Nanosized Ni/SBA-15 Catalysts for CO₂ Reforming of CH₄

Ahmed A. Ibrahim 1,*, Ashraf Amin 2, Ahmed S. Al-Fatesh 1, Nadavala Siva Kumar 1, Samsudeen Olajide Kasim 1, Abdulrhman S. Al-Awadi 1, Ahmed M. El-Toni 3, Ahmed Elhag Abasaeed 1 and Anis H. Fakeeha 1,*

1 Chemical Engineering Department, College of Engineering, King Saud University, P.O. Box 800, Riyadh 11421, Saudi Arabia; aalfatesh@ksu.edu.sa (A.S.A.-F.); shivanadavala@gmail.com (N.S.K.); SOFKOLAJIDE2@GMAIL.COM (S.O.K.); alawadi@ksu.edu.sa (A.S.A.-A.); abasaeed@ksu.edu.sa (A.E.A.)
2 Chemical Eng. & Pilot Plant Department, Eng Res Division, National Research Centre, El Buhouth St., Dokki, 12622 Cairo, Egypt; ashmukhtar@yahoo.com
3 King Abdullah Institute for Nanotechnology, King Saud University, Riyadh 11451, Saudi Arabia; aamohammad@ksu.edu.sa

* Correspondence: aidid@ksu.edu.sa (A.A.I.); anishf@ksu.edu.sa (A.H.F.); Tel.: +966-534278905 (A.A.I.); +966-505369691 (A.H.F.); Fax: +966-114678770 (A.A.I. & A.H.F.)

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Abstract: Ni, Co, and Co–Ni bimetallic catalysts supported over SBA-15 and over SBA-15 doped with Zn or Ce oxides were prepared and tested in a methane dry reforming reaction. The loading of the metals in the catalyst was 5 wt % for either mono or bimetallic catalysts. The prepared catalysts were tested in a continuous-flow fixed-bed reactor at 800 °C under atmospheric pressure. XRD, TPR, TPD, and SEM characterization techniques were employed to investigate the catalytic properties of fresh catalysts. SEM and TGA were used to study the catalytic properties of spent catalysts. A remarkable effect on the reduction properties and catalytic performance of catalysts was observed after adding Zn and Ce. Over an 8 h test, Ni/SBA-15 showed the best activity and stability. The conversion was 90% for CH₄ and CO₂. Co–Ni/SBA-15 and Co–Ni/Ce–SBA-15 have shown a reasonable activity and stability. Selectivity of the Ni/SBA-15 catalyst was higher than all other catalysts as indicated by the H₂/CO ratio. Co/SBA-15 and Co–Ni/Zn–SBA-15 showed a low activity and selectivity. TPD–NH₃ profiles indicated that doping SBA-15 with Ce and/or Zn increased the catalyst acidic sites. Ni/SBA-15 is an excellent potential catalyst for commercial methane dry reforming processes.

Keywords: catalyst; CO₂; H₂; methane reforming; SBA-15

1. Introduction

Hydrogen is produced mostly by steam reforming of methane [1–3]. CO₂ reforming of methane can reduce the emissions of CO₂ and CH₄, the main greenhouse gases [1,4–6]. Methane reforming is an interesting method for converting biogas (methane and carbon dioxide) to a mixture of CO and H₂ that is recognized as a synthesis gas (syngas) [1–3,7–10]. CO₂ reforming of methane produces equal amounts of carbon monoxide and hydrogen which can be converted into a variety of chemicals and fuels, such as methanol and liquid fuel, via the Fischer–Tropsch process [10–12]. However, CO₂ reforming of methane is an endothermic reaction; it requires high temperature levels as indicated by the following reaction [13–15]:

\[
CH₄(gas) + CO₂(gas) \leftrightarrow 2CO(gas) + 2H₂(gas)ΔH₂₉₈ = 261 kJ mol⁻¹.
\]
A catalyst is essential for converting the highly stable methane molecules into synthetic gas, and then into liquid fuels \[4,16,17\]. Due to the high reaction temperatures, the catalyst may suffer from deactivation due to sintering, and may also be deactivated by carbon deposition \[5,9,13,18\]. Supported nickel and noble metal catalysts have been used successfully in research for catalyzing CO\(_2\) reforming of methane \[1,6,9,13\]. Although nickel catalysts are sensitive to coke formation and are less active, nickel is more economical and widely available \[15,19\]. Adding Co to Ni improves dispersion and catalytic enactment due to the synergetic effect of Ni and Co \[10,13\].

Developing stable nickel catalysts with higher resistance to coke formation and sintering is the key to commercializing the process \[20–22\]. The stability and performance of nickel catalysts can be improved by alloying them with another active metal. The support critically affects the catalyst stability and activity. Different factors should be considered when selecting a support material. The support surface area is considered a dominant factor \[15,18,23,24\]. A higher surface area provides better dispersion for the metallic active sites, thereby reducing the sintering effect. Other factors should be considered in the selection of a support, including larger pores, thermal stability, chemical composition, and wall thickness \[15,25\]. The support can be modified by doping other metal oxides that can provide oxygen for the formation of CO, which reduces the carbon deposition \[26,27\]. Oxides with higher oxygen capacity and mobility, such as CeO\(_2\), are preferred catalyst promoters for CO\(_2\) reforming of methane \[24\].

SBA-15, referred to also as S15, is a mesoporous support distinguished by its thick walls and a narrow, well-ordered, two-dimensional hexagonal pore network that is stable even after reaction \[12,23\]. The active sites are distributed within the high-surface-area pores of S15, leading to improved catalyst dispersion. Good interface between active sites and support should ensure reduced active site mobility and sintering which, in turn, decrease the extent of carbon deposition and catalyst deactivation \[19,27–29\]. In addition, better dispersion should reduce the extent of carbon deposition, which is the main barrier to developing a stable catalyst in the CO\(_2\) reforming of methane \[6,15,19,30,31\]. Albarazi et al. \[6\] doped Ni/S15 with ceria and zirconia modifiers, resulting in a remarkable improvement in the stability of the doped catalysts. The authors reported better conversion with Ni/S15, which is credited to the availability of more nickel active sites for catalyzing the reaction. Al-Fatesh et al. \[15\] used a bimetallic catalyst (Co–Ni) supported on S15 for the CO\(_2\) reforming of methane. They compared the performance of Co–Ni/S15 with that of Co–Ni/S15 doped with Mg, La, and Sc. The results indicated that Mg and Sc are excellent support dopants. Adding Mg and Sc increased the CH\(_4\) conversion achieved using Co–Ni/S15 by 28% and 26%, respectively. The Mg- and Sc-doped catalysts exhibited stable performance during a 50 h test, whereas the undoped Co–Ni/S15 was stable for only 20 h. The authors found that La addition had almost no effect on the activity of Co–Ni/S15. Pompeo et al. \[21\] reported a noticeable positive outcome on the overall enactment of Ni/SiO\(_2\) when adding Li. It was concluded that the effect of a certain promoter/dopant is dependent on the textural properties, support material, electronic state, and reaction conditions. Wang et al. \[12\] reported different effects of introducing Ce into the hexagonal structure of S15 for promoting Ni/S15. The variation of the Ce effect was attributed to the Ce/Si ratio. The best catalytic stability and activity was observed at a Ce/Si molar ratio of 0.04, around 80% CH\(_4\) conversion at 700 °C for 40 h. Wang et al. \[11\] examined the effects of MgO addition to Ni/S15, whereby MgO addition enriched catalytic enactment and carbon resistance of Ni/S15.

In this study, various nickel and cobalt catalysts supported on S15 are evaluated in the CO\(_2\) reforming of methane. Ce and Zn oxides are used as support dopants. The effect of the catalyst/support and promoters/dopants combination was studied to optimize the catalyst performance and conversion. Different characterization techniques were employed to probe the effect of adding cobalt and promoters on the catalyst structure and textural properties. The prepared catalysts were assessed in CO\(_2\) reforming of methane in a fixed bed reactor, over the course of 8 h, to examine the effect of the addition of cobalt and dopants.
2. Materials and Methods

2.1. Catalyst Preparation

To prepare mesoporous nanoparticle S15 silica, 600 mL distilled water and 120 mL concentrated HCl (37%) were mixed by stirring at room temperature in a 1 L glass bottle. Twenty-four grams of Pluronic 123* (MW = 5800, Aldrich) was placed in HCl solution and stirred for half an hour until homogenization. Then, 48 g TEOS (tetraethoxysilane, 98%, Alfa Aesar) was added under stirring at 45 °C for 24 h. During this time, the clear solution changed to a white suspension. Finally, the solution was aged at 90 °C for 48 h without stirring. Cooled dispersion was filtered using a glass frit (G3). The filter cake (S15) was dried at room temperature for 24 h then at 120 °C for 4 h. The dry S15 was calcined in air at a 50 °C/h heating rate for up to 550 °C for 6 h, in a muffle.

S15 was doped with 5 wt % of Ce and Zn using Ce(NO₃)₃ and Zn(NO₃)₂, respectively, by the wet impregnation method. The modified support was dried overnight at 120 °C and calcined at 600 °C in air for 4 h. The support was co-impregnated by a solution of the metal precursor (Ni(NO₃)₂·6H₂O and Co(NO₃)₂·6H₂O), with a total loading of 5 wt %. The mole ratio of Co and Ni in the bimetallic catalyst was 1:1 Co/Ni. The prepared catalysts were reduced at 600 °C for 1 h under a 20% H₂/Ar atmosphere. The unmodified catalysts are referred to as 5% Co/S15 (Co/S15), 5% Ni/S15 (Ni/S15), and 5% Co–Ni/S15 (Co–Ni/S15). The modified bimetallic catalysts are denoted as 2.5% Co–2.5% Ni/Ce–S15 (Co–Ni/Ce–S15), and 2.5% Co–2.5% Ni/Zn–S15 (Co–Ni/Zn–S15).

2.2. Catalytic Testing

The activity of the catalyst (0.15 g) was evaluated at 1 atm in a continuous-flow fixed-bed reactor. The reactor was shaped from a SS tube (9.4 mm i.d. and 30 cm in length). A thermocouple was fixed in the middle of the catalyst bed to display the reaction temperature and the metallic thermocouple was placed inside a small quartz tube to eliminate any contribution of the catalytic activity of the metal component. Pretreatment of the catalysts (before starting the reaction) was conducted by introducing hydrogen at 500 °C for 1 h at a flow rate of 30 mL/min. Subsequently, the reactor was purged with flowing nitrogen (N₂) at a rate of 20 mL/min for 20 min at 750 °C to remove any residual H₂ in the reactor. The nitrogen purge was continued until the reactor temperature reached 800 °C. The feed gas, CH₄/CO₂/N₂, with a volume ratio of 22/22/6, was introduced and maintained at a rate of 50 mL/min throughout the reaction at a space velocity of 20,000 mL/(h·gcat). The concentration of products and unconverted feed gases from the reactor was evaluated using an online GC (GC-Shimadzu 2014) attached to a thermal conductivity detector (TCD).

2.3. Catalyst Characterization

X-ray diffraction (XRD) outlines were obtained via a Panalytical X’Pert Pro diffractometer fitted with RTMS detector (X’Celerator) and Cu Ka X-ray radiation (40 kV, 40 mA; scan mode: continuous; step range: 10–90° 2θ; step size: 0.0167°, counting time: 25 s/step).

The BET surface area of the fresh catalyst was calculated from the N₂ adsorption–desorption data by a Micromeritics Tristar II 3020 surface area and porosity analyzer. The pore distribution was computed using the Barrett–Joyner–Halenda (BJH) method.

Temperature-programmed reduction (H₂-TPR) and ammonia temperature-programmed desorption (NH₃-TPD) analyses were conducted via a Micromeritics Auto Chem II 2920 instrument. The measurements were conducted after heating the catalysts at 200 °C for 1 h under an argon atmosphere, and subsequent cooling to room temperature. In the case of H₂-TPR, 0.07 g of the sample was heated at a rate of 10 °C/min to a temperature of 900 °C under a gas mixture of H₂/Ar (v/v, 10/90) at a flow rate of 40 mL/min. The H₂ consumption signal was recorded using a thermal conductivity detector (TCD). The adsorption of NH₃ was evaluated at a temperature of 50 °C over the course of half an hour under a mixture of NH₃/He (v/v, 10/90) at a flow rate of 30 mL/min. The desorption...
signal (NH$_3$) was recorded with a TCD by gradually increasing the temperature to 800 °C at a rate of 10 °C/min.

The quantity of coke deposited in the used catalysts was assessed by burning in air using an EXSTAR SII TG/DTA 7300 thermogravimetric/differential analyzer (TGA). The spent catalyst (10–20 mg) was heated from 25 °C to 800 °C at a rate of 20 °C/min. TEM measurements were performed for the catalyst samples using a JEOL (JEM-2100F, JEOL Ltd., Tokyo, Japan) transmission electron microscope operated at 120 KV accelerating voltage.

3. Results and Discussion

Table 1 summarizes the catalyst surface areas under investigation, measured using N$_2$ adsorption. The bare support, S15, had the highest surface area of 819.3 m$^2$/g. The surface area loss on supporting Ni, Co, and Co–Ni with and without the modifiers was in the range of 33–35%. The results denote that the surface areas of all the catalysts were comparable, irrespective of the catalyst composition. The high surface area of the catalysts is attributed to the high area of the support, S15, as shown in Table 1.

| Catalyst       | Surface Area (m$^2$/g) |
|----------------|------------------------|
| S15            | 819                    |
| Ni/S15         | 547                    |
| Co/S15         | 532                    |
| Co–Ni/S15      | 549                    |
| Co–Ni/Ce–S15   | 551                    |
| Co–Ni/Zn–S15   | 548                    |

The XRD of the fresh calcined catalyst samples are displayed in Figure 1. The XRD pattern of the bare S15 carrier showed the amorphous nature of the mesoporous silica nanoparticles which is clearly in the 2θ range of 20–30° (Figure 1a). Upon loading with 5 wt % Ni oxide (Figure 1b), the characteristic peaks matching to the (1 1 1), (2 0 0), and (2 2 0) planes of face-centered-cubic NiO appeared at 2θ = 37.3, 43.3, and 62.9° [32,33]. On the other hand, loading 5 wt % Co oxide into S15 (Figure 1c) produced peaks at 2θ = 36.8, 44.8, 55.6, 59.4, and 65.2°, corresponding to the (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), and (4 4 0) planes of the cubic phase of Co$_3$O$_4$ spinel [33]. Upon doping with a mixture of 2.5 wt % of both Ni and Co oxide, characteristic peaks of Co and Ni oxide were detected, similar to what was observed with samples doped with Ce and Zn (Figure 1d,e, respectively). However, no characteristic peaks were observed for Ce and Zn as they might be highly dispersed, or the Ce and Zn species may have been included into the mesoporous framework of S15 [34]. The peak intensity of the modified supports is slightly higher compared to the non-modified, due to their being calcined two times.

The catalysts were characterized using NH$_3$ desorption to examine the surface acidity of the prepared solids. Figure 2 illustrates the NH$_3$-TPD profiles of the different catalysts. A major peak was observed at 100 °C for Co–Ni/S15, Co–Ni/Co–S15, and Co–Ni/Zn–S15, and a minor peak was found at 100 °C for Ni/S15 and Co/S15. In the 260–350 °C range, minor peaks were detected for all catalysts. The two peaks observed for each catalyst in the range of 25–500 °C are attributed to the weak acidic sites. In the 600–700 °C range, peaks were detected for Co–Ni/S15, Co–Ni/Co–S15, and Co–Ni/Zn–S15, which can be attributed to the strong acidic sites. The NH$_3$-TPD profiles indicate that the modified support bimetallic catalysts showed stronger acidic sites compared to the non-modified samples. The acidic sites, especially the strong acidic sites, are expected to have a negative effect on CO$_2$ adsorption and to reduce the CO$_2$/CH$_4$ conversion rate and the completion of CO$_2$ reforming of methane [7,33,35]. The lower CO$_2$ adsorption rate may facilitate other reaction pathways, thus reducing the catalyst selectivity. Overall, the NH$_3$-TPD profiles suggest that the catalysts doped with Ce/Zn should exhibit lower activity than the non-doped catalyst.
Co–Ni/Zn–S15, which can be attributed to the strong acidic sites. The NH$_3$-TPD profiles indicate that the modified support bimetallic catalysts showed stronger acidic sites compared to the non-modified samples. The acidic sites, especially the strong acidic sites, are expected to have a negative effect on CO$_2$ adsorption and to reduce the CO$_2$/CH$_4$ conversion rate and the completion of CO$_2$ reforming of methane [33,35]. The lower CO$_2$ adsorption rate may facilitate other reaction pathways, thus reducing the catalyst selectivity. Overall, the NH$_3$-TPD profiles suggest that the catalysts doped with Ce/Zn should exhibit lower activity than the non-doped catalyst.

Figure 1. XRD patterns of calcined samples: (a) S15, (b) 5% Ni/S15, (c) 5% Co/S15, (d) 2.5% Ni + 2.5% Co/Ce + S15, (e) 2.5% Ni + 2.5% Co/Zn + S15.

Figure 2 shows the elucidated TPR profiles of the catalysts under study. The decreasing temperature is a sign of the presence of a certain species and indicates the degree of interaction with the support [35]. Two peaks were observed at 300 and 530 °C for Ni/S15, respectively, corresponding to two different NiO species. The first peak was assigned to NiO species that are weakly attached to the support, while the one at 530 °C was for the NiO species that are strongly interacting with the support [15,32]. For Co/S15, two low temperature peaks were observed for the two-step reduction of Co$^{3+}$ to Co$^{2+}$, and then to Co$^{0}$. Additionally, another peak was observed at 850 °C, which indicates a firm interaction between smaller Co oxide crystals and the support, or the formation of cobalt silicates. The profile of Co–Ni/S15 showed two low temperature peaks at 217 and 370 °C which could be due to the formation of an alloy between Co and Ni. Hence, reduction occurs more easily in the bimetallic system than in the monometallic system. It seems that the addition of Co as an active component weakens the interaction between Ni and the support. Therefore, catalyst reduction takes place easily, and more active sites are provided for the catalytic reaction [15].

Figure 2. NH$_3$ temperature-programmed desorption profiles of catalysts.

Figure 3 shows the elucidated TPR profiles of the catalysts under study. The decreasing temperature is a sign of the presence of a certain species and indicates the degree of interaction with the support [35]. Two peaks were observed at 300 and 530 °C for Ni/S15, respectively, corresponding to two different
NiO species. The first peak was assigned to NiO species that are weakly attached to the support, while the one at 530 °C was for the NiO species that are strongly interacting with the support [15,32]. For Co/S15, two low temperature peaks were observed for the two-step reduction of Co$^{3+}$ to Co$^{2+}$, and then to Co$^{0}$. Additionally, another peak was observed at 850 °C, which indicates a firm interaction between smaller Co oxide crystals and the support, or the formation of cobalt silicates. The profile of Co–Ni/S15 showed two low temperature peaks at 217 and 370 °C which could be due to the formation of an alloy between Co and Ni. Hence, reduction occurs more easily in the bimetallic system than in the monometallic system. It seems that the addition of Co as an active component weakens the interaction between Ni and the support. Therefore, catalyst reduction takes place easily, and more active sites are provided for the catalytic reaction [15].

![Temperature-programmed reduction using a mixture of hydrogen and argon.](image)

The incorporation of Zn and Ce oxides led to a better efficiency and better reduction of the active sites at lower temperatures. The TPR profiles of Co–Ni/ Ce–S15 and Co–Ni/Zn–S15 indicate the presence of four and three peaks, respectively, in contrast to two peaks only for Co–Ni/S15. NiO and/or Co in Co–Ni/ Ce–S15 and Co–Ni/Zn–S15 catalysts were reduced at 220 and 240 °C, respectively, as shown in Figure 3. The cobalt oxides were reduced at lower temperatures in Co–Ni/ Ce–S15 compared to Co–Ni/S15. Figure 3 shows that the catalyst doped with Ce was more completely reduced at lower temperatures than the Zn doped catalyst, indicating that the surface oxygen species on Co–Ni/ Ce–S15 samples have higher mobility and activity due to the redox property of Ce [12]. Based on the TPR results, 500 °C was chosen as the reduction temperature at which all the free NiO was reduced. However, Co could not be completely reduced at this temperature, and higher temperature levels were avoided to reduce the sintering effect.

Figures 4 and 5 illustrate the CH$_4$ and CO$_2$ conversions versus time-on-stream respectively, calculated from the onset of the reaction (CH$_4$/ CO$_2$/N$_2$ mixture flowing). The reported conversion of both reactants over different catalysts varied significantly depending on the catalyst. This indicates that the promoter/dopants exerted a remarkable influence on the catalyst activity. As indicated by the TPD and TPR results for NH$_3$, the variation of the degree of reduction and acidity of the catalyst surface...
may affect the catalyst selectivity. The catalytic activity based on the conversion of both reactants was observed according to the following order (from high to low): Ni/S15 > Co–Ni/S15 > Co–Ni/Ce–S15 > Co–Ni/Zn–S15 > Co/S15.

![Figure 4. CH₄ conversion against time-on-stream (min).](image)

![Figure 5. CO₂ conversion versus time-on-stream (min).](image)
Figures 4 and 5 show that Ni/S15 exhibited the maximum activity among the tested catalysts, which can be assigned to the high amount of nickel supported on S15, leading to the accessibility of more nickel active sites for the reaction compared to that of the other catalysts. In addition, Ni/S15 exhibited complete reduction and fewer acidic sites. \( \text{CH}_4 \) and \( \text{CO}_2 \) conversions were 90%, 78%, and 72% over Ni/S15, Co–Ni/S15, and Co–Ni/Ce–S15, respectively. For Co–Ni/Zn–S15, the \( \text{CH}_4 \) and \( \text{CO}_2 \) conversion was 20% and 37%, respectively. For Co/S15, the \( \text{CH}_4 \) and \( \text{CO}_2 \) conversion was 10% and 13%, respectively. The conversion of \( \text{CO}_2 \) was slightly greater than that of \( \text{CH}_4 \) due to the involvement of a reversed water–gas shift (RWGS) reaction.

The conversion achieved with Co–Ni/S15 and Co–Ni/Ce–S15 was slightly less than that obtained with Ni/S15. The low conversion observed with Co–Ni/S15 and Co–Ni/Ce–S15 was attributed to the lower amount of nickel. The catalyst doped with CeO\(_2\) showed better activity than the catalyst doped with ZnO, as CeO\(_2\) has a greater oxygen capacity and mobility than ZnO, which improves the activity and carbon capacity [36]. Higher oxygen mobility facilitates \( \text{CO}_2 \) conversion and reduces the extent of carbon formation on the catalyst.

As shown in Figure 2, Co–Ni/Zn–S15 has a high concentration of acidic sites, which reduces \( \text{CO}_2 \) adsorption on the catalyst surface, leading to lower reaction rates [7,36,37]. In addition, the low adsorption of \( \text{CO}_2 \) on Co–Ni/Zn–S15 may affect \( \text{CO}_2 \) reforming of the methane reaction, leading to different side reactions owing to the unbalanced availability of \( \text{CH}_4 \) and \( \text{CO}_2 \) on the catalyst surface, as presented in Figure 6. The lower \( \text{H}_2/\text{CO} \) ratio for Co–Ni/Zn–S15 and Co/S15 indicates lower catalyst selectivity, as displayed in Figure 6. However, the low activity of Co/S15 can be attributed to the Co oxidation state. The TPR data showed that reduction of Co in Co/S15 started after 800 °C, whereas the employed reduction temperature was 500 °C.

![Figure 6](image_url)  
Figure 6. The molar \( \text{H}_2/\text{CO} \) ratio of the product stream.

To provide extra details about the characteristics of the fresh S15 and loaded fresh Ni/S15 catalysts, TEM images were acquired, as displayed in Figure 7. It is clear that S15 had a well-ordered mesoporous
structure of S15 supports (long-parallel channels in hexagonal array), as shown in Figure 7a,b. Higher magnification showed that the metal catalyst nanoparticles were homogeneously distributed on S15 with a fine particle size of around 6–10 nm, as shown in Figure 7b. After using the catalyst, the metal nanoparticles maintained their particle size (6–10 nm) with the appearance of larger carbon nanoparticles (20 nm), as shown in Figure 7c,d.

Figure 6. The molar H$_2$/CO ratio of the product stream. Thus, it is postulated that the side reaction pathways led to the same reaction products, since no other reaction products have been detected. CeO$_2$ addition should confer strong basic sites, leading to enhanced CO$_2$ adsorption and improved carbon gasification. ZnO supported over S15 has shown remarkable catalytic activity in the cyclic addition of CO$_2$ to hydrocarbons [37]. Thus, it is expected that Zn-doping should support carbon/hydrocarbon deposition.

To investigate the amount of carbon formed over each catalyst, the deposited carbon was subjected to a temperature-programmed oxidation (TPO) test, using air, in TGA. The weight loss against the temperature is displayed in Figure 8 for the Co–Ni/S15 and Co/S15 catalysts, and an analogous trend was seen for the other catalysts. When the temperature was raised to 1000 °C, almost no weight loss was detected for the catalysts under study. The small weight changes illustrated in Figure 8 are attributed to noise in the TGA instrument. Figure 8 shows that no carbon was deposited over the catalyst samples. Carbon deposition is considered to be the main cause for catalyst deactivation. As shown in Figures 4–6, all catalysts exhibited stable performance throughout the 8 h test. The stable performance is assigned to the high catalytic surface area, ensuring better catalyst distribution and a lower thermal aging rate. In addition, the detection of almost no carbon deposition indicates that carbon fouling does not influence the catalyst performance. Figure 8 indicates that the prepared catalysts show excellent resistance to carbon deposition and a higher selectivity for CO$_2$ reforming of methane. Thus, such catalysts, especially Ni/S15, are potentially applicable in the commercial CO$_2$ reforming of methane.
Several catalysts were prepared using S15 as a support, including Ni, Co, and Ni–Co. The support was also modified by doping S15 with Ce or Zn for Co–Ni bimetallic catalysts. A metallic catalyst loading of 5 wt % was used for all experiments. The catalysts were activated at 500 °C using a mixture of H2 and He. The prepared catalysts were tested for CO2 reforming of methane under atmospheric pressure at 800 °C. Different characterization methods were used to investigate the textural and chemical properties of all categories of catalysts.

Over 8 h of reaction time, Ni/S15 demonstrated the best activity and stability, where the observed conversion was 90% for CH4 and CO2. Co–Ni/S15 and Co–Ni/Ce–S15 exhibited reasonable activity and stability. Regarding the H2/CO ratio in the product stream, Ni/S15 exhibited the highest selectivity among all catalysts. Promoting/doping Ni/S15 had a remarkable effect on the catalyst activity. Co/S15 and Co–Ni/Zn–S15 exhibited low activity and selectivity. The addition of Zn/Ce oxides had a remarkably negative influence on the reduction properties and catalytic performance of the catalysts. All catalysts showed a high surface area, which is attributed to the high surface area of S15 support. The NH3-TPD profiles indicated that doping S15 with Ce/Zn oxides increased the catalyst acidic sites. Ni/S15 exhibits excellent potential for the commercial CO2 reforming of methane.

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