Promotional effect of magnesium oxide for a stable nickel-based catalyst in dry reforming of methane

Ahmed S. Al-Fatesh1*, Rawesh Kumar2, Anis H. Fakeeha3, Samsudeen O. Kasim1, Jyoti Khatri2, Ahmed A. Ibrahim1, Rasheed Arasheed1, Muhamad Alabdulsalam3, Mahmud S. Lanre1, Ahmed I. Osman4*; Ahmed E. Abasaeed1 & Abdulaziz Bagabas3

The generation of synthesis gas (hydrogen and carbon monoxide mixture) from two global warming gases of carbon dioxide and methane via dry reforming is environmentally crucial and for the chemical industry as well. Herein, magnesium-promoted NiO supported on mesoporous zirconia, 5Ni/xMg–ZrO2 (x = 0, 3, 5, 7 wt%) were prepared by wet impregnation method and then were tested for syngas production via dry reforming of methane. The reaction temperature at 800 °C was found more catalytically active than that at 700 °C due to the endothermic feature of reaction which promotes efficient CH4 catalytic decomposition over Ni and Ni–Zr interface as confirmed by CH4–TSPR experiment. NiO–MgO solid solution interacted with ZrO2 support was found crucial and the reason for high CH4 and CO2 conversions. The highest catalyst stability of the 5Ni/3Mg–ZrO2 catalyst was explained by the ability of CO2 to partially oxidize the carbon deposit over the surface of the catalyst. A mole ratio of hydrogen to carbon monoxide near unity (H2/CO ~ 1) was obtained over 5Ni/ZrO2 and 5Ni/5Mg–ZrO2, implying the important role of basic sites. Our approach opens doors for designing cheap and stable dry reforming catalysts from two potent greenhouse gases which could be of great interest for many industrial applications, including syngas production and other value-added chemicals.

The production of syngas (a mixture of H2 and CO) through dry reforming of methane is an excellent strategy to reduce the global warming effects of carbon dioxide (CO2) and methane (CH4). Noble metals such as palladium (Pd), platinum (Pt), and ruthenium (Ru) have been used for this purpose, but costly precursors and instability of catalyst, at high reaction temperature around 800 °C, have limited their application1. On the other hand, cost-effective nickel (Ni) metal, supported on an appropriate supports such as alumina2, mesoporous silicates3–7, and zirconia8–10, has been found to withstand at this reaction temperature (800 °C). In this context, many researchers have followed the surface modification methodology to optimise the catalyst performance because Ni-based catalyst is also prone to deactivation. The first series of modifications were carried out over alumina supports with K11,12, Mg, Ca, Ba, Sr13–16, Y17, La18, Ce19, K-Ce20, Ti21, Zr22,23, Mo, W21, Mn24, Co & Cu25, Zn26, B27, Si28, and Sn14. Due to the extended pore network (from micro to meso) and easy pore tunable synthetic methodology of silicates, silica support is preferable over alumina support28. Therefore, the second series of modifications were carried out over mesoporous silicates supports with Li29, K30, Mg31,32, Ca30, Ba13, La14, Ce30,35,36, Zr37,38, Mn38, Co39,40, Cu41,42, Zn30, Al38 and Sn43. However, neither alumina nor silica supports can utilize their lattice oxygen during carbon deposit oxidation at the surface, but zirconia support does and is thus used as oxygen carrier materials. Zirconia support is characterized by its thermal stability, an expanded network, and the ability to utilize its mobile oxygen during the surface reaction45. The third series of modifications were carried out over

1Chemical Engineering Department, College of Engineering, King Saud University, P.O. Box 800, Riyadh 11421, Saudi Arabia. 2Sankalchand Patel University, Visnagar, Gujarat 384315, India. 3National Petrochemical Technology Center (NPTC), Materials Science Research Institute (MSRI), King Abdulaziz City for Science and Technology, P.O. Box 6086, Riyadh 11442, Saudi Arabia. 4School of Chemistry and Chemical Engineering, Queen’s University Belfast, Belfast BT9 5AG, Northern Ireland, UK. *Email: aalfatesh@ksu.edu.sa; aosmanahmed01@qub.ac.uk
zirconia supports with K\textsuperscript{46}, Mg\textsuperscript{47–50}, K-MgO\textsuperscript{51}, Ca\textsuperscript{52,53}, La\textsuperscript{54,55}, and Ce\textsuperscript{56–58}. A brief literature survey of promoter/modifiers that were utilized over Ni-doped different supports is given in Table 1. Use of strong solid base as CaO and MgO showed significant improvement and facilitated the catalytic performance with prompt adsorption of slightly acidic CO\textsubscript{2} during dry reforming reaction over Ni-based catalysts. CaO coprecipitated Ni supported ZrO\textsubscript{2} was well studied for different types of carbon species deposited over the catalyst surface during dry reforming of methane\textsuperscript{59}. MgO modified Ni system is known for outstanding coking tolerance\textsuperscript{60}. Chunwen Sun et al. showed that MgO modification might help to stabilize the lattice oxygen sites of NiO which effectively decrease the carbon deposition or graphitic layer formation\textsuperscript{61}. Garcia et al. prepared the Ni/MgO–ZrO\textsubscript{2}–MgO (MgO loading in the range of 1–5 wt\%) catalysts by co-precipitation method and found out that the CO\textsubscript{2} and CH\textsubscript{4} conversions were less than 35\%\textsuperscript{47}. Asencios and Assaf loaded Ni and Mg with different ratios on zirconia support by wet impregnation method and found out that catalyst with 20 wt\% Ni and 20 mol\% Mg has the best performance, where the activity was less than 80\% in the oxidative reforming of methane\textsuperscript{49}. Most of the research outputs in the literature used high loading of Ni or MgO (as high as 35 mol\%) for the dry reforming reaction as Montoya et al. via sol–gel method\textsuperscript{56} and Titus et al. via melt impregnation\textsuperscript{50}. Herein, we prepared four catalysts via incipient wetness impregnation method, where the support was mesoporous zirconia, nickel as the active catalyst, and magnesium oxide as a promoter. We varied the amount of magnesium oxide to find its optimum loading for the best catalytic performance. Furthermore, we optimised the performance by varying reaction temperature. Catalysts were characterized by TGA, N\textsubscript{2} physisorption, XRD, H\textsubscript{2}-TPR, and CO\textsubscript{2}-TPD. To understand the surface chemistry in optimizing the catalytic activity along with the stability of the modified catalyst, CO\textsubscript{2}-TPD, H\textsubscript{2}-TPD and O\textsubscript{2}-TPO of spent catalyst were also performed. A very fine-tuning, among catalytic activity and characterization results were performed; this will help to better understand the surface behaviour towards syngas production from dry reforming of methane.

Results and discussion
The catalytic activity of SnixMgZr catalysts (x = 0, 3, 5, 7) in terms of CH\textsubscript{4} conversion, CO\textsubscript{2} conversion, and H\textsubscript{2}/CO mole ratio at 700 °C are shown in Fig. 1(A–C) and at 800 °C are shown in Fig. 1(D–F). The TGA results of spent catalysts are shown in Fig. 1(G,H), respectively. It is worth noting that without magnesium oxide modification, catalyst SnNi/ZrO\textsubscript{2} shows lower catalytic activity than that of magnesium oxide modified catalyst in all cases. At the reaction temperature of 700 °C, SnNi/xMg–ZrO\textsubscript{2} catalysts showed approximately 50–60\% CH\textsubscript{4} conversion and 65–75\% CO\textsubscript{2} conversion which were comparable to those in the recent publications\textsuperscript{50,47,49,54,62,63}. The TGA results of these spent catalysts also showed carbon deposition. Interestingly, when the reaction temperature was set at 800 °C, it gave a stable performance with constant high conversion up to 500 min in the time-on-stream test (TOS) and no noticeable carbon deposition. Over SnNi/3Mg–ZrO\textsubscript{2} catalyst, 85\% CH\textsubscript{4} conversion, 92\% CO\textsubscript{2} conversion and 0.94 H\textsubscript{2}/CO ratios were achieved constantly up to 500 min in the TOS. On the target of H\textsubscript{2}/CO = 1, the performance of the SnNi/5Mg–ZrO\textsubscript{2} catalyst was found to be the best as it showed 82\% CH\textsubscript{4} conversion, 87\% CO\textsubscript{2} conversion. The SnNi/7Mg–ZrO\textsubscript{2} catalyst performance was a little bit lower than that of SnNi/5Mg–ZrO\textsubscript{2} (78\%)

| Table 1. A brief literature survey of promoter/modifier Ni-doped different supports. |
|---------------------------------|----------------|----------------|----------------|
| Active metal | Modified/ | Support: Al\textsubscript{2}O\textsubscript{3} | Support: SiO\textsubscript{2} | Support: ZrO\textsubscript{2} |
| Ni | Group I | Li | 29 |
| Ni | Group I | K | 11,31 |
| Ni | Group II | Mg | 13–16 |
| Ni | Group II | Ca | 13–16 |
| Ni | K | 36 |
| Ni | Sr | 13–16 |
| Ni | Ba | 13–16 |
| Ni | Y | 17 |
| Ni | La | 18 |
| Ni | Ce | 19,20 |
| Ni | Ti | 21 |
| Ni | Zr | 22,25 |
| Ni | Mo | 23 |
| Ni | W | 21 |
| Ni | Group VII | Mn | 24 |
| Ni | Group IX | Co | 25 |
| Ni | Group XI | Cu | 25 |
| Ni | Group XII | Zn | 26 |
| Ni | Group XIII | B | 27 |
| Ni | Al | – |
| Ni | Si | 21 |
| Ni | Sn | 14 |
| Ni | Sn | 14 |
CH$_4$ conversion, 86% CO$_2$ conversion and H$_2$/CO = 0.98). Whether to check the thermal decomposition of CH$_4$ at 800 °C, reaction without catalyst was carried out with substrate CH$_4$. It gave 3% CH$_4$ conversion with 1.8% H$_2$ yield in 3 h time on stream. Further again, a blank reaction was carried out with substrates CH$_4$ and CO$_2$ together at 800 °C. It resulted in 1.6% CH$_4$ conversion, 3.6% CO$_2$ conversion, H$_2$ yield 0.63%, CO yield 4.25% and H$_2$/CO = 0.14. As our catalytic systems are highly active towards DRM, so the thermal decomposition of CH$_4$ as an intermediate step in DRM could be neglected.

To understand the surface behaviour of the DRM reaction, we characterised the catalyst thoroughly and discussed the characterization results herein. The surface area analysis indicated that after the addition of MgO, type IV adsorption–desorption curve with H1 hysteresis loop (Figure S1) was built up. It indicates the narrow distribution of mesopores.

Figure 1. Catalytic activity profiles for methane dry reforming over various catalysts (A–F); (A) CH$_4$ conversion at 700 °C reaction temperature, (B) CO$_2$ conversion at 700 °C reaction temperature, (C) H$_2$/CO mole ratio at 700 °C reaction temperature, (D) CH$_4$ conversion at 800 °C reaction temperature, (E) CO$_2$ conversion at 800 °C reaction temperature, (F) H$_2$/CO mole ratio at 800 °C along with TGA curves of spent catalysts, (G) TGA results of spent catalyst carried out at 700 °C reaction temperature, (H) TGA results of spent catalysts carried out at 800 °C reaction temperature.
XRD patterns of 5NiₓMgZr catalysts (x = 0, 3, 5, 7) are shown in Fig. 2(A–D). The diffraction lines at 2θ = 24.2°, 28.34°, 31.45°, 34.2°, and 55.4° were attributed to the monoclinic zirconia (m-ZrO₂) whereas diffraction lines at 2θ = 30.48° and 50.24° were attributed to tetragonal zirconia (t-ZrO₂). Cubic nickel oxide showed diffraction lines at 2θ = 37.2°, 43.28° and 62.9° for (111), (200) and (220) crystallographic planes, respectively. After the addition of basic promoter 3 wt% MgO, the crystalline peak intensity of ZrO₂ remarkably increased as well as the selected plane of NiO (200) about 43.28° bragg angle also intensified and shifted to the lower angle 43.12°. It indicated the rapid growth of NiO-MgO solid solution after addition of MgO. Further addition of MgO did not show such a rapid rise of NiO-MgO solid solution.

The H2-TPR surface reduction profiles of fresh 5Ni/xMg–ZrO₂ catalysts are shown in Fig. 3A. 5Ni/ZrO₂ has one small reduction peak in the temperature range of 140–200 °C that attributed to the free NiO species, a shoulder reduction peak at the temperature range of 200–300 °C for “NiO weakly interacted with ZrO₂ support” and a strong peak at 300–450 °C for “NiO that interacted strongly with ZrO₂ support”. After the addition of 3.0 wt% MgO, these three peaks diminished and reduction peaks in the intermediate and high-temperature ranges appeared. The high reduction temperature for MgO modified samples could be correlated to the high inherent stability expected for NiO–MgO-solid solution with respect to pure NiO. From the XRD results, also after MgO modification, NiO–MgO-solid solution was found. The intermediate temperature reduction peak in the range of 450–700 °C could be attributed to “NiO–MgO-solid solution weakly interacted with ZrO₂ support” whereas high-temperature reduction peak in the range of 700–900 °C could be claimed to “NiO–MgO-solid solution strongly interacted with ZrO₂ support”. As MgO loading was increased from 3.0 wt% to 5.0 wt%, the TCD signal intensity of the intermediate temperature reduction peak was decreased and high-temperature reduction peak was increased. These observations indicated that a higher amount of “NiO-MgO-solid solution strongly interacted on ZrO₂” was present in 5Ni/5Mg–ZrO₂ than 5Ni/3Mg–ZrO₂, thus 5 wt% MgO was the optimum loading. At 7 wt% MgO loading, both types of high-temperature peaks were suppressed in comparison to those for 5Ni/5Mg-ZrO₂. The H₂-TPR surface reduction profile of spent 5Ni/3Mg-ZrO₂ is shown in Fig. 3B. It showed that TPR peaks in the intermediate and high-temperature regions had got suppressed. Also, it was noticeable
that a lower reduction temperature peak (0–400 °C) remained preserved as well as shifted to a lower temperature. The H₂-TPR surface reduction profile of spent 5Ni/5Mg–ZrO₂ indicated the suppression and shifting of high-temperature region peaks to intermediate temperature regions (Fig. S2). These observations indicated that NiO supported on ZrO₂ was less involved whereas “NiO-MgO-solid solution interacted with ZrO₂ support” are significantly involved in DRM. Apart from that, the elimination of carbon deposit by hydrogen gas during methane gasification reaction (C + 2H₂ → CH₄) over spent catalyst system was also possible.

The CO₂-TPD profiles of 5Ni/xMg–ZrO₂ are shown in Fig. 3C. Without magnesium oxide modification, the catalyst showed a sharp peak at lower temperature (weak basic sites) region and in intermediate temperature (medium basic sites) regions, but a broad peak in higher temperature regions (strong basic sites). This profile indicated a wide distribution of basic sites. However, after loading of 3.0 wt% MgO, only weak basic sites remained preserved; the rest disappeared. Surprisingly, basic modifier addition caused the disappearance of basicity. XRD of the same sample showed the appearance of NiO–MgO-solid solution as well as the rise of ZrO₂ crystallinity. This means that after the addition of basic 3.0 wt% MgO, basic MgO was engaged in the nurture of NiO–MgO solid solution and supported the crystallinity, thus it caused the disappearance of basicity. It caused the removal of intermediate strength as well as strong strength basic sites from the surface. Again, at 5 wt% MgO loading, peak reappeared in the intermediate temperature region whereas it broadened in high-temperature regions. As the TGA profile of the spent catalyst did not show markable carbon deposition, it is interesting to observe the basic profile of the spent catalyst.

The CO₂-TPD profile of fresh as well as spent 5Ni/3Mg–ZrO₂ & 5Ni/5Mg–ZrO₂ catalyst are shown in Fig. 3D and Figure S3 respectively. Figures 3D and S3 also include O₂-TPO and “CO₂-TPO followed by O₂-TPO” of spent 5Ni/3Mg–ZrO₂ and 5Ni/5Mg–ZrO₂ catalysts, respectively. It is obvious from the fresh and spent CO₂-TPD samples that there was a significant decrease in the intensity of basic sites after the reaction over the spent catalysts. However, unlike the fresh samples, the spent catalysts showed a small peak in CO₂-TPD. Again, a consumption (negative) peak in O₂-TPO of spent 5Ni/3Mg–ZrO₂ and spent 5Ni/5Mg–ZrO₂ catalyst samples were also seen at about the same temperature region. Interestingly, O₂-TPO (carried out after CO₂-TPD) of spent 5Ni/3Mg–ZrO₂ and spent 5Ni/5Mg–ZrO₂ catalysts had no such O₂ consumption peak. It can be explained that
O2 consumption peak in O2-TPO was due to oxidation of residual carbon by O2 into CO2. So, the small evolution peak in CO2-TPD profile also indicated the oxidation of residual carbon deposit by CO2. As the carbon deposit on the surface of the catalyst was already oxidized by CO2 during CO2-TPD profile so when O2-TPO was carried out after CO2-TPD, no evolution peak was found. This confirmed the oxidation of the carbon deposit by CO2 over the surface of the catalyst. Oxidation of carbon deposit by lattice oxygen of ZrO2 and thereafter simultaneous compensation of the oxygen vacant sites by CO2 (through losing one of its oxygen to the vacant site) might be a possible route of oxidation of carbon deposit by CO2.

To study the conditions and sites of CH4 decomposition, CH4-temperature programmed surface reaction (CH4-TPSR) experiment over ZrO2, 5Ni/ZrO2 and 5Ni/3Mg–ZrO2 were carried out (Fig. 4). It shows a decrease in the methane concentration with temperature over catalysts due to methane decomposition reaction on the surface. For ZrO2, a single prominent consumption peak at 870 °C temperature was noticed due to CH4 interaction at ZrO2 surface53. After the addition of Ni, apart from the high-temperature peak, a lower temperature CH4 consumption peak at about 350 °C and an intermediate temperature broad peak in the range of 400–800 °C were observed. Low temperature and intermediate temperature temperatures could be claimed to the catalytic decomposition of CH4 over Ni active sites as well as Ni–Zr interface53. MgO containing catalysts (i.e. 5Ni/3Mg–ZrO2) also showed the intense peak at high temperature (about 800 °C), attributed to the effect of the temperature. At higher reaction temperature (about 800 °C), an endothermic feature of DRM reaction promotes more efficient catalytic decomposition of CH4 over Ni and Ni–Zr interface and thereafter oxidation of deposit by CO2. So, at 800 °C, all catalysts showed high CH4 and CO2 conversion as well as nearly no carbon deposit over the surface of the catalysts. Yang et al.60 also claimed MgO modified Ni system as outstanding coking tolerance and Chunwen et al.61 explained the effective reduction of carbon deposit by MgO modified Ni system by stabilization of lattice oxygen sites of NiO by MgO.

5Ni/ZrO2 had free NiO species, “NiO species interacted with support” and a wide range of basicity. CO2 uptake at basic sites, catalytic decomposition of CH4 at Ni and Ni–Zr and oxidation of deposits by CO2 pivoted the way of high-performance dry reforming reaction. It showed a constant 76% CH4 conversion, constant 84% CO2 conversion and 0.99 H2/CO ratios for 130 min, then a ratio of 0.98 for 300 min and finally a ratio of 0.96 for 500 min.

After modifying the catalyst with 3.0 wt% MgO, NiO–MgO-solid solution was built up. With a wide range of NiO–MgO-solid solution interaction (weakly as well as strongly with support ZrO2), 5Ni/3 Mg–ZrO2 promoted the efficient catalytic decomposition of CH4 over Ni, Ni–Zr interface and thereafter oxidation of deposit by CO2. Thus, 5Ni/3Mg–ZrO2 showed high 85% CH4 conversion and 92% CO2 conversion with H2/CO ratio ~ 0.96. The CO2-TPD, as well as O2-TPO profile of spent catalysts, showed an extra peak in TPD and a negative (consuming) peak in TPO, respectively which both related to the oxidation of residual carbon deposits on the
surface of the catalyst. The CO₂-TPD along with the O₂-TPO results showed that CO₂ is capable of oxidizing carbon deposit over the surface of the catalyst. Removal of carbon deposits by hydrogen gas through methane gasification reaction (C + 2H₂ → CH₄) is also possible. It resulted in stable catalytic activity up to 500 min in the TOS test. Furthermore, modifying the catalyst with 5 wt%MgO in 5Ni/5Mg–ZrO₂, it showed more amount of “NiO–MgO solid solution strongly interacted with ZrO₂ support” as well as a wide variety of basic sites. That catalyst showed a constant conversion (82% CH₄ conversion and 89% CO₂ conversion) as well as H₂/CO ratio = 1 for 250 min in the TOS then slightly decreased to 0.99 for another 250 min, with overall 500 min TOS. Thus, it could be concluded that 5 wt%MgO loading is optimum loading for an active and stable catalyst for methane dry reforming reaction. Further increase in magnesium oxide loading to 7 wt%MgO caused a decrease in NiO–MgO-solid solution that interacted weakly or strongly with the ZrO₂ support and consequent the loss of strong basic sites. Thus, decreasing the CH₄ conversion to 79% as well as CO₂ conversion to 86% and H₂/CO ratio to 0.98 were noticed.

Conclusion
Magnesium promoted NiO supported mesoporous zirconia, 5Ni/xMg–ZrO₂ (x = 0, 3, 5, 7) were prepared and tested for the methane dry reforming reaction. Higher activity was found at 800 °C than that at 700 °C due to favourable endothermic feature of DRM reaction which promotes efficient CH₄ decomposition over Ni and Ni–Zr interface and successive oxidation of carbon deposits by CO₂. By modifying the catalyst (5Ni/ZrO₂) with MgO as a promoter, NiO–MgO-solid solution was formed. It was found that for high constant CH₄ and CO₂ conversions, NiO–MgO-solid solution played a significant role during the DRM. The 5Ni/3Mg–ZrO₂ catalyst showed a constant 85% CH₄ conversion and 92% CO₂ conversion up to 500 min on stream at H₂/CO mole ratio ~ 0.96. The highly constant performance of magnesium oxide modified catalysts was due to the ability of CO₂ to oxidize the carbon deposits during the DRM, thus maintaining the catalytic stability. However, with a further loading (> 5.0 wt%Mg) such as in 5Ni/5Mg–ZrO₂ which showed a higher amount of ”NiO–MgO-solid solution strongly interacted with ZrO₂ support” along with a wide variety of basic sites as well. Thus, it showed a constant 82% CH₄ conversion and 89% CO₂ conversion and H₂/CO mole ratio ~ 1. It is hoped that these findings could inspire finding more stable and less expensive synthesis gas production catalysts, including from two potent greenhouse gases emissions such as methane and carbon dioxide.

Experimental
Materials. Nickel nitrate hexahydrate [Ni(NO₃)₂.6H₂O, 98%, Alfa Aesar], magnesium acetate tetra-hydrate [Mg(O₂CCH₃)₂.4H₂O, 99.5–102.0%, Merck], mesoporous zirconia (meso-ZrO₂, 1/8” pellets, Alfa Aesar) were commercially available and were used without further purification. Ultrapure water was acquired from a Milli-Q water purification system (Millipore).

Catalyst preparation. A two-step procedure, based on incipient wetness impregnation as described elsewhere, was followed for synthesizing the desired catalysts. The first step was to dope the support with a metal oxide promoter, while the second step was to load nickel oxide over the promoted support. The detailed description of each synthesis step is given below.

Synthesis of mesoporous zirconia promoted with magnesia (MgO-meso-ZrO₂). The required amount of Mg(CH₃CO₂)₂.4H₂O for 3.0, 5.0, or 7.0 wt/wt% loading of MgO was mixed and pulverized with the required amount of meso-ZrO₂. To this resultant solid mixture, drops of ultrapure water were added until the
formation of a colourless paste, which was mechanically stirred until complete dryness at room temperature. The addition of water and drying processes were performed three times to ensure homogeneous distribution of Mg(CH₃CO₂)₂ within the matrix of meso-ZrO₂. The solid mixture was then grounded and calcined in a muffle furnace, at 600 °C for 3 h in the static air atmosphere. The resultant materials were designated as xMg–ZrO₂ catalysts where x is wt% of MgO (x = 0, 3, 5, 7).

Synthesis of mesoporous zirconia supported nickel oxide promoted with magnesia (NiO/ MgO-meso-ZrO₂). The required amount of Ni(NO₃)₂.6H₂O to obtain 5.0 wt/wt% of NiO loading was mixed and was crushed with the required amount of MgO-meso-ZrO₂ of the desired MgO wt/wt% loading, forming a green solid mixture. Drops of ultrapure water were then added to get a paste. By continuous mechanical stirring, the paste was dried at room temperature. The wetting and drying processes were repeated three times. Afterwards, calcination was performed at 600 °C for 3 h in static air atmosphere. Overall, 5 wt% NiO loaded catalyst sample is designated as 5Ni/xMg–ZrO₂ catalysts where x is wt% of MgO (x = 0, 3, 5, 7).

Catalyst characterization. The details of instrument specifications and procedures are described in the supporting information and described elsewhere²¹.

Catalyst test. DRM was carried out in a fixed-bed stainless steel tubular micro-reactor (ID = 9 mm) at atmospheric pressure. A load of 0.10 g catalyst was activated under 20 SCCM H₂ flow at 800 °C for 60 min. Then 20 sccm of N₂ was fed to the reactor for 20 min at 800 °C to remove adsorbed H₂. Afterwards, CH₄, CO₂, and N₂ were dosed at flow rates of 30, 30 and 5 sccm, respectively. A GC (GC-2014 Shimadzu) unit, equipped with a thermal conductivity detector and two columns, Porapak Q and Molecular Sieve 5A, was connected in series/bypass connections to have a complete analysis of the reaction products. The following equations were used to calculate the conversion of each reactant and the H₂/CO mole ratio, respectively²¹.

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

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

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

Received: 7 May 2020; Accepted: 4 August 2020
Published online: 17 August 2020

References
1. Osman, A. I. Catalytic hydrogen production from methane partial oxidation: mechanism and kinetic study. Chem. Eng. Technol. 43, 641–648. https://doi.org/10.1002/cet.201900339 (2020).
2. Zhou, L., Li, L., Nini, W., Jun, L. & Basset, J. M. Effect of NiAl₂O₄ formation on NiAl₂O₄ stability during dry reforming of methane. ChemCatChem 7, 2508–2516. https://doi.org/10.1002/cctc.201500379 (2015).
3. Wang, C. et al. The importance of inner cavity space within Ni@SiO₂ nanocapsule catalysts for excellent coking resistance in the high-space-velocity dry reforming of methane. Appl. Catal. B Environ. 259, 118019–118029. https://doi.org/10.1016/j.apcatb.2019.118019 (2019).
4. Liu, D. et al. Carbon dioxide reforming of methane over nickel-grafted SBA-15 and MCM-41 catalysts. Catal. Today 148, 243–265. https://doi.org/10.1016/j.cattod.2009.08.014 (2009).
5. Quek, X. Y. et al. Nickel-grafted TUD-1 mesoporous catalysts for carbon dioxide reforming of methane. Appl. Catal. B Environ. 95, 374–382. https://doi.org/10.1016/j.apcatb.2010.01.016 (2010).
6. Zhang, J. & Li, F. Coke-resistant Ni@SiO₂ catalyst for dry reforming of methane. Appl. Catal. B Environ. 176–177, 513–521. https://doi.org/10.1016/j.apcatb.2015.04.039 (2015).
7. Li, Z., Mo, L., Kathiraser, Y. & Kow, S. Yolk–Satellite–Shell structured Ni–Yolk@Ni@SiO₂ nanocomposite: superb catalyst toward methane CO₂ reforming reaction. ACS Catal. 5, 1526–1536. https://doi.org/10.1021/acscatal.4c01027p (2014).
8. Zhang, M. et al. Insight into the effects of the oxygen species over Ni/ZrO₂ catalyst surface on methane reforming with carbon dioxide. Appl. Catal. B Environ. 244, 427–437. https://doi.org/10.1016/j.apcatb.2018.11.068 (2019).
9. Delacruz, V. M. G., Pereñiguez, R., Ternero Juan, F., Holgado, P. & Caballero, A. Modifying the size of nickel metallic particles by H₂/CO treatment in Ni/ZrO₂ Methane dry reforming catalysts. ACS Catal. 1(2), 82–88. https://doi.org/10.1021/cs100116m (2011).
10. Tathod, A. P., Hayek, N., Shpasser, D., Simakov, D. S. A. & Gazit, O. M. Mediating interaction strength between nickel and zirconia using a mixed oxide nanosheets interlayer for methane dry reforming. Appl. Catal. B Environ. 249, 106–115. https://doi.org/10.1016/j.apcatb.2019.02.040 (2019).
11. Luna, A. E. C. & Iriarte, M. E. Carbon dioxide reforming of methane over a metal modified Ni-Al₂O₃ catalyst. Appl. Catal. A Gen. 343, 10. https://doi.org/10.1016/j.apcata.2007.11.041 (2008).
12. Juan, J. J., Martínez, M. C. R. & Gómez, M. J. I. Effect of potassium content in the activity of K-promoted Ni/Al₂O₃ catalysts for the dry reforming of methane. Appl. Catal. A Gen. 301, 9. https://doi.org/10.1016/j.apcata.2005.11.006 (2006).
13. Alipour, Z., Rezaei, M. & Meshkani, F. Effect of Ni loadings on the activity and coke formation of MgO-modified Ni/Al₂O₃ nano-catalyst in dry reforming of methane. J. Energy Chem. 23, 633. https://doi.org/10.1016/j.j energychem.2013.08.009 (2014).
14. Alipour, Z., Rezaei, M. & Meshkani, F. Effects of support modifiers on the catalytic performance of Ni/Al₂O₃ catalyst in CO₂ reforming of methane. Fuel 129, 197. https://doi.org/10.1016/j.fuel.2014.03.045 (2014).
15. Alonso, D. S. J., Gómez, M. J. I. & Martínez, M. C. R. K and Sr promoted Co alumina supported catalysts for the CO₂ reforming of methane. Catal. Today 176, 187. https://doi.org/10.1016/j.cattod.2010.11.093 (2011).
16. Fatesh, A. S. A., Naeem, M. A., Fakheea, A. H. & Abasaee, A. E. CO₂ reforming of methane to produce syngas over γ-Al₂O₃-supported Ni-Sr catalysts. Bull. Chem. Soc. Jpn. 86, 742. https://doi.org/10.1246/bcsj.20130002 (2013).
53. Sun, N. et al. Catalytic performance and characterization of Ni–CaO–ZrO₂ catalysts for dry reforming of methane. Appl. Surf. Sci. 257, 9169 https://doi.org/10.1016/j.apsusc.2011.05.127 (2011).

54. Yabe, T., Mitarai, K., Oshima, K., Ogo, S. & Sekine, Y. Low-temperature dry reforming of methane to produce syngas in an electric field over La-doped Ni/ZrO₂ catalysts. Fuel Process. Technol. 158, 96. https://doi.org/10.1016/j.fuproc.2016.11.013 (2017).

55. Sokolov, S., Kondratenko, E. V., Pohl, M.-M. & Rodemerck, U. Effect of calcination conditions on time on-stream performance of Ni/La₂O₃-ZrO₂ in low-temperature dry reforming of methane. Int. J. Hydrogen Energy 38, 16121. https://doi.org/10.1016/j.ijhydene.2013.10.013 (2013).

56. Montoya, J. A., Pascual, E. R., Gimon, C., Angel, P. D. & Monzón, A. Methane reforming with CO₂ over Ni/ZrO₂–CeO₂ catalysts prepared by sol–gel. Catal. Today 63, 71. https://doi.org/10.1016/S0920-5861(00)00447-8 (2000).

57. Arslan, A. & Dogu, T. Effect of calcination/reduction temperature of Ni impregnated CeO₂-ZrO₂ catalysts on hydrogen yield and coke minimization in low temperature reforming of ethanol. Int. J. Hydrogen Energy 41, 16752. https://doi.org/10.1016/j.ijhydene.2016.07.082 (2016).

58. Potdar, R. H. S. & Jun, K. W. Carbon dioxide reforming of methane over co-precipitated Ni–CeO₂, Ni–ZrO₂ and Ni–Ce–ZrO₂ catalysts. Catal. Today 93–95, 39. https://doi.org/10.1016/j.catod.2004.05.012 (2004).

59. Wang, C., Sun, N., Wei, W. & Zhao, Y. Carbon intermediates during CO₂ reforming of methane over Ni-CaO-ZrO₂ catalysts: a temperature-programmed surface reaction study. Int. J. Hydrogen Energy 41, 19014. https://doi.org/10.1016/j.ijhydene.2016.08.128 (2016).

60. Yang, Q. et al. Enhanced coking tolerance of a MgO-modified Ni cermet anode for hydrocarbon fuelled solid oxide fuel cells. J. Mater. Chem. A 4, 18031. https://doi.org/10.1039/C6TA08031F (2016).

61. Sun, C. W., Su, R., Chen, J., Lu, L. & Guan, P. F. Carbon formation mechanism of C₃H₈ in Ni-based catalysts revealed by in situ electron microscopy and molecular dynamics simulations. ACS Omega 3, 8413. https://doi.org/10.1021/acsomega.9b00798 (2019).

62. Mette, K. et al. Stable performance of Ni catalysts in the dry reforming of methane at high temperatures for the efficient conversion of CO₂ into syngas. ChemCatChem 6, 100. https://doi.org/10.1002/cctc.201300699 (2014).

63. Kambolis, A., Matralis, H., Trovarelli, A. & Papadopoulou, C. Ni/CeO₂-ZrO₂ catalysts for the dry reforming of methane. Appl. Catal. A 377, 16. https://doi.org/10.1016/j.apcata.2010.01.013 (2010).

64. Chung, U.-C. Effect of H₂ on formation behavior of carbon nanotubes. Bull. Korean Chem. Soc. 25(10), 1521. https://doi.org/10.4028/www.scientific.net/MSF.475-479.3559 (2004).

Acknowledgements
The KSU authors would like to extend their sincere appreciation to the Deanship of Scientific Research at the King Saud University for funding this research group project # No. RGP-119. Dr Ahmed I. Osman would like to thank Prof. David Rooney for the given support and acknowledge the support given by the EPSRC project “Advancing Creative Circular Economies for Plastics via Technological-Social Transitions” (ACCEPT Transitions, EP/S025545/1). RK wants to acknowledge the administration of Sankalchand Patel University for providing research environment.

Author contributions
Experiment test, A.S.A.-F. and S.O.K. writing—original draft, R.K. and A.S.A.-F., Preparation of Catalyst, A.A.B., M.A. and R.A. Characterization, A.A.B., A.A.I., M.S.L., J.K., R.A. and A.H.F., writing—review and editing. R.K., M.A., A.A.B., A.E.A., A.I.O.

Competing interests
The authors declare no competing interests.

Additional information
Supplementary information is available for this paper at https://doi.org/10.1038/s41598-020-70930-1.

Correspondence and requests for materials should be addressed to A.S.A.-F. or A.I.O.

Reprints and permissions information is available at www.nature.com/reprints.

Publisher’s note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

© The Author(s) 2020