Yttria Modified ZrO₂ Supported Ni Catalysts for CO₂ Reforming of Methane: The Role of Ce Promoter

Anis H. Fakeeha, Ahmed S. Al Fatesh,* Ahmed A. Ibrahim, Abdulrahman N. Kurdi, and Ahmed E. Abasaeed*

ABSTRACT: Yttria modified zirconia (YZ) supported on 5 wt % of Ni-based catalysts promoted with ceria (1−3 wt %) were prepared by the impregnation process to investigate their performance for dry reforming of methane. The reforming reactions, conducted at 700 °C and at atmospheric pressure using a CO₂/CH₄/N₂ fixed feed ratio of 3/3/1, with a total flow rate of 70 mL/min, revealed that the ceria-promoted catalysts (xCe−Ni−YZ; x = 1−3 wt %) enhanced the CH₄ and CO₂ conversions as compared to the reference catalyst (Ni−YZ). A CO₂ conversion of 85% was exhibited by the 3Ce−Ni−YZ catalyst. Despite increased conversions, xCe−Ni−YZ catalysts showed more amounts of carbon deposition as evidenced by the values of TGA, and hence were found to be less stable as compared to the reference Ni−YZ catalyst. The used and fresh catalysts were characterized by BET, H₂-TPR, XRD, TEM, Raman, TPD, and TGA. TEM images displayed nanoparticle sizes of Ni in the fresh catalysts, while carbon filaments were formed on the spent catalysts. The CO₂-TPD, H₂-TPR, and BET results revealed the existence of only weak and moderate basic sites, the increase of total hydrogen consumption, and the surface area values with the addition of the Ce promoter, respectively. The TGA analysis showed that the Ce promoter increased the carbon deposition, while the Raman results indicated the dominance of crystallinity due to the graphitized carbon.

1. INTRODUCTION

Researchers have recently focused on the conversion of cheaper raw materials including methane and carbon dioxide into syngas by a reaction commonly known as methane reforming via CO₂ or dry reforming of methane (DRM).¹,² Mitigating greenhouse gases responsible for global warming and generating sustainable hydrogen through purified biogas are the main benefits that attracted the scientific community to DRM.³,⁴ Considering the balance between catalytic performance, availability, and price, Ni-based catalysts are reported to have the potential to compete favorably against noble metals catalysts.⁵ Nonetheless, the existence of side reactions such as carbon monoxide disproportionation and methane decomposition brings a challenge that relates to deactivation of Ni-based catalysts because of coke deposits.⁶ Hence, catalyst performance is mainly evaluated not only by the conversion of CH₄ and CO₂ but also by the tendency of the catalyst to minimize carbon deposition. Vasiliades et al. investigated the CO₂ reforming of methane over Ni and Pt and their bimetallic alloys supported on CeₓPr₀.5ZrₓO₂−δ.⁷ The authors quantified the origin of carbon. It was found that the supported bimetallic Ni−Pt catalyst offered overall a superb performance and stability after 50 h in DRM at 750 °C. Charisiou et al. addressed the carbon formation in the reforming of biogas.⁸ The calculation of catalytic stability upon unpromoted Ni/Al₂O₃, Ni/ZrO₂, and Ni/SiO₂ catalysts was performed using different reaction temperatures in terms of particle sintering and carbon formation. The results exhibited that the development and type of carbonaceous formed on catalytic surfaces were determined by the relationship aspects of the acidity/basicity, metal support interaction, active phase particle
size, and O2− lability. In a different investigation, Charisiou et al. examined Ni/Al2O3 and Ni/La2O3−Al2O3 catalysts for the biogas reforming reaction using CH4/CO2. The study of stability tests at various reaction temperatures revealed the formation of graphitized nanotubes and amorphous carbon on all spent catalysts. Doping Al2O3 with La2O3 stabilizes the catalyst.

The improvement of catalytic performance can be achieved by employing various strategies including catalyst design, for instance, using singular synthetic methods, adding promoters, and/or selecting suitable oxide support. Berdilo et al. studied the effect of CaO on ZrO2 support for the DRM performance of Ni-based catalysts. Based on catalyst characterizations, they revealed that the electrical features of the support and the creation of the tetragonal phases of CaO−ZrO2 solid solutions were the main factors affecting catalytic activity. Taherian et al. prepared via one-pot method, yttria promoted Ni catalyst supported on MgO-modified MCM-41 and tested for CO2 reforming of methane. Their results displayed that the ordered mesoporous structure of the support stayed even after the combination of the metallic ions. Yttria improved catalyst reducibility, while the MgO weakened the acidity of the support and increased the interactions of the support and the metal. Petuning and Korovin investigated the stabilization of the zirconia powder in a high-temperature phase state. Y2O3 (7 wt% ) was used to increase the stability of this state at ambient temperature. In a previous investigation, Yan et al. reported that the addition of ZrO2 containing 3% mole fraction of Y2O3 into an Al2O3 matrix of ceramic improved the thermal shock resistance and mechanical properties. In the fuel cells for power generations, it is improved the thermal shock resistance and mechanical properties and O2− adequate medium. Furthermore, ceria reveals the features of discharging and storing O2. Consequently, the reduction of Ce4+ − Ce3+ causes the creation of O2 vacancies. The discharge of O2 takes place in an O2-insufficient medium, while reoxidation happens in an O2-adequate medium.

The addition of Ce as a promoter to a Pt/ZrO2 catalyst for DRM was evaluated at different feed compositions and reaction temperatures. The effect of the synthesis method i.e., impregnation approach and the extent of the Ce promoter on the catalyst activity and stability showed that co-impregnating 1% cerium to the Pt/ZrO2 catalyst displayed the optimum catalytic stability and activity. The strong interaction between Ce and Pt phases was established to be mainly responsible for the high activity performance. In the automotive catalysts, adding the CeO2 promoter permits the catalyst to work over an extensive range of air/fuel fractions, specifically, CeO2 can offer O2 to oxidize HCs and CO. Also, CeO2 is identified to improve the conversions of NO and CO, support water gas shift at lower temperature, stabilize the dispersion of active metal, and decrease the sintering of supports induced by the heat.

Markaryan et al. studied the characterization of redox features and the phase structure of Y2O3−CeO2−ZrO2 and CeO2−ZrO2 solid solutions via electron paramagnetic resonance (EPR), X-ray diffraction (XRD), and temperature-programmed reduction (TPR) methods. Goula et al. elaborated the catalytic efficiency of Ni dispersed on ZrO2, La2O3−ZrO2, and CeO2−ZrO2 supports for the dry reforming of methane in the temperature range of 500–800 °C. Ni supported on La + Zr and Ce + Zr displayed improved basicity and oxygen ion lability, which led to excellent catalytic efficiency and stability. The spent catalysts of Ni−La + Zr and Ni−Zr generated the carbon deposit of filamentous tube, while N/Ce + Zr produced carbon tubes.

It has been found that doping of 10 mol % of Y2O3 stabilizes a cubic structure and helps the reduction of the catalyst. The development of O2− anion radicals on the surface of Y2O3−CeO2−ZrO2 and CeO2−ZrO2 was considered. Higher activity of O2− in the reoxidation of the catalysts and toward CO was noticed for yttria doped CeO2−ZrO2.

In this contribution, we evaluate the effect of Ce promoter over Ni-based catalysts supported on zirconia modified with yttria in the catalytic reforming of CH4 with CO2. We demonstrate that the Ce addition to the supported Ni catalysts improves the catalytic performance through enhanced reducibility of promoted catalysts. These findings further correlate with the characterization results before and after the reaction.

Table 1. Physicochemical Properties of Ce Promoted Ni−YZ Catalysts

| Catalysts | BET (m²/g) | Pore Volume (cm³/g) | Pore Size (nm) | Monolayer Capacity (cm³/g) | Overall H2 Consumption (μmol/g) | DF (%) |
|-----------|------------|---------------------|---------------|---------------------------|-------------------------------|-------|
| Ni−YZ     | 5.8        | 0.027               | 21.5          | 1.33                      | 1200                          | 4.93  |
| 1Ce−Ni−YZ | 6.9        | 0.042               | 27.0          | 1.59                      | 1324                          | 8.16  |
| 2Ce−Ni−YZ | 8.0        | 0.042               | 22.9          | 1.84                      | 1740                          | 7.32  |
| 3Ce−Ni−YZ | 9.0        | 0.050               | 23.9          | 2.07                      | 1885                          | 10.05 |

*From BET. From H2-TPR. DF (%) = \( \frac{\text{initial CH conversion} - \text{final CH conversion}}{\text{initial CH conversion}} \times 100 \)
2. RESULTS AND DISCUSSION

Table 1 exhibits the pore volume, BET, and monolayer capacity data. The results demonstrate that the BET increases slightly after the addition of the Ce promoter to Ni–YZ catalysts. It is moreover evident that the pore volume increased as the amount of Ce increased, which shows that the Ce promoter enhanced the porosity. The monolayer capacity data show that Ce addition promotes monolayer adsorption, which may influence the catalytic activity performance of these catalysts. It is well established that the increase in the specific surface area is associated with the increase in catalytic activity. The increase of the hydrogen consumption and the deactivation factor with the increase of the cerium loadings denotes that the promoter enhances the BET of the catalysts and the increase of carbon formation, respectively.

Figure 1 displays the XRD profiles of the synthesized catalysts. It is evident from the given XRD patterns that both the reference (Ni–YZ) and Ce-promoted Ni–YZ catalysts exhibit characteristic peaks of NiO (JCPDS: 01-073-1519) and tetragonal phase of YZ (JCPDS: 00-017-0923). It is worthy to notice that Ce-promoted catalysts caused a decline in the intensity of NiO peaks at 37.2 and 43°, which can be credited to better dispersion of NiO species over the support surface through the promotion of a monolayer as indicated by BET results (Table 1). Furthermore, no peaks of CeO₂ are detected, which can be ascribed to the small amount of Ce that is beyond the detection limits of XRD. Table 2 shows the crystalline size calculation of various catalysts using the Debye–Scherrer method. 2Ce–Ni–YZ gives the smallest size.

The reduction or activation temperature of the metal oxide is an important parameter, which is computed via hydrogen-based H₂-TPR. Moreover, reduction profiles provide an insight into the metal support interaction, which also contributes to determining the catalytic performance. Figure 2 presents the reduction profiles of reference (Ni–YZ) and Ce-promoted Ni–YZ catalysts. The reduction profiles can be deconvoluted into two peaks: peak 1 (red) and peak 2 (green). For the reference Ni–YZ catalyst, the first peak (350 °C) is assigned to the reduction of NiO species with a weaker interaction with...
the YZ support, and peak 2 (455 °C) is ascribed to the moderately reduced NiO species intermingling with the YZ support. It is noteworthy that Ce promotion affected the reducibility of NiO species and the first peak is shifted from 350 to 290 °C toward left, indicating that the addition of 1 wt % of Ce enhanced NiO reducibility or metal support interaction becomes weaker as compared with the reference catalyst (Ni−YZ). The increase in the amount of Ce to 2 and 3 wt % also demonstrates the enhanced NiO reducibility.

The catalytic activity results in terms of conversions of the feed and the product against the reaction time for Ce-promoted Ni−YZ catalysts are presented in Figures 3–5. From Figures 3 and 4, it is clear that Ce-promoted catalysts xCe−Ni−YZ (x = 1–3 wt %) outperformed the reference catalyst (Ni−YZ). For instance, 2Ce−Ni−YZ and 3Ce−Ni−YZ catalysts showed the initial CH₄ conversion (after 20 min) of 84.5 and ~82%, respectively, while the 1Ce−Ni−YZ catalyst displayed the initial CH₄ conversion (after 20 min) of ~73.5% as compared to ~71% for the Ni−YZ catalyst. It is noteworthy that final CH₄ conversions (after 450 min) were found to be the same (67.5%) for 1Ce−Ni−YZ and Ni−YZ. Similarly, the final CH₄ conversions for 2Ce−Ni−YZ and 3Ce−Ni−YZ were ~76%. Figure 4 shows that all the catalysts (xCe−Ni−YZ and Ni−YZ) that exhibited CH₄ conversions are less than the corresponding CO₂ conversions, confirming the existence of a reverse water gas shift reaction (CO₂ + H₂ ↔ CO + H₂O).
Promoter combination plays a helpful role in catalytic activity, crediting to their capabilities in upgrading active metal scattering and enhancing the dispersion of metal Ni and resisting sintering. Cerium is a versatile promoter due to its strong reducibility features. This may be attributed to its ability to store/release oxygen in O₂ excess/deficient situation, triggering the redox between Ce³⁺ and Ce⁴⁺ along with the generation of O₂ vacancies. O₂ vacancies are at one point of view on the effective active sites for the adsorption/activation of DRM reactants, and conversely, it is the origin of gasification/oxidation of formed carbon, producing CO. In the O₂ deficiency circumstance, Ce oxide as an O₂ donor may permit oxygen atoms to flow liberally on the catalyst surface on which formed carbon as an O₂ acceptor uses O₂, thus gasifying into species like CO and CO₂. In other words, ceria releases lattice oxygen while varying the oxidation state from Ce⁴⁺ to Ce³⁺, consequently creating oxygen vacancies.36

\[ \text{Ce}^{4+} - \text{O} - \text{Ce}^{4+} \rightarrow \text{Ce}^{3+} - \text{O} - \text{Ce}^{4+} + 1/2\text{O}_2 \]

where \( \text{O}_2 \) lattice O₂; O₂ = O₂ vacancy.

On the other hand, in O₂ plentiful situations, O₂ vacancies are refilled, as Ce could keep O₂ as lattice O₂ while changing Ce³⁺ to Ce⁴⁺.

\[ \text{Ce}^{3+} - \text{O} - \text{Ce}^{3+} + 1/2\text{O}_2 \rightarrow \text{Ce}^{4+} - \text{O} - \text{Ce}^{4+} \]

CeO₂ forms solid solutions with support elements (ZrO₂ and Y₂O₃) that produce abundant O₂ vacancies and strong metal support interaction to render thermal stability. However, as the time increases, owing to the thermal aging and high temperature operation, oxygen vacancies begin to diminish, finally triggering the high rate of carbon formation.37 Hence, the formed O₂ is not adequate to contest with the carbon accumulation and the rate of carbon growth surpasses the rate of its gasification. This explains the higher amounts of carbon deposits for the Ce-promoted catalysts as depicted by the TGA analysis.

The deactivation factor (DF) is the measure of catalyst stability. Table 1 indicates that despite enhanced conversions, Ce-promoted catalysts showed lower stability performance as compared to the reference catalyst. This can be described with H₂/CO ratio results displayed in Figure 5. The H₂/CO ratios less than unity mean more CO₃ at the outlet, which generates more CO. Since Ce-promoted catalysts exhibited better dispersion (Figure 1) and more reducibility (Figure 2) than a reference catalyst, they enhanced the catalytic activity but they also promoted side reactions such as methane decomposition (\( \text{CH}_4 \rightarrow \text{C} + 2\text{H}_2 \)) and CO disproportionation (2CO → C + CO₂) that caused more carbon deposition over Ce-promoted catalysts. Further, from the XRD diffractogram, the absence of peaks that could be assigned to pure ceria or zirconia could mean that a bonding has occurred between these two to form a CeO₂−ZrO₂ solid solution. This solid solution would hinder the oxygen storage/donation capability of CeO₂ that leads to the reverse shift in the redox behavior between Ce⁴⁺ and Ce³⁺, which is responsible for the creation of oxygen vacancy. This redox behavior is thought to be the driving force for the oxidation of carbon deposits. These findings further validate with the TGA of the catalysts post-reaction, as presented in Figure 6. The TGA-based quantitative measurement of carbon deposition in terms of weight loss shows that 3Ce−Ni−YZ had the highest weight loss (57%) while the reference catalyst (Ni-YZ) just had 18% weight loss, indicating a stable performance.

Raman is a tool that provides additional information about the graphitization degree and nature of the carbon deposited over the spent samples. Figure 7 shows the Raman spectra of the spent samples. In this figure, the spectra can be classified into two regions. The first region is between 1200 and 1700 cm⁻¹ and the second region lies between 2000 and 2800 cm⁻¹. In the area between 1200 and 1700 cm⁻¹, the occurrence of distinctive two peaks, D-band and G-band, is prevailing; the first positioned at 1340 cm⁻¹ is for D-band, which denotes imperfections due to a disorder double resonance technique attributable to the collapse of the normal wave vector selection.
rule\(^{38}\) and the second positioned at 1575 cm\(^{-1}\) is for G-band, which symbolizes graphite. It is the output of vibration of adjacent carbon atoms on the seamless hexagonal graphite. Meanwhile, the band at 2675 cm\(^{-1}\) is for 2D, which was formed from the merges and overtones of the bands of the first region.\(^{38}\) The amount of crystallinity of the carbon made in the course of a reaction may be properly estimated from the comparative intensity measurements of the D and G bands (I\(_D\)/I\(_G\)). Lower ratios indicate the dominance of crystallinity due to the graphitized carbon. For the investigated catalysts here, the values of I\(_D\)/I\(_G\) were 0.63, 0.69, 0.53, and 0.79 for the Ni–YZ, 1Ce–Ni–YZ, 2Ce–Ni–YZ, and 3Ce–Ni–YZ, respectively. The crystallinity of the 2Ce–Ni–YZ catalyst is more pronounced than other catalysts, and its graphitization degree was obviously enhanced. These results elucidated the enhanced activity and the 2Ce–Ni–YZ catalyst stability in terms of time-on-stream (TOS).

2.1. CO\(_2\)-Temperature-Programmed Desorption (CO\(_2\)-TPD). To comprehend the basic profile of the catalyst surface, CO\(_2\)-TPD has been performed and displayed in Figure 8. The desorption peaks qualitatively classified the catalyst surface into four categories of basic regions.\(^{39}\) The peak below 100 °C specifies weak basic sites associated with surface hydroxyl, below 200 °C for medium strength basic sites associated with carbonates, the peak at 250–350 °C for strong basic sites related to isolated O\(_2^-\) species and above 400 °C for super basic sites of carbonates.\(^{39}\) All catalysts have somewhat weak and medium strength basic sites. Remarkably, the 2Ce–Ni–YZ catalyst exhibited higher intensity of medium basic sites. This could be a strong revealing of the best activity among the rest of the catalysts.

Comprehensive examination of the morphology of catalysts was conducted by TEM. Typical TEM overviews of the fresh catalysts, 9A and 9C, and spent catalyst samples, 9B and 9D, obtained after 450 min of reaction time in the dry reforming of CH\(_4\) at 700 °C is presented in Figure 9. From qualitative perspective, carbon deposits on the nonpromoted Ni–YZ and promoted 2Ce–Ni–YZ is prevalently carbon tubes. The TEM image of the fresh Ni–YZ catalyst is shown in Figure 9A. It is obvious that the TEM image displays that the Ni is homogeneously scattered over the surface of the support. The particle size distribution as shown in Figure 10A, is between 2 and 9 nm with an average value of 4.67 nm. On the contrary, for its used sample as shown in Figure 9B, the Ni particles are not visible. Its particle size distribution as depicted in Figure 10B lies between 2 and 20 nm, with a mean value of 5.30 nm. Large amounts of coke are formed mostly in the form

![Graphene](image-url)
of carbon tubes. Figure 9 C presents the TEM image of the freshly promoted 2Ce−Ni−YZ catalyst. The Ni particles are found to be homogeneously deposited on the support surface, and the particle size distribution as depicted in Figure 10C ranges between 2 and 16 nm, with an average value of 5.00 nm. For the used 2Ce−Ni−YZ catalyst in Figure 9D, the Ni particle continues to be visible on the support, which demonstrates that this catalyst is relatively more resistant to leaching. The particle distribution for this spent catalyst is displayed in Figure 10D. The distribution values scatter in the range of 2−18 nm with a mean value of 6.50 nm. Despite the analogous structure of carbon deposits on both promoted and nonpromoted catalysts, it is immediately obvious that Ce strongly favors the coking process of the Ni−YZ catalyst during DRM at 700 °C.

3. CONCLUSIONS

Yttria modified ZrO2 supported Ni-based catalysts promoted with 1−3 wt % of Ce were successfully synthesized via the impregnation method and tested for DRM. The activity and stability tests on the catalysts revealed that, despite the improved activity of Ce-promoted catalysts, these catalysts were found to be less stable than the reference catalyst (Ni−YZ). An optimum Ce loading of 2% was achieved. The TGA analysis showed that the addition of the Ce promoter enhanced the carbon formation. TEM images of the spent catalysts displayed carbon filaments. The CO2-TPD analysis pointed out the lack of strong basic sites. The TGA and the Raman analysis showed that the Ce promoter increased the carbon deposition, while the Raman indicated the dominance of crystallinity due to the graphitized carbon. Besides the changes in the preparation and operating conditions, the combination of Ce and Ni in the form of bimetallic catalysts is suggested using the same support. The replacement of Ce with other elements that do not favor the formation of carbon such as Ca and Mg are advised. We also recommend the addition of pure oxygen in the feed so that partial and dry reforming of methane occurs simultaneously.

4. EXPERIMENTAL SECTION

4.1. Catalyst Preparation. The wet impregnation technique was implemented for the formation of the catalysts. The mixed supports of zirconium oxide and 13% Y2O3 along with the Ni acquired from the nickel nitrates [Ni(NO3)2·6H2O; 99.7% pureness] formed the desired ingredients. Distilled water was used to dissolve the ingredients. A 5 wt % Ni was fixed in the catalyst preparation. The solution temperature was raised to 90 °C. The mixing of the solution was kept for 3 h. After that, the drying and the calcination of the samples were performed at 125 °C for 12 h and at 600 °C for 3 h, respectively. Promoted cerium (1, 2, and 3 wt %) catalysts were prepared by co-impregnating Ce(NO3)3·6H2O and nickel with the support using the identical way stated earlier. For simplicity, Ce-promoted Ni supported on modified zirconium oxide by 13% Y2O3 catalysts will be designated as xCe−Ni−YZ (where x symbolizes the % of Ce in the catalyst).

4.2. Catalyst Characterization. The catalysts were characterized by various experimental skills. The specific surface area of catalysts was computed via nitrogen (N2) physisorption at −197 °C. A Micromeritics Tristar II 3020 unit was used to obtain the surface area via standard Brunauer−Emmett−Teller (BET). X-ray diffraction of Rigaku (Miniflex), employing the radiations of Cu Kα, was used to examine the configuration of the produced catalysts. Diffraction peaks documented in a 2θ range between 11 and 81° were employed to classify the phases of the catalysts. Carbon deposition over
the surface of spent catalysts was quantified by means of thermogravimetric analysis (TGA) in atmospheric air via an EXSTAR SII TG/DTA 7300 analyzer. For estimating catalyst reducibility, the H2-TPR measurements were conducted on Micromeritics Auto Chem II 2920 apparatus. Raman spectroscopy provided the graphitization degree and the type of carbon deposited over the used catalysts. A laser Raman spectrometer (JASCO, Japan) was employed to record the Raman spectra of the spent catalysts. An excitation beam with a 532 nm wavelength was used.

The structure of the used samples was seized using a transmission electron microscope “120 kV JEOL JEM-2100F”. Transmission electron microscopy (TEM) micrographs were documented at 120 kV.

4.3. Catalytic Reaction. The DRM reactions were accomplished using a stainless steel fixed reactor (9.1 mm diameter and 300 mm long) operated at 1 atm. The reactor was from PID Eng. & Tech Microactivity Reference Company. A 0.1 g of the catalyst was activated by a H2 flow of 1200 mL/h for 1 h at 700 °C. Then, N2 treatment of the bed for 15 min was followed to eliminate the physisorbed H2. In a typical test, the proportion CO2/CH4/N2 was set to 3/3/1 at 4.2 L/h, generating 42 L (h•gcat)−1 of gas hourly space velocity. A conductivity detector “GC-2014 SHIMADZU” determined the feed and output gas compositions. Afterward, N2 gas was used to cool the reactor. Then, the characterization of the catalysts was analyzed. Finally, the reproducibility was executed by taking the mean value of three runs. The expressions for CO2 and CH4 conversions and the hydrogen to carbon monoxide ratio are given as:

\[
\%\text{CH}_4 \text{ conversion} = \frac{\text{CH}_4 \text{ in} - \text{CH}_4 \text{ out}}{\text{CH}_4 \text{ in}} \times 100
\]

\[
\%\text{CO}_2 \text{ conversion} = \frac{\text{CO}_2 \text{ in} - \text{CO}_2 \text{ out}}{\text{CO}_2 \text{ in}} \times 100
\]

\[
\frac{\text{H}_2}{\text{CO}} = \frac{\text{moles of H}_2 \text{ produced}}{\text{moles of CO produced}}
\]

■ AUTHOR INFORMATION

Corresponding Authors

Ahmed S. Al Fatesh — Chemical Engineering Department, College of Engineering, King Saud University, Riyadh 11421, Saudi Arabia; orcid.org/0000-0002-5521-5741; Email: aalfatesh@ksu.edu.sa

Ahmed E. Abasaed — Chemical Engineering Department, College of Engineering, King Saud University, Riyadh 11421, Saudi Arabia; Email: abasaed@ksu.edu.sa

Authors

Anis H. Fakecha — Chemical Engineering Department, College of Engineering, King Saud University, Riyadh 11421, Saudi Arabia; King Abdullah City for Atomic & Renewable Energy, Energy Research & Innovation Center (ERIC) in Riyadh, Riyadh 11451, Saudi Arabia

Ahmed A. Ibrahim — Chemical Engineering Department, College of Engineering, King Saud University, Riyadh 11421, Saudi Arabia

Abdulrahman N. Kurdi — Chemical Engineering Department, College of Engineering, King Saud University, Riyadh 11421, Saudi Arabia; King Abdullah City for Atomic & Renewable Energy, Energy Research & Innovation Center (ERIC) in Riyadh, Riyadh 11451, Saudi Arabia

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors extend their appreciation to the National Plan for Science, Technology and Innovation (MAARIFAH), King Abdulaziz City for Science and Technology, Kingdom of Saudi Arabia, award no. (13-PET1056-02).

■ REFERENCES

(1) Bradford, M. C. J.; Vannice, M. A. CO2 reforming of CH4. Catal. Rev. 1999, 41, 1–42.

(2) Ross, J. R.; Van Keulen, A. N. J.; Hegarty, M. E. S.; Seshan, K. The catalytic conversion of natural gas to useful products. Catal. Today 1996, 30, 193–199.

(3) Guerra, C.; Lanzini, A.; Leone, P.; Santarelli, M.; Beretta, D. Experimental study of dry reforming of biogas in a tubular anode-supported solid oxide fuel cell. Int. J. Hydrogen Energy 2013, 38, 10559–10566.

(4) Khodee, W.; Wongsakulphasatch, S.; Kiatkittipong, W.; Powell, J.; Laosirisopanaj, N.; Bumroongkulasawat, P.; et al. Investigation of Biogas Decomposition Process for Fuel Cell Applications (PEMFC and SOFC): Thermodynamic Approach. J. Chem. Eng. Jpn. 2016, 49, 728–733.

(5) Rostrup-Nielsen, J. R.; Hansen, J. H. B. CO2-reforming of methane over transition metals. J. Catal. 1993, 144, 38–49.

(6) Forzatti, P.; Lietti, L. Catalytic deactivation. Catal. Today 1999, 52, 165–181.

(7) Vasilades, M. A.; Damaskinos, C. M.; Kyprianou, K. J.; Kollia, M.; Efthathiou, A. M. The effect of Pt on the carbon pathways in the dry reforming of methane over Ni-Pt/Ce0.8Pr0.2O2 catalyst. Catal. Today 2020, 355, 788–803.

(8) Charisiou, N. D.; Douvatrides, S. L.; Siakavelas, G. I.; Tsoumis, L.; Sebastian, V.; Stoilovan, V.; et al. The relationship between reaction temperature and carbon deposition on nickel catalysts based on Al2O3 as support. Catalysts 2019, 9, 676.

(9) Charisiou, N. D.; Siakavelas, G.; Tsoumis, L.; Sebastian, V.; Monzon, A.; Baker, M. A.; et al. An in depth investigation of deactivation through carbon formation during the biogas dry reforming reaction for Ni-supported on modified with CeO2 and La2O3 zirconia catalysts. Int. J. Hydrogen Energy 2018, 43, 18955–18976.

(10) García-Díezquez, M.; Pieta, I. S.; Herrera, M. C.; Larrubia, M. A.; Alemany, L. J. Improved Pt-Ni nanocatalysts for dry reforming of methane. Appl. Catal., A 2010, 377, 191–199.

(11) Ribeiro, N. F. P.; Neto, R. C. R.; Moya, S. F.; Souza, M. M. V.; Schmal, M. Synthesis of NiAl2O4 with high surface area as precursor of Ni nanoparticles for hydrogen production. Int. J. Hydrogen Energy 2010, 35, 11725–11732.

(12) Chen, H.-W.; Wang, C.-Y.; Yu, C.-H.; Tseng, L.-T.; Liao, P.-H. Carbon dioxide reforming of methane reaction catalyzed by stable nickel copper catalysts. Catal. Today 2004, 173–180.

(13) Jeong, D.-W.; Jang, W.-J.; Shim, J.-O.; Roh, H.-S.; Son, I. H.; Lee, S. J. The effect of preparation method on the catalytic performance over superior MgO-promoted Ni-Ce0.8Pr0.2O2 catalyst for CO2 reforming of CH4. Int. J. Hydrogen Energy 2013, 38, 13649–13654.

(14) Damyanova, S.; Pawelec, B.; Aristihtrova, K.; Fierro, J. L. G. Ni-based catalysts for reforming of methane with CO2. Int. J. Hydrogen Energy 2012, 37, 15966–15975.
Effect of adding CaO to ZrO2 support on nickel catalyst activity in dry reforming of methane. Appl. Catal. A 2009, 358, 215−223.
(16) Taherian, Z.; Khataee, A.; Orooji, Y. Facile synthesis of yttria-promoted nickel catalysts supported on MgO-MCM-41 for syngas production from greenhouse gases. Renewable Sustainable Energy Rev. 2020, 134, 110130.
(17) Petrunin, V. F.; Korovin, S. A. Preparation of nanocrystalline powders of ZrO2 stabilized by Y2O3 doped for ceramics. Phys. Procedia 2015, 544−547.
(18) Yan, M.; Wei, W.; Zuoren, N. Influence of pH on Morphology and Formation Mechanism of CeO2 Nanocrystalline. J. Rare Earths 2007, 25, 53−57.
(19) Abdalla, A. M.; Hossain, S.; Azad, A. T.; Petra, P. M. I.; Begum, F.; Eriksson, S. G.; Azad, A. K. Nanomaterials for solid oxide fuel cells: A review. Renewable Sustainable Energy Rev. 2018, 82, 353−368.
(20) Asencios, Y. J. O.; Rodella, C. B.; Assaf, E. M. Oxidative reforming of model biogas over NiO-Y2O3-ZrO2 catalysts. Appl. Catal. B 2013, 132-133, 1−12.
(21) Charisiou, N. D.; Siakavelas, G.; Tzounis, L.; Dou, B.; Sebastian, V.; Hinder, S. J.; et al. Ni/Y2O3−ZrO2 catalyst for hydrogen production through the glycerol steam reforming reaction. Int. J. Hydrogen Energy 2020, 45, 10442−10460.
(22) Yao, L.; Galvez, M. E.; Hu, C.; Da Costa, P. Synthesis Gas Production via Dry Reforming of Methane over Manganese Promoted Nickel/Cerium−Zirconium Oxide Catalyst. Ind. Eng. Chem. Res. 2018, 57, 16645.
(23) Xu, G.; Shi, K.; Gao, Y.; Xu, H.; Wei, Y. Studies of reforming natural gas with carbon dioxide to produce synthesis gas. J. Mol. Catal. A: Chem. 1999, 147, 47−54.
(24) Özkar-Aydınoğlu, S.; Özensoy, E.; Aksoyul, A. E. The effect of impregnation strategy on methane dry reforming activity of Ce promoted Pt/ZrO2. Int. J. Hydrogen Energy 2009, 34, 9711−9722.
(25) Su, E. C.; Montreuil, C. N.; Rothschild, W. G. Oxygen storage capacity of monolith three-way catalysts. Appl. Catal. 1985, 17, 75−86.
(26) Diwell, A. F.; Rajaram, R. R.; Shaw, H. A.; Truex, T. J. The role of ceria in three-way catalysts. Stud. Surf. Sci. Catal. 1991, 71, 139−152.
(27) Harrison, B.; Diwell, A. F.; Hallett, C. Promoting Platinum Metals by Ceria - metal-support interactions in autocatalysts. Platinum Met. Rev. 1988, 32, 73−83.
(28) Li, Y. X.; Klabunde, K. J.; Davis, B. H. Alloy formation in supported Pt Sn catalysts: Mossbauer studies. J. Catal. 1991, 128, 1−12.
(29) Markaryan, G. L.; Ikrannikova, L. N.; Muravieva, G. P.; Turakulova, A. O.; Kostyuk, B. G.; Lunina, E. V.; Lunin, V. V.; Zhilinskaya, E.; Aboukais, A. Red-ox properties and phase composition of CeO2-ZrO2 and Y2O3-CeO2-ZrO2 solid solutions. Colloids Surf., A 1999, 151, 435−447.
(30) Goula, M. A.; Charisiou, N. D.; Siakavelas, G.; Tzounis, L.; Tsiaousis, I.; Panagiotopoulou, P.; Goula, G.; Yentekakis, I. V. Syngas production via the biogas dry reforming reaction over Ni supported on zirconia modified with CeO2 or La2O3 catalysts. Int. J. Hydrogen Energy 2017, 42, 13724−13740.
(31) Naem, M. A.; Al-Fatesh, A. S.; Abasaeeed, A. E.; Fakeeha, A. H. Activities of Ni-based nano catalysts for CO2−CH4 reforming prepared by polyol process. Fuel Process. Technol. 2014, 122, 141−152.
(32) Al-Fatesh, A. S.; Arafat, Y.; Kasim, S. O.; Ibrahim, A. A.; Abasaeeed, A. E.; Fakeeha, A. H. In situ auto-gasification of coke deposits over a novel Ni–Ce/W-Zr catalyst by sequential generation of oxygen vacancies for remarkably stable syngas production via CO2-reforming of methane. Appl. Catal. B 2021, 280, 119445.
(33) Muñoz, M. A.; Calvino, J. J.; Rodríguez-Izquierdo, J. M.; Blanco, G.; Arias, D. C.; Pérez-Omí, J. A.; et al. Highly stable ceria-zirconia-yttria supported Ni catalysts for syngas production by CO2 reforming of methane. Appl. Surf. Sci. 2017, 426, 864−873.
(34) Jang, W. J.; Jeong, D. W.; Shim, J. O.; Kim, H. M.; Roh, H. S.; Son, I. H.; et al. Combined steam and carbon dioxide reforming of methane and side reactions: Thermodynamic equilibrium analysis and experimental application. Appl. Energy 2016, 173, 80−91.
(35) Gury, H. R.; Dama, S.; Samuel, V.; Chilakuri, S. Influence of preparation method on activity and stability of Ni catalysts supported on Gd doped ceria in dry reforming of methane. J. CO2 Util. 2017, 20, 357−367.
(36) Kang, S.; Sub Kwak, B.; Kang, M. Synthesis of Ni-alkaline earth metals particles encapsulated by porous SiO2 (NiMO@SiO2) and their catalytic performances on ethanol steam reforming. Ceram. Int. 2014, 40, 14197−14206.