steps sites than at terrace sites [55]. Rates of carbon polymerization are higher on terrace sites and therefore, on bigger crystal particles [56,57]. Hence, it was unexpected to observe such an effect of particle size for Ni/TiO₂ catalysts.

It has been suggested that the presence of TiO₂ species does not only change the adsorption capacities of H₂ and CO, but also their dissociation properties [49]. Zielinski [58] suggested that CO dissociation is promoted due to the acceptance of oxygen atoms by these TiO₂ species at the nickel support interphase. Therefore, if the carbon hydrogenation rates are not large enough, higher rates of carbon deposition and polymerization for Ni/TiO₂ catalysts may be expected. In fact, van de Loosdrecht et al. [27] related these statements with experimental results which showed that the presence of TiO₂ species was enhancing both the formation and polymerization of carbon. In addition, they found that the carbon deposition on Ni/TiO₂ catalysts increased with decreasing nickel particle size, which is in accordance with the results of this study. We suggest that this controversial effect of nickel particle size is a consequence of a stronger metal support interaction with small crystals. In fact, the metal dispersion values obtained from H₂ chemisorption on the Ni/TiO₂ catalysts presented in Table 2 indicate that the interaction may be stronger for the catalyst with smaller nickel particle size. The stronger the metal support interaction, the weaker the chemisorption of H₂ and the higher the carbon coverage on the nickel surface, which results in a higher rate of carbon deposition.

Finally, it should be noted again that the study from van de Loosdrecht et al. [27] showed that Ni/TiO₂ catalysts reduced at high temperatures promoted the formation of carbon species with higher hydrogenating temperatures. However, this study was performed at atmospheric pressure and an inlet H₂/CO ratio = 2. Thus, the carbon hydrogenation rate at these conditions is probably significantly lower than the one of the present study [55,59].

Temperature-programmed oxidation (TPO) measurements were performed after TPH in order to determine if any carbon was left after the hydrogenation treatment. No remaining carbon was detected from the TPO measurements for any of the spent samples. Therefore, a complete removal of carbon was achieved by TPH.

3.4. Sintering of the nickel particles during the methanation synthesis

X-ray diffraction measurements (XRD) were performed on the spent samples after TPH. The average Ni particle sizes of the samples after 24 h of methanation synthesis are presented in Table 3. The results show that the increase of the nickel particle size after one day of reaction is larger for Ni/γ-Al₂O₃ and Ni/SiO₂ than for

---

**Fig. 5.** TPH profile of 20Ni/TiO₂ batch 2 after: a) 2 h on stream b) 24 h on stream.

**Fig. 6.** TPH profile after 24 h of methanation synthesis of the catalysts: a) 20Ni/γ-Al₂O₃, b) 10Ni/γ-Al₂O₃, c) 20Ni/TiO₂ batch 2 and d) 20Ni/TiO₂ batch 1.
Table 3
Sintering of nickel particles during the methanation synthesis.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>(d(Ni)_{XRD} ) (nm)</th>
<th>Reaction time on stream (h)</th>
<th>(d(Ni)_{XRD} ) after reaction (nm)</th>
<th>Crystal growth (%)</th>
<th>Loss of Ni surface area (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20Ni/(\alpha)-Al(_2)O(_3)</td>
<td>25</td>
<td>24</td>
<td>39</td>
<td>56</td>
<td>36</td>
</tr>
<tr>
<td>20Ni/TiO(_2) batch 1</td>
<td>25</td>
<td>24</td>
<td>36</td>
<td>44</td>
<td>31</td>
</tr>
<tr>
<td>20Ni/TiO(_2) batch 2</td>
<td>13</td>
<td>24</td>
<td>34</td>
<td>162</td>
<td>62</td>
</tr>
<tr>
<td>20Ni/TiO(_2) batch 2</td>
<td>13</td>
<td>24</td>
<td>20</td>
<td>54</td>
<td>35</td>
</tr>
<tr>
<td>20Ni/SiO(_2)</td>
<td>13</td>
<td>24</td>
<td>46</td>
<td>254</td>
<td>72</td>
</tr>
<tr>
<td>20Ni/(\gamma)-Al(_2)O(_3)</td>
<td>10</td>
<td>24</td>
<td>44</td>
<td>340</td>
<td>77</td>
</tr>
<tr>
<td>10Ni/(\gamma)-Al(_2)O(_3)</td>
<td>&lt;8</td>
<td>24</td>
<td>&gt;338</td>
<td>&gt;77</td>
<td></td>
</tr>
</tbody>
</table>

Precision of the XRD instrument: ±1 nm.

\(^a\) Calculated according to: \(d(Ni)_{XRD} \)after reaction – \(d(Ni)_{XRD}\) before reaction /
\(d(Ni)_{XRD}\) before reaction.

\(^b\) Calculated from the XRD measurements assuming spherical particles.

Ni/\(\alpha\)-Al\(_2\)O\(_3\) and Ni/TiO\(_2\) catalysts. It can be easily deduced, by comparing the crystal growth of the 20Ni/TiO\(_2\) batch 2 and the 20Ni/SiO\(_2\), that there is an effect of the support on the sintering rate. This is in line with some results achieved by Vannice and Garten [17], who found differences on nickel carbonyl formation rates between SiO\(_2\) and TiO\(_2\) supported nickel catalysts.

In addition, there is a clear relation between the initial particle size and crystal growth. The Ni/TiO\(_2\) and Ni/\(\alpha\)-Al\(_2\)O\(_3\) catalysts with the highest initial particle sizes, presented the lowest losses of Ni surface area. Moreover, the growth of Ni particles is different for the two batches of 20Ni/TiO\(_2\). In addition, the loss of Ni surface area of the second batch of 20Ni/TiO\(_2\) after 2 h and one day of reaction indicates that the rate of crystal growth decreases with time on stream. These facts prove that the rate of sintering is also dependent on the nickel surface area. In fact, it seems that sintering is more affected by the initial crystal size than by the support.

It must be mentioned that some methanation experiments were repeated without performing TPH on the samples in order to check if sintering occurs during the TPH procedure. The XRD measurements showed no difference in Ni particle size between the samples exposed and not exposed to TPH. This suggests that the main sintering mechanism present may be due to the presence of reaction species, such as H\(_2\)O and/or CO. According to Bartholomew et al. [19], water vapor enhances sintering rates above 800 K (significantly above the reaction temperature of this study) and that the loss of metallic surface area is mainly due to collapse of the support instead of nickel crystal growth. On the other hand, formation of nickel carbonyls occurs at relatively low temperature and high pressure conditions [5,20,60] and is probably the main sintering mechanism occurring during reaction. Moreover, Shen et al. [20], established a criteria to evaluate the regions of “safe” operating conditions. According to this study, the operating conditions of the present work (583 K and 500 kPa of CO) are far from the “safe region”. Therefore, nickel carbonyl formation should occur.

Finally, it should be noted that formation of Ni(CO)\(_4\) is significantly suppressed in the case of using large catalyst pellets [5]. In exothermic reactions, the temperature of catalyst pellets may considerably exceed that of the surrounding bulk fluid [61]. Moreover, depending on the operating conditions, there can also be present a CO concentration gradient from the bulk gas to the catalyst surface through the gas film. These two phenomena result in a lower partial pressure of CO and a higher temperature on the nickel surface which, in consequence, reduce the potential of nickel carbonyl formation.

4. Conclusions

In this study different supported nickel catalysts were prepared and tested under methanation conditions in order to study their resistance towards carbon deposition and nickel particle sintering. The catalysts presented significant differences in their initial nickel particle size due to the large differences in the physical properties of the selected supports. Nevertheless, the authors prepared two batches of Ni/TiO\(_2\) which differed significantly on their average nickel particle diameter. This difference in their initial nickel crystal size provided not only a more comprehensive study of the actual impact of different supports on catalyst deactivation but also an indication of the effect of the initial nickel particle size.

It was found that there is an effect of the support both on the amount and the type of carbon formed. The Ni/TiO\(_2\) catalysts presented low formation of deactivating carbon in comparison with the other tested catalysts. The TPH results showed that the carbon species formed on Ni/TiO\(_2\) catalysts present the lowest hydrogenation temperature in comparison with the carbon species formed on the other supported catalysts. Moreover, the effect of particle size on carbon formation was evaluated for Ni/\(\gamma\)-Al\(_2\)O\(_3\) and Ni/TiO\(_2\) catalysts. For Ni/\(\gamma\)-Al\(_2\)O\(_3\), a higher carbon formation rate was observed on the sample with higher initial particle size. However, the opposite behavior was observed for the two Ni/TiO\(_2\) catalysts with different initial particle size. Apparently, the formation of Ti\(_x\) species after reduction at high temperatures can have a significant effect on carbon formation. This effect may be enhanced on small particles which present a stronger metal-support interaction and, in consequence, a higher carbon deposition rate.

It was found that both the support and the nickel particle size have an effect on crystal growth. It could be observed that the sintering rate is more dependent on particle size than on the support. Nevertheless, it was shown that the rate of sintering is lower for titania-supported nickel catalysts than for the other catalysts tested.

In conclusion, Ni/TiO\(_2\) catalysts are significantly more stable than the other supported catalysts under the studied operating conditions. This higher stability could be explained with the TPH and XRD measurements which proved its higher resistance towards carbon formation and sintering. The product yield after one day on stream resulted to be almost one order of magnitude higher for the Ni/TiO\(_2\) catalysts than for the others.

However, none of these catalysts was actually stable under the studied reaction conditions. Nevertheless, the exposure of these catalysts to higher temperatures and/or the use of larger pellets shapes could significantly decrease the deactivation due to nickel carbonyl formation and perhaps, increase the catalyst stability. Future work will focus on the effect of different operating conditions, especially at higher temperatures and longer time on stream, in order to evaluate the suitability of Ni/TiO\(_2\) catalysts at industrial operation.

Acknowledgments

The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2013) under grant agreement n° 308733. The authors acknowledge the financial support provided by the Swedish Energy Agency.