Effects of Selected Promoters on Ni/ γ -Al₂O₃ Catalyst Performance in Methane Dry Reforming

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Abstract: The Ni catalysts supported on γ -Al₂O₃ were synthesized by an impregnation method. Their catalytic performance in methane dry reforming was investigated. The reforming reactions were carried out in a microreactor using a CO₂:CH₄ feed ratio of 1:1, a F/W = 2640 ml/(h·g), reaction temperatures between 500–850 °C, and at atmospheric pressure. The influence of Ca, Ce, and Zr promoters on catalyst stability, coke deposition, and the H₂/CO ratio were also studied. Effluents were analyzed using an online gas chromatograph equipped with a thermal conductivity detector. The spent and fresh catalysts were characterized by scanning electron microscopy and thermogravimetric analysis. It was found that 3%Ni/ γ -Al₂O₃ promoted with 0.15% Ce and 0.05% Ca gave the best performance and resulted in less coke formation. The highest CH₄ and CO₂ conversion activities were found to be 94.1% and 98.3% at 850 °C, respectively. Stability tests were carried out for 130 h and this provided a H₂ yield of 91%. Moreover, the amount of formed carbon was negligible and did not increase to more than 1.5 wt%.

Key words: methane; dry reforming; coke; nickel; synthesis gas; stability

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The carbon dioxide reforming of CH₄, also known as dry reforming, has received a large amount of attention because of its positive industrial and environmental impact. CH₄ and CO₂ are greenhouse gases that cause the warming of the earth and climate change. These two gases can be consumed by reforming reactions leading to a significant reduction in their concentrations in the atmosphere [1,2]. The primary products are H₂ and CO, which are suitable for industrial processes such as methanol, dimethyl ether, or Fisher-Tropsch reactions [3–9]. Fisher-Tropsch has been recognized as an important alternate technology to petroleum refining [10]. The main process reactions include:

The major drawback of the reforming process is the rapid coke deposition that causes catalyst deactivation, catalyst destruction, and/or reactor blockage. The coke originates mainly from two reactions:

The reaction is exothermic and is favored at temperatures below 700 °C and at higher pressures.

The methane decomposition reaction is endothermic and is favored by high temperatures and low pressures. Carbon formation by CH₄ decomposition is a structure sensitive reaction [2]. Several investigators have attributed catalyst

instability and deactivation in reforming reactions to coke formation [10–13]. Numerous supported metal catalysts have been evaluated (Ni, Rh, Ru, Ir, Pd, and Pt) for this process [14–22]. Their catalytic performance can be affected by many factors such as promoters and operating conditions [23–28]. The incorporation of small amounts of oxygen to the feed was found to have significant effects on catalyst stability, carbon formation, and methane conversion for low CO₂ to CH₄ feed ratios [29–31].

Bellido et al. [32] investigated the effect of adding CaO to the ZrO₂ support on nickel catalyst activity for the dry reforming of methane. During the characterization of the catalyst containing the oxide precursor (NiO) they found a tetragonal phase consisting of CaO-ZrO₂ solid solutions. They also observed that the electrical properties of the support have a proportional effect on catalytic activity. Moreover, a direct relation was found between variations in the electrical conductivity of the support and the nickel species supported on it. Oezkara-Aydinoglu et al. [33] investigated the dry reforming of methane over Pt/ZrO₂ catalysts promoted with Ce at different temperatures and feed compositions. They investigated the influence of the impregnation strategy and the amount of cerium on the activity and stability of the catalyst. They found that the introduction of 1% Ce to the Pt/ZrO₂ catalyst via co-impregnation led to the optimum catalytic activity and stability. The reason for the

high activity was the intensive interaction between Pt and Ce phases in the co-impregnated sample. Chen et al. [34] studied a Ce_{0.75}Zr_{0.25}O₂ solid solution supported Ru catalysts for CH₄-CO₂ reforming. The effect of Ru content on the properties of the catalysts was investigated by N₂ adsorption-desorption, H₂-TPR/MS, XRD, XPS, CO chemisorption, and H₂-TPD/MS. The highly dispersed Ru species was found to favor the interaction between Ru and Ce_{0.75}Zr_{0.25}O₂ and contributed positively to catalyst activity and stability, and it provided excellent resistance to carbon deposition during reforming.

Much effort has been put into the development of metal catalysts that provide high catalytic performance for synthesis gas formation and that are also resistant to carbon deposition. They are expected to provide a stable long-term operation. Thermodynamic consideration suggests that operation at high temperatures is required to minimize carbon formation in the CO₂ reforming of methane [35].

Transition elements combined with a Ce promoter have attracted the attention of researchers because of their high oxygen storage capacity [36]. It has been established that the elimination of lattice oxygen in Ce oxide under reducing conditions produces anionic vacancies that can be correlated to high lattice oxygen mobility. These oxygen vacancy defects are considered to be reactive sites on the surfaces of metal oxides [37,38].

The objective of this study is to develop supported Ni-based catalysts that maintain high activity and stability while minimizing the formation of coke during the dry reforming of methane. We investigated the effect of promoters and reaction temperatures on the activity, stability, and coke formation of Ni/ γ -Al₂O₃ catalysts. Various characterization techniques were employed to substantiate the findings.

1 Experimental

1.1 Preparation of the catalysts

Wet impregnation was used to prepare the catalysts. Supported Ni/ γ -Al₂O₃ catalysts were prepared using nickel nitrate salt (Ni(NO₃)₂·6H₂O) as a precursor and high surface area alumina (SA-6175, A_{BET} = 230 m²/g) as a support. Precursors for the Ce, Ca, and Zr promoters were cerous nitrate (Ce(NO₃)₃·6H₂O), calcium nitrate (Ca(NO₃)₂·4H₂O), and zirconium nitrate (Zr(NO₃)₄·5H₂O), respectively. The catalyst was dried for 10 h at 120 °C and calcined at 900 °C for 2 h. The catalysts were then activated inside the reactor at 700 °C by passing hydrogen at a rate of 40 ml/min for 2 h followed by 20 min of N₂ at a rate of 30 ml/min.

1.2 Methane dry reforming reaction

The CO₂ reforming of methane was carried out at atmospheric pressure in a 9.4 mm i.d. and 48 cm long stainless steel fixed-bed microreactor (Zeton Altamira 2000) packed with 0.75 g of the catalyst. The reaction temperature was measured by a thermocouple placed at the center of the catalyst bed. The volume ratio of the feed gases (CH₄:CO₂:N₂) was 5:5:1. The total flow rate was 33 ml/min with a space velocity of 2640 ml/(h·g). The investigation covered the reaction temperatures of 500, 600, 700, 800, and 850 °C. Effluents were analyzed using an online gas chromatograph (Varian Star cx 3400) equipped with a thermal conductivity detector.

We calculated conversions, H₂/CO ratio, yields, and the deactivation factor (DF) according to the following formulae:

$$\text{CH}_4 \text{ conversion (\%)} = (\text{CH}_4^{\text{in}} - \text{CH}_4^{\text{out}}) / \text{CH}_4^{\text{in}} \times 100$$

$$\text{CO}_2 \text{ conversion (\%)} = (\text{CO}_2^{\text{in}} - \text{CO}_2^{\text{out}}) / \text{CO}_2^{\text{in}} \times 100$$

$$\frac{\text{H}_2}{\text{CO}} = \frac{\text{mole of H}_2 \text{ produced}}{\text{mole of CO produced}}$$

$$\text{H}_2 \text{ yield (\%)} = \frac{\text{mole of H}_2^{\text{out}}}{2 \times \text{mole of CH}_4^{\text{in}}} \times 100$$

$$\text{DF} = \frac{\text{Final CH}_4 \text{ conversion} - \text{Initial CH}_4 \text{ conversion}}{\text{Initial CH}_4 \text{ conversion}}$$

1.3 Characterization of the catalysts

The catalysts (before and after the reaction) were characterized by different techniques. To investigate carbon deposition the morphology of the catalysts was investigated using a scanning electron microscope (SEM, JEOL JSM-6360A). The amount of surface carbon was evaluated by thermogravimetric analysis (TGA) and differential thermal analysis (DTA) in an air atmosphere at up to 800 °C on a Perkin-Elmer Pyris Diamond thermogravimetric-differential analyzer TG/DTA 6300 at a heating rate 20 °C/min.

2 Results and discussion

A blank experiment without a catalyst and with only quartz wool at 800 °C showed a CH₄ conversion of less than 2%. In an earlier investigation the optimum Ni loading for the highest catalyst activity and the lowest amount of coking was a 3% Ni loading [39] and the optimum calcination temperature was 900 °C [40].

2.1 Effect of promoters on the 3%Ni/ γ -Al₂O₃ catalyst

Promoters such as ceria or other rare earth metal oxides can improve the behavior of nickel based catalysts since they possess a higher oxygen storage capacity and therefore

contribute to the inhibition of carbon formation. The catalytic performance of the Ca, Zr, and Ce-promoted 3%Ni/ γ -Al₂O₃ catalyst are presented in Table 1.

Table 1 Catalytic performance of the Ca, Zr, and Ce-promoted 3%Ni/ γ -Al₂O₃ catalyst

Promoter	$X(\text{CH}_4)/\%$		$X(\text{CO}_2)/\%$		H_2/CO ratio ^c	Coke ^d (%)	DF (%)
	Initial ^a	Final ^b	Initial ^a	Final ^b			
—	73.7	73.0	80.1	79.0	0.91	6.9	−0.95
0.05%Ca	74.1	73.6	81.8	80.3	0.91	6.0	−0.67
0.15%Ca	74.4	74.0	80.8	79.4	0.92	4.1	−0.54
0.30%Ca	71.8	70.7	83.7	83.0	0.79	9.2	−1.50
0.05%Zr	73.4	73.0	83.3	76.7	0.84	6.4	−0.55
0.15%Zr	72.3	71.0	82.3	79.1	0.87	9.2	−1.80
0.30%Zr	75.2	71.9	81.2	75.4	0.93	12.4	−4.40
0.05%Ce	74.5	73.8	82.8	81.4	0.82	6.4	−0.94
0.15%Ce	76.1	75.1	84.9	84.5	0.86	8.9	−1.30
0.30%Ce	74.0	73.0	84.2	80.1	0.80	10.4	−1.40

Reaction temperature: F/W = 2640 ml/(h·g), 700 °C, CH₄ 15 ml/min, CO₂ 15 ml/min, N₂ 3 ml/min, catalyst 0.75 g, Calcination temperature 900 °C. ^a0.5 h on stream; ^b9 h on stream; ^cAverage data during time on stream; ^dDetermined by TGA.

The initial and final conversions of methane and carbon dioxide for the unpromoted 3%Ni/ γ -Al₂O₃ catalyst changed from 73.7% to 73.0% and 80.1% to 79.0%, respectively. The calculated deactivation factor and coke were −0.95% and 6.9%, respectively. For the catalysts promoted with 0.05% and 0.15% calcium there was no significant enhancement in the conversions of methane and carbon dioxide (< 2%). A significant drop in carbon formation (from 6.9% to 4.1%) and a drop in the deactivation factor (from −0.95% to −0.54%) were observed upon increasing the Ca content to 0.15%. However, for the 0.30% Ca-promoter, the conversion of methane dropped slightly by 2.5% initially and 3.2% after 9 h on stream, and for the same time intervals the conversion of CO₂ increased by 4.5% and 5%, respectively. Upon increasing the calcium content to 0.30% the Ca-promoted catalyst gave a lower H₂/CO ratio (0.79) and higher carbon formation (9.2%) compared with the unpromoted catalyst at 0.91% and 6.9%, respectively. These findings are in agreement with the results obtained by Hou et al. [41] who showed that the presence of small quantities of Ca in the Ni/ α -Al₂O₃ catalyst enhanced catalyst activity and stability; however, the methane decomposition reaction is favored at a higher Ca content. The 0.15% Ca-promoted catalyst gave the lowest deactivation factor and coke deposition of −0.54% and 4.1%, respectively, and the H₂/CO ratio was practically unaffected.

Upon promoting the catalyst with 0.05% Zr, the conversion of methane showed insignificant change (73.4% to 73.0%). However, carbon dioxide showed an 8% drop in conversion from 83.3% to 76.7%. The calculated deactivation

factor and coke deposition were −0.55% and 6.4%, respectively. When the catalyst was promoted with 0.15% Zr the conversions of methane and carbon dioxide varied from 72.3% to 71.0% and 82.3% to 79.1%, respectively. The calculated deactivation factor and coke were −1.8% and 9.2%, respectively. The addition of 0.15% Zr to the catalyst did not result in an improvement in activity or carbon formation; however, upon increasing the amount of promoter to 0.30% the conversions of methane and carbon dioxide dropped by 4.4% (from 75.2% to 71.9%) and by 7.1% (from 81.2% to 75.4%), respectively. The calculated deactivation factor and coke were 4.4% and 12.4%, respectively. Compared with the unpromoted catalyst, the initial conversion of CH₄ increased, however, the final CO₂ conversion decreased. As is evident from Table 1, the 0.05% of Zr-promoted catalyst was less prone to carbon deposition. However, as the Zr content was further increased more carbon deposition was observed.

For the Ce-promoted catalyst the initial and final conversions of methane and carbon dioxide obtained during the time on stream experiments varied from 74.5% to 73.8% and 82.8% to 81.4%, respectively. The calculated deactivation factor and coke were −0.94% and 6.4%, respectively. Increasing the Ce content to 0.15% improved the conversions of both methane and carbon dioxide to 76.1% and 84.9%, respectively, at the expense of the H₂/CO ratio (from 0.91 to 0.86) and more carbon deposition (8.9% compared with 6.9%). A further increase in the Ce content to 0.30% resulted in lower activity (74% for CH₄ and 84.2% for CO₂), a lower H₂/CO ratio (0.80), and higher coke deposition (10.4%), and thus a higher deactivation factor (−1.4%) compared with the 0.15% Ce-promoted catalyst.

Therefore, the 0.15% Ce-promoted catalyst was chosen for further modification by the addition of different amounts of Ca and Zr, and the results are given in Table 2. When 0.05% Ca was added to the 0.15% Ce-promoted catalyst matrix the activity did not change significantly, however, the amount of deposited coke was reduced by 69% (from 8.9% to 2.5%) and lower deactivation factors were obtained (−0.9% vs. −1.3%). The final CO₂ conversion was lower (81.9%) compared with the Ce-only promoted catalyst

Table 2 Catalytic performance of (3%Ni+0.15%Ce)/ γ -Al₂O₃ modified with Ca or Zr

Promoter	$X(\text{CH}_4)/\%$		$X(\text{CO}_2)/\%$		H_2/CO ratio	Coke (%)	DF (%)
	Initial	Final	Initial	Final			
—	76.1	75.1	84.9	84.5	0.86	8.9	−1.3
0.05%Ca	76.6	75.9	85.6	81.9	0.91	2.5	−0.9
0.10%Ca	75.3	74.4	85.9	85.9	0.91	4.1	−1.2
0.05%Zr	75.7	73.9	85.5	75.0	0.92	12.2	−2.4
0.10%Zr	74.0	72.0	84.9	63.5	0.94	16.5	−2.7

Reaction conditions are the same as in Table 1.

(84.5%). A higher H₂/CO ratio was obtained with the 0.05% Ca-doped catalyst (0.91) compared with the undoped catalyst (0.86). Upon increasing the Ca content to 0.10% the activity remained the same but the amount of coke was reduced to less than one half. Upon doping the 0.15% Ce-promoted catalyst with 0.05% Zr, the initial activity did not change significantly. However, the final CO₂ conversion dropped significantly (> 11%) and carbon deposition increased by 37%. Upon a further increase in the amount of Zr to 0.10%, the final activity of the catalyst (especially for CO₂) deteriorated appreciably and more carbon deposition was evident (increased by 85.4%). It is clear from data presented in Tables 1 and 2 that the Zr-containing catalysts are more prone to carbon formation. Therefore, by considering all these factors, especially carbon formation, the (3%Ni+0.15%Ce+0.05%Ca)/ γ -Al₂O₃ was selected for further investigation. The addition of Ca and Ce oxides to the catalyst increased its Lewis basicity leading to an enhanced absorption of CO₂ resulting in higher stability and lower carbon deposition.

2.2 Effect of reaction temperature on the (3%Ni+0.15%Ce+0.05%Ca)/ γ -Al₂O₃ catalyst

The effect of temperature on the activity and stability of the catalyst for the methane reforming reaction with carbon dioxide was conducted for 9, 105, and 130 h on stream at five different reaction temperatures (500, 600, 700, 800, and 850 °C) as presented in Fig. 1, Fig. 2, and Table 3. Figure 1

Fig. 1. CH₄ (a) and CO₂ (b) conversions with time over (3%Ni+0.15%Ce+0.05%Ca)/ γ -Al₂O₃ at different temperatures.

Fig. 2. Stability test for (3%Ni+0.15%Ce+0.05%Ca)/ γ -Al₂O₃ at 800 °C (a) and 850 °C (b).

shows the conversions of CH₄ and CO₂ respectively at 500, 600, and 700 °C over a period of 9 h. Figure 2 shows the stability test results at 800 and 850 °C. It is clear that this catalyst is stable. The results in Table 3 (only initial and final conversions of Figs. 1 and 2) show that the initial and final conversions of the reactants (CH₄ and CO₂) and the yields of H₂ and CO increase with temperature. The initial methane and carbon dioxide conversions reached 91.0% and 93.6%, respectively, and the H₂ and CO yields were 0.87 and 0.88 respectively at a reaction temperature of 800 °C and for a time on stream of 105 h. Upon a further increase in the reaction temperature to 850 °C and with a longer duration (130 h) the initial methane and carbon dioxide conversions increased to 94.1% and 98.3%, respectively. The H₂ and CO yields were 0.91 and 0.92 respectively giving a H₂/CO ratio of 0.99. The conversion of carbon dioxide was

Table 3 Catalytic performance of (3%Ni+0.15%Ce+0.05%Ca)/ γ -Al₂O₃ catalyst

T/°C	t/h	X(CH ₄)/%		X(CO ₂)/%		H ₂ /CO ratio	Y(H ₂)/%	Y(CO)/%	Coke (%)
		Initial	Final	Initial	Final				
500	9	16.0	15.4	26.8	25.1	0.55	0.10	0.18	2.6
600	9	40.3	38.3	52.2	51.4	0.71	0.31	0.40	2.8
700	9	76.6	75.9	85.6	81.9	0.91	0.74	0.80	2.5
800	105	91.0	87.6	93.6	86.6	0.98	0.87	0.88	2.6
850	130	94.1	92.2	98.3	91.0	0.99	0.91	0.92	1.5

found to be higher than that of methane and the H_2/CO ratios are similar indicating the dominance of the water gas shift reaction ($CO_2 + H_2 \rightarrow CO + H_2O$).

The CO_2 reaction consumed H_2 and the reduced carbon deposition on the catalyst was due to steam formation. As is evident from Table 3, the synthesis gas ratio increased with reaction temperature. Coke formation was relatively high at lower reaction temperatures (500 to 800 °C). However, upon increasing the reaction temperature to 850 °C, coke formation decreased even over longer periods of time on stream (130 h). The decrease in coke can be attributed to the increased rate of coke removal by gasification agents such as H_2O and CO_2 during the reaction ($C + H_2O \rightarrow CO + H_2$).

The developed supported catalyst was characterized by its resistance to coke formation. The TG curves for the spent catalysts described in Table 1 (3%Ni/ γ - Al_2O_3 , 3%Ni+0.15%Ce/ γ - Al_2O_3) and Table 2 (3%Ni+0.15%Ce+0.05%Ca/ γ - Al_2O_3) are shown in Fig. 3. The profiles of the three spent catalysts show mass losses of 6.9%, 8.9%, and 2.5%, respectively, at a reaction temperature of 700 °C. These results confirm the supremacy of the catalyst promoted with Ce and Ca (3%Ni+0.15%Ce+0.05%Ca/ γ - Al_2O_3) with regard to carbon formation and catalyst stability.

Figure 4 shows the SEM images of the fresh (3%Ni/ γ - Al_2O_3) and the spent 3%Ni/ γ - Al_2O_3 , 3%Ni+0.15%Ce/ γ - Al_2O_3 , and 3%Ni+0.15%Ce+0.05%Ca/ γ - Al_2O_3 catalysts. The used 3%Ni/ γ - Al_2O_3 and 3%Ni+0.15%Ce/ γ - Al_2O_3 catalysts show a considerable amount of carbon deposition.

Fig. 3. TG curves for the spent catalysts.

However, the spent 3%Ni+0.15%Ce+0.05%Ca/ γ - Al_2O_3 catalyst was almost identical to the fresh catalyst indicating the absence of coke formation. This further confirms our previous findings regarding this catalyst, and it is thus industrially preferable to use 3%Ni+0.15%Ce+0.05w%Ca/ γ - Al_2O_3 at temperatures higher than 800 °C.

3 Conclusions

Dry reforming of CH_4 to produce CO-rich synthesis gas was investigated. Promoters such as Ca, Ce, and Zr were used for the preparation of supported catalysts. Carbon

Fig. 4. SEM images of fresh 3%Ni/ γ - Al_2O_3 (a), spent 3%Ni/ γ - Al_2O_3 (b), spent (3%Ni+0.15%Ce)/ γ - Al_2O_3 (c), and spent (3%Ni+0.15%Ce+0.05%Ca)/ γ - Al_2O_3 (d) catalysts.

deposition was the major factor that influenced catalyst activity and stability. CH₄ and CO₂ conversions increased with an increase in the reaction temperature. The lowest coke formation and the best stability were obtained at 800 and 850 °C. Based on catalyst stability, Ce was found to be the best promoter for the 3%Ni/ γ -Al₂O₃ catalyst. The addition of Ca to the Ce-promoted catalyst with the following composition (3%Ni+0.15%Ce+0.05%Ca/ γ -Al₂O₃) gave the best activity and stability results. Moreover, the same catalyst gave the lowest amount of coke formation as confirmed by TGA and SEM.

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