**Enhanced methane reforming activity of a hydrothermally synthesised co-doped perovskite catalyst**

Majida H. Khazaal\*, John Z. Staniforth, Zainab A. Alfatlawi, R. Mark Ormerod and Richard. J. Darton\*

Catalysis and Sustainable Materials Group, School of Chemical and Physical Sciences, Keele University, Keele, Staffordshire, ST5 5BG, UK.

Email: r.j.darton@keele.ac.uk

\*Corresponding Authors

**Abstract**

A catalyst for the direct reforming of methane and simulated biogas has been prepared using a green and low temperature hydrothermal method. The nickel and iron co-doped SrZrO3 perovskite shows catalytic activity comparable to 10% Ni/Al2O3, but with an almost 50% saving in nickel content and a significant reduction in unwanted carbon deposition through thermal decomposition of methane and the Boudouard reaction.

The use of a catalyst with a low active metal content produced via a hydrothermal route provides an attractive and sustainable method of production of synthesis gas from both methane and biogas for potential use in solid oxide fuel cells.

**1. Introduction**

As the simplest hydrocarbon, methane has a high hydrogen to carbon ratio making it a cleaner fossil fuel than coal or oil. Methane can be considered a renewable energy resource that can be produced naturally by the fermentation of organic compounds, under anaerobic conditions such as is found in wastewater sludge and sewage. The resulting “biogas” is a variable mixture of mainly methane and carbon dioxide, usually in a 2:1 ratio, and often accompanied with ppm quantities of sulphur compounds and higher hydrocarbons and is saturated with water. The direct utilisation of greenhouse gases such as methane or biogas in a solid oxide fuel cell system to produce electrical energy via internal reforming reactions followed by oxidation of the resultant syngas would help to reduce the impact of global warming as well as help to avoid the energy crisis.(1, 2)

Three main catalytic methane reformation reactions can be utilized to produce syngas from hydrocarbon fuels, shown in equations (1) partial oxidation of methane (POM), (2) dry reforming of methane (DRM), and (3) steam reforming of methane (SRM).

(1)

(2)

(3)

One of the most serious problems in methane reforming is catalyst deactivation due to unwanted carbon formation, which can lead to a substantial reduction in performance, especially when using materials such as nickel which are known to catalyse carbon deposition. There are several reaction pathways that participate in the accumulation of solid carbon on the catalyst surface, or other forms of carbon which can lead to deactivation of the available active sites or physical blocking and interference of the gas delivery system.(3)

Thermal decomposition (4)

Boudouard reaction (5)

Carbon monoxide reduction (6)

Many factors affect the quantity of carbon deposition observed, including reaction temperature as thermodynamically there is no specific temperature at which carbon will not be deposited due to either the Boudouard reaction or thermal decomposition; thus to negate carbon deposition, kinetic factors must be utilised, usually by the formulation of the catalyst which should be optimised for reforming reactions whilst unreactive for carbon formation reactions.(4) The ratio of O/C and H/C also affects the amount of carbon deposition with a higher propensity towards coke formation being observed in lower O/C and H/C ratios. For example, dry reforming of methane has a 2O/2C=1 and 4H/2C=2 compared to steam reforming that has 1O/1C=1 and 6H/1C=6, showing that dry reforming has a greater tendencyto form carbon than steam reforming. (5, 6)

Generally, there are two ways for lowering the level of coke formation: changing reaction conditions such as different temperatures, or by changing the formulation of the catalyst involved. The development of new active and selective anode catalyst materials for methane reforming with a high ability for suppressing coke formation has become one of the major challenges in the development of a new generation of solid oxide fuel cells. Specifically, base metal catalysts are often preferred over noble metal catalysts as they are more widely available and significantly cheaper.(7) It has also been reported that nickel based catalysts are considered more effective, as nickel has a high catalytic activity and selectivity towards partial oxidation over total oxidation of methane.(8, 9) However Ni-based catalysts often suffer from deactivation due to the accumulation of carbon on the surface and therefore many studies have focused on synthesising catalysts that have a high resistance to carbon formation as well as good catalytic activity for hydrogen production.(10)

Hydrothermal synthesis has been widely used in the preparation of catalysts such as mixed metal oxide materials. This method has been shown to offer several benefits over other conventional methods of production, including the ability to synthesize high-quality crystals that are thermodynamically stable using lower synthesis temperatures and in a single step process.(11) Perovskite type oxides with the general formula ABO3 have demonstrated very good catalytic activity as they can suppress coke formation compared to Ni supported catalysts.(12 - 14) Moreover, partial substitution of the A or B site by dopant cations can significantly change the catalytic behaviour and stability of the perovskite materials. The activity of the catalyst towards reformation reactions depends on the type of metal used, the surface area of the catalyst, particle size, reaction temperature and the preparation method of the catalyst.(15) For example, noble metals such as Rh and Ru are very active towards DRM and are much more stable against coke formation compared to other transition metals.(16, 17) But, due to high prices, it is often more practical and economical to improve the activity and stability of non-noble metal catalysts.

In this paper, it has been shown that a small amount of two active metals (4 mol% Ni and 1 mol% Fe) incorporated into a strontium zirconate synthesised via a hydrothermal method(18) produces a perovskite materialwhich exhibits excellent catalytic POM and DRM performance and a good carbon deposition resistance as well as showing good stability under reaction conditions without any decrease in methane conversion up to 20 hours of reaction.

**2. Experimental**

**2.1 Catalyst Synthesis**

Ni-Fe doped SrZrO3 (5.3 wt% Ni) was prepared by a hydrothermal method based on previously published work.(18,19) 3.1 mmol ZrOCl2•8H2O (Alfa Aesar, 98%), 2.5 mmol Sr(NO3)2 (Alfa Aesar, 99%), 0.62 mmol Ni(NO3)2•6H2O (Aldrich, 99%) and 0.16 mmol Fe(NO3)3.9H2O (Aldrich, 98%), were dissolved in deionized water at room temperature within a 23 ml Teflon-lined stainless steel autoclave. NaOH (Aldrich, >97%) was then added and thoroughly mixed to produce a homogeneous gel with pH=13. The autoclave was then heated for 24 hours at 150°C before being cooled to room temperature and the product transferred into 50 mL centrifuge tubes and subjected to three cycles of washing with ultra-pure water and centrifuging at 4500 rpm for 15 minutes. Finally, the samples were dried at 60 °C for 24 hours.

Nickel supported on alumina 10 wt% Ni/Al2O3 was prepared by a wet impregnation technique using alumina powder as previously described to give a powdered sample with an average particle size of 10 m.(20)

**2.2 Perovskite Characterization**

The powder X-ray diffraction patterns for all samples were recorded using a Bruker D8 Advance powder x-ray diffractometer using Cu Kα radiation with a wavelength of 1.5406 Å using a 2θ range of 10° to 90° in 0.02° steps.

Brunauer-Emmett-Teller (BET) surface areas for the catalytic samples were determined using a Quantachrome Autosorb-1 apparatus, the samples of approximately 200 mg were outgassed at 350 °C in vacuum for 5 hours and then nitrogen gas was used as the adsorbent.

The morphologies and structures of the samples were characterized by scanning electron microscopy that was undertaken on a Hitachi TM3000 scanning electron microscope with a magnification of up to x30K and a Bruker Quantax 70 EDS system.

**2.3 Evaluation of Catalytic Activity**

To achieve maximum catalytic activity, the catalyst was first reduced by using a temperature programmed reduction (TPR) technique. In this technique, 2 mL min-1 of hydrogen in 18 mL min-1 of helium carrier was passed over 20 ± 0.5 mg of catalyst which was loaded in a fixed-bed quartz reactor tube and held in place with quartz wool, while the temperature was raised linearly from room temperature at 10 °C min-1 up to 900 °C. On reaching 900 °C the catalyst was quickly cooled under the same flow rate of hydrogen in helium until reaching room temperature to prevent re-oxidation. TPR profiles were gained by measuring hydrogen consumption and water production as a function of temperature. The characteristics of the TPR profile, including the peak area and the reduction temperature profile depend on the nature of the oxides, the sensitivity to the experimental conditions, the hydrogen concentration and the flow rate of the reducing gas mixture, therefore the profiles for the same material could be significantly different if the measurement was performed under different conditions. The area of the reduction peak gives an indication about the levels of the reduction occurring.

Temperature programmed reaction was performed using a mixture of 1 mL min-1 of CH4 and 0.5 mL min-1 of O2 in 18 mL min-1 of helium carrier for methane partial oxidation, 1 mL min-1 of CH4 and 0.5 mL min-1 of CO2 in 18 mL min-1 helium carrier for biogas reforming and 1 mL min-1 of CH4 and 1 mL min-1 of CO2 in 18 mL min-1 helium carrier for dry reforming. For each run, the streams of reactant gases were passed through the reactor tube over 20 ± 0.5 mg of catalyst sample and the flow rates of the gases were accurately adjusted by use of mass flow controllers. The space velocity in all cases was approximately 60000 mL hr-1 gcat-1.

The furnace temperature was ramped from room temperature up to 900 °C at 10 °C min-1 and then reversed at 5 °C min-1 down to room temperature(21) The furnace temperature was controlled and monitored by a Eurotherm 310 system with a K-type thermocouple which also has the capability to perform temperature controlled reactions either constant temperature isothermally or by linear temperature programmed reaction from 2 °C/min up to 20 °C/min. Yields of H2 and CO were calculated based on a 100% methane conversion.

Temperature programmed oxidation (TPO) was used following catalytic reaction to characterise and quantify the mass of carbon deposited on the catalyst surface during the reforming reaction. This TPO reaction was carried out in an analogous manner to the TPR reaction, with the temperature raised to 900 °C at 10 °C min-1, whilst 2mL min-1 oxygen in 18 mL min-1 helium was passed over the catalyst. The resulting profile for carbon dioxide and carbon monoxide production were quantified using the peak area and a pre-determined calibration, which gives information about the mass of carbon and the nature of the carbon deposition.

**3. Results and Discussion**

**3.1 Catalyst characterization**

Powder X-ray diffraction patterns for the Ni-Fe doped, Ni-doped and the un-doped SrZrO3 perovskites are shown in Figure 1. The x-ray powder pattern of the Ni-Fe doped SrZrO3 shows the expected orthorhombic (P*bnm*) unit cell structure with lattice parameters of a = 5.8118 Å, b = 5.8067 Å and c = 8.2187 Å and cell volume = 277.36 A3. This compares well with the patterns for the un-doped SrZrO3 and Ni-doped SrZrO3 (a = 5.7920 Å, b = 5.8130 Å, c = 8.1960 Å) (a = 5.7948 Å, b = 5.8014 Å, c = 8.1985 Å) respectively and indicates some doping of the pervoskite structure has occurred.

A standard catalyst of 10 wt% Ni supported on Al2O3 (Ni/Al2O3) was chosen for comparison purposes with the Ni-Fe doped SrZrO3 perovskite. In situ high temperature XRD studies using an Anton-Parr XRK 900 reaction chamber were carried out to investigate the thermal stability of the Ni-Fe doped SrZrO3 and the Ni/Al2O3 samples, with diffraction patterns collected every 100 °C up to 900 °C as shown in the supplementary information. The perovskite sample remains stable at all calcination temperatures with no phase transformation or separation occurring under the reaction temperatures employed in this study (100 – 900 °C). In contrast the Ni/Al2O3 sample shows additional small peaks at 36.9○ and 62.1○ by 400 ○C, which are attributed to the formation of nickel oxide and these become more intense by 900 ○C.

The particle sizes for the co-doped perovskite were found to be in the range of 2-5 µm by SEM images and BET nitrogen absorption experiments gave an average surface area of 47.4 m2 g-1 whilst the 10% Ni/Al2O3 sample was 17.8 m2 g-1. EDX analysis measurements (Supplementary Information) on the as-prepared samples were used to confirm the composition of the catalysts. These results combined with the powder X-ray diffraction measurements indicate that both the Ni and Fe have been successfully incorporated into the perovskite structure at levels consistent with the original synthesis formulations. In order to confirm the nickel contents of the catalysts, reduction measurements were carried out as shown in Figure 2.

The TPR profile for 10 wt% Ni/Al2O3 shows a broad peak at around 420°C which can be assigned to the reduction of surface NiO species weakly interacting with the Al2O3 support and are consistent with studies by Li.(22) In comparison the perovskite shows a different reduction profile more consistent with previous studies of Ni only doped SrZrO3 perovskites but with an additional peak at around 540 °C believed to be due to the reduction of the Fe species.(23)

The co-doped perovskite was further characterized after reduction using powder XRD to determine any changes in phase composition and to gain a deeper understanding of the reduction process. As can be seen from Figure 3 there is only a small change in the structure of the Ni-Fe doped perovskite shown by the formation of Ni0 at 2θ=51○.

**3.2 Partial oxidation of methane**

The reforming characteristics of the catalysts were investigated by analysing the reforming reaction profiles as shown in Figure 4. The reaction over Ni/Al2O3 changes from total oxidation to predominantly partial oxidation at ~530 °C with a sharp drop in methane and oxygen coinciding with the production of a 2:1 ratio of H2 and CO, reaching a maximum at ~800°C. The co-doped perovskite shows a similar profile but with the switch over between total and partial oxidation occurring at ~630°C and reaching a maximum at ~900°C. In addition there is some evidence of total oxidation occurring above 550 °C, although this begins to drop away above 600 °C. As the temperature is increased, methane conversion and selectivity toward CO and H2 production increases resulting in a high yield of synthesis gas at 900○C. Conversion of reactants for Ni/Al2O3 and Ni-Fe doped SrZrO3 begins at 530 ○C and 630○C respectively. Although the Ni/Al2O3 is more active than the co-doped perovskite at lower temperatures, both catalysts produced the same amount of synthesis gas (H2 and CO) at 900○C. This lower initial activity of co-doped perovskite is possibly due to the significantly lower Ni content of the catalyst.

All reactions show an increase in synthesis gas with increasing temperature as reforming become more thermodynamically favoured. It is possible that the reaction mechanism involves total oxidation followed by carbon dioxide and steam reforming of the remaining methane but that has not been elucidated by this study.

The conversion of methane for the undoped SrZrO3 perovskite was found to be less than 3% at 900 °C. This is expected since there is no catalytically active metal on SrZrO3, whilst the CH4 conversion for just Fe as the active metal doped perovskite and only Ni-doped perovskite were 27% and 75% respectively. Methane conversion for both of the monometallic-doped perovskite catalysts is lower than the co-doped catalyst and the experimental conversion for the co-doped catalyst is slightly lower than the equilibrium values. H2-TPR results show higher amounts of reducible Ni on the Ni/Al2O3 surface compared to that of Ni-Fe doped SrZrO3, this leads to lower methane conversion over Ni-Fe doped SrZrO3 compared to Ni/Al2O3 where significant methane dissociation is occurring most likely due to the much higher nickel content (Figure 5). Interestingly the hydrogen production for the Ni/Al2O3 catalyst over the 20 hours of reaction shows a decrease, which we have attributed to the selective oxidation of the H2 to produce water.

The catalyst materials were tested for stability over 20 hours of reforming at 900°C, and the results are shown in Figure 5. Ni/Al2O3 catalyst had a higher initial H2 yield than the co-doped perovskite, but over time the hydrogen yield from Ni/Al2O3 decreased whilst the hydrogen yield over Ni- Fe doped SrZrO3 increased slightly.

A temperature programmed oxidation (TPO) reaction was used to quantify the deposited carbon on each catalyst and the results are shown in Figure 6. The co- doped perovskite was shown to be comparable in activity to the 10%Ni/Al2O3catalyst in terms of production of H2, whilst displaying significantly lower deposits of solid carbon. The TPO profile shows large peaks for Ni/Al2O3 catalyst at approximately 650°C whereas only a small peak for the co-doped perovskite catalyst can be seen, which suggests that the nature of the deposited carbon species might be similar and most likely amorphous carbon.(24)

These results demonstrate that the substitution of iron into a nickel doped strontium zirconate increases the stability and reduces carbon accumulation on the surface, possibly due to creating structural defects in the lattice structure and providing higher oxygen ion mobility, which may help oxidize any carbonaceous species formed via the promotion of total oxidation.(25, 26)

**3.3 Dry reforming of methane and biogas reforming**

The catalysts were also investigated for their dry reforming of methane capability as shown in Figure 7. The reaction over both the perovskite and supported nickel catalyst are very similar and both demonstrate that the reactants (CH4, CO2) decrease simultaneously with the increase of products starting at approximately 450°C resulting in the formation of CO/H2 and a limited amount of water due to the reverse water gas shift reaction.

Temperature programmed reaction over the different catalysts using a mixture of 2:1 CH4/CO2, to simulate biogas, are shown in Figure 8. These results also show similar profiles with reaction initiation at approximately 500 °C generating H2 and CO, whilst CH4 and CO2 are consumed and a limited amount of water is produced, most likely due to the reverse water gas shift reaction. Some evidence of methane decomposition over both catalysts can be observed, but to a greater extent over Ni/Al2O3 with a starting temperature of ~800°C over the Ni/Al2O3 catalyst and ~870°C over the perovskite. Reverse water gas shift reaction was greater on the co-doped perovskite than Ni/Al2O3, resulting in the production of a higher amount of CO than H2.

The activity and long term stability of the catalysts was monitored by means of CH4 and CO2 conversions during isothermal reactions at 700, 800 and 900 °C, Figure 9. A high stability and activity of the perovskite was obtained under CH4:CO2 mixtures for 20 hours at different temperatures. At 900 °C and 800 °C, both catalysts show the maximum CH4 conversion near to the equilibrium value and the catalytic activities remains almost constant over the 20 h reaction time.

**3.4 The effects of temperature on catalytic activity and carbon formation.**

The quantity of deposited carbon was found to be lower for the co-doped perovskite than the Ni supported catalyst. Deposition of carbon is one of the main causes of deactivation of methane reforming catalysts. Carbon is mainly formed by either disproportionation of CO or decomposition of hydrocarbons. The rate of carbon deposition varies according to material whether it is a metal or metal oxide, which depends on the type of metal, the promoters, the particle size, and the interaction between the metal and the support.

In general, higher resistance against carbon build-up was observed for the co-doped perovskite compared to the Ni/Al2O3 catalyst as shown in Figure 10. This result is in agreement with previous work, which suggested that both CO disproportionation and methane cracking contribute to coke formation on Ni/Al2O3.(27) However, slightly more carbon was deposited on the co-doped catalyst during dry reforming at 800°C and this is believed to be due to a combination of the Boudouard reaction and thermal decomposition both occurring at this particular temperature. It can be seen from Table 1 that the methane conversions for both catalysts are approximately close to the maximum theoretical values and that there is no direct relation between the amount of carbon deposition and catalytic activity.

In order to investigate the stability of the catalysts, both materials were subjected to powder XRD and SEM analysis post-reaction. The results of these are shown in the supplementary information and suggest that the perovskite undergoes minimal changes in structure or morphology, whilst the Ni/Al2O3 catalyst shows some structural changes that can be attributed to the sintering of NiO. SEM images were collected for catalysts before and after reforming reactions. These show that the supported catalyst has less uniform and larger particle sizes than the perovskite catalyst (Supplementary Info.). The SEM images for Ni-Fe doped SrZrO3 samples show minimal differences before and after reaction with no obvious signs of agglomeration or sintering of the particles, indicating a thermally resistant catalyst.

**4. Conclusions**

This work has shown that a Ni-Fe co-doped SrZrO3 perovskite catalyst can be successfully synthesised by hydrothermal methods and shows excellent catalytic activity and selectivity towards partial oxidation and dry reforming of methane to synthesis gas with excellent coke resistance, yielding very low levels of deposited carbon on the catalyst surface. The effect of partial substitution of iron into the perovskite structure was found to play a significant role in reducing the quantity of unwanted carbon deposition during methane reforming and is believed to be due to the formation of oxygen vacancies and further work to investigate this is currently underway. The co-doped perovskite catalyst has been shown to have a similar catalytic performance to 10% Ni/Al2O3, but with less carbon deposition particularly for dry reforming reactions, whilst also using 50% less active metal within the catalyst. These results show that perovskite based reforming catalysts have the potential to provide a more sustainable method of hydrogen production for either industrial use or in solid oxide fuel cells.

**Acknowledgements**

The authors would like to thank the Iraqi Ministry of Higher Education and Scientific Research (MOHESR) for funding MHK and ZAA.

**Supporting Information**

Additional catalyst characterisation data: SEM, EDX and powder X-ray diffraction.

**References**

1. Serrano-Lotina, A.; Daza, L. Highly stable and active catalyst for hydrogen production from biogas. *J. Power Sources*, 2013, 238, 81–86.

2. Ormerod, R. M. Solid oxide fuel cells. *Chem. Soc. Rev*., 2003, 32, 17–28.

3. Chen, T.; Wang, W.G.; Miao, H.; Li, T.; Xu, C. Evaluation of carbon deposition behavior on the nickel/yttrium-stabilized zirconia anode-supported fuel cell fueled with simulated syngas. *J. Power Sources*. 2011, 196, 2461–2468.

4. Wang, C.; Sun, N.; Zhao, N.; Wei, W.; Sun, Y.; Sun, C.; Liu, H.; Snape, C. E. Coking and deactivation of a mesoporous Ni–CaO–ZrO2 catalyst in dry reforming of methane: A study under different feeding compositions. *Fuel*, 2015, 143, 527–535.

5. Wang, W.; Chao, S.; Yuzhou, W.; Ran, R.; Zongping, S. Progress in Solid Oxide Fuel Cells with Nickel-Based Anodes Operating on Methane and Related Fuels. *Chem. Rev*., 2013, 113, 8104−8151.

6. Li, D.; Nakagawa, Y.; Tomishige, K. Methane reforming to synthesis gas over Ni catalysts modified with noble metals. *Appl. Catal. A: Gen*., 2011, 408, 1–24.

7. Pakhare, D.; Spivey, J. A review of dry (CO2) reforming of methane over noble metal catalysts. *Chem. Soc. Rev.,* 2014, 43, 7813-7837.

8. Staniforth, J.; Evans, S. E.; Good, O. J.; Darton R. J.; Ormerod, R. M. A novel perovskite based catalyst with high selectivity and activity for partial oxidation of methane for fuel cell applications. *Dalton Trans.,* 2014, 43, 15022–15027.

9. Mishra, A.; Galinsky, N.; He, F.; Santiso, E.; Li, F. Perovskite-structured AMnxB1−xO3 (A = Ca or Ba; B = Fe or Ni) redox catalysts for partial oxidation of methane. *Catal. Sci. Technol.,* 2016, 6, 4535-4544.

10. Gallego, G. S.; Mondrago, F.; Barrault, J.; Tatiboue, J.; Dupeyrat, C. CO2 reforming of CH4 over La–Ni based perovskite precursors. *Appl. Catal. A.,* 2006, 311, 164-711.

11. Modeshia, D. R.; Darton, R. J.; Ashbrook S. E.; Walton, R. I. Control of polymorphism in NaNbO3 by hydrothermal synthesis. *Chem. Commun.,* 2009, 68–70.

12. Modeshia, D. R.; Walton, R. I. Solvothermal synthesis of perovskites and pyrochlores: crystallisation of functional oxides under mild conditions. *Chem. Soc. Rev.,* 2010, 39, 4303–4325.

13. Zhu, J.; Li, H.; Zhong, L.; Xiao, P.; Xu, X.; Yang, X.; Zhao, Z.; Li, J. Perovskite Oxides: Preparation, Characterizations, and Applications in Heterogeneous Catalysis. *ACS. Catal.,* 2014, 4, 2917−2940.

14. Maneerung, T.; Hidajat, K.; Kawi, S. LaNiO3 perovskite catalyst precursor for rapid decomposition of methane: Influence of temperature and presence of H2 in feed stream. *Catal. Today,* 2011, 171, 24-35.

15. Ballarini, A. D.; deMiguel, S. R.; Jablonski, E. L.; Scelza, O. A.; Castro, A. A. Reforming of CH4 with CO2 on Pt-supported catalysts: Effect of the support on the catalytic behaviour. *Catal. Today*. 2005, 107, 481–486.

16. Kehres, J.; Jakobsen, J. G.; Andreasen, J. W.; Wagner, J. B.; Liu, H.; Molenbroek, A.; Sehested, J.; Chorkendorff, I.; Veggel, T. Dynamical Properties of a Ru/MgAl2O4 Catalyst during Reduction and Dry Methane Reforming. *J. Phys. Chem. C.*, 2012, 116 21407–21415.

17. Zhang, J.; Wang, H.; Dalai, A.; Development of stable bimetallic catalysts for carbon dioxide reforming of methane. *J. Catal.,* 2007, 249, 300–310.

18. Evans, S. E.; Good, O. J.; Staniforth, J. Z.; Ormerod; R. M.; Darton, R. J. Overcoming carbon deactivation in biogas reforming using a hydrothermally synthesised nickel perovskite catalyst. *RSC Adv.*, 2014, 4, 30816–30819.

19. Evans, S. E.; Staniforth, J. Z.; Darton, R. J.; Ormerod, R. M. A nickel doped perovskite catalyst for reforming methane rich biogas with minimal carbon deposition. *Green Chem.,* 2014, 16, 4587-4594.

20. Diskin, A. M. PhD Thesis, Keele University, 2000.

21. Laycock, C. J.; Staniforth, J. Z.; Ormerod, R. M. Biogas as a fuel for solid oxide fuel cells and synthesis gas production: effects of ceria-doping and hydrogen sulfide on the performance of nickel-based anode materials. *Dalton Trans.,* 2011, 40, 5494–5504.

22. Li, C.; Chen, Y-W. Temperature-programmed-reduction studies of nickel oxide/alumina catalysts: effects of the preparation method. *Thermochimica Acta*, 1995, 256, 457-465.

23. Evans, S. E. PhD Thesis, Keele University, 2017.

24. Silverwood, I. P.; Hamilton, N. G.; Laycock, C. J.; Staniforth, J. Z.; Ormerod, R. M.; Frost, C. D.; Parker, S. F.; Lennon, D. Quantification of surface species present on a nickel/alumina methane reforming catalyst. *Phys. Chem. Chem. Phys.,* 2010, 12, 3102-3107.

25. Zhu, H.; Wang, W.; Ran, R.; Sua, C.; Shi, H.; Shao, Z. Iron incorporated Ni–ZrO2 catalysts for electric power generation from methane. *Int. J. Hydrogen Energ.* 2012, 37, 9801–9808.

26. Sutthiumporn, K.; Maneerung, T.; Kathiraser, Y.; Kawi, S. CO2 dry-reforming of methane over La0.8Sr0.2Ni0.8M0.2O3 perovskite (M = Bi, Co, Cr, Cu, Fe): Roles of lattice oxygen on C–H activation and carbon suppression. *Int. J. Hydrogen Energ.*, 2012, 37, 11195-11207.

27. Therdthianwong, S.; Siangchin, C.; Therdthianwong, A. Improvement of coke resistance of Ni/Al2O3 catalyst in CH4/CO2 reforming by ZrO2 addition. *Fuel Processing Technol.*, 2008, 89, 160–168.

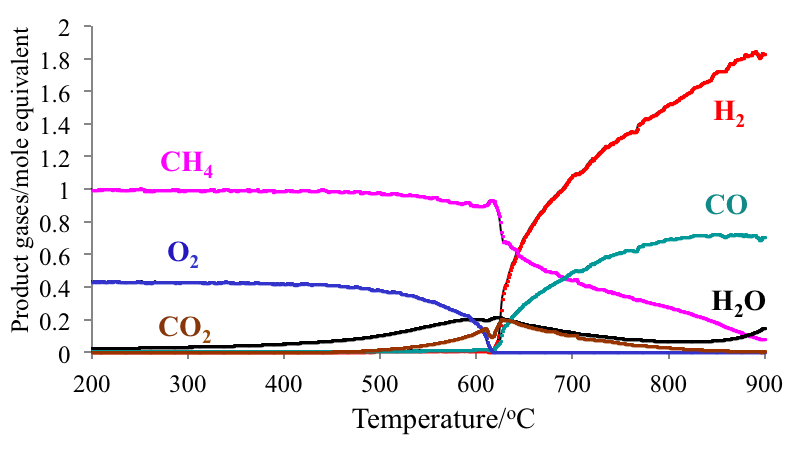
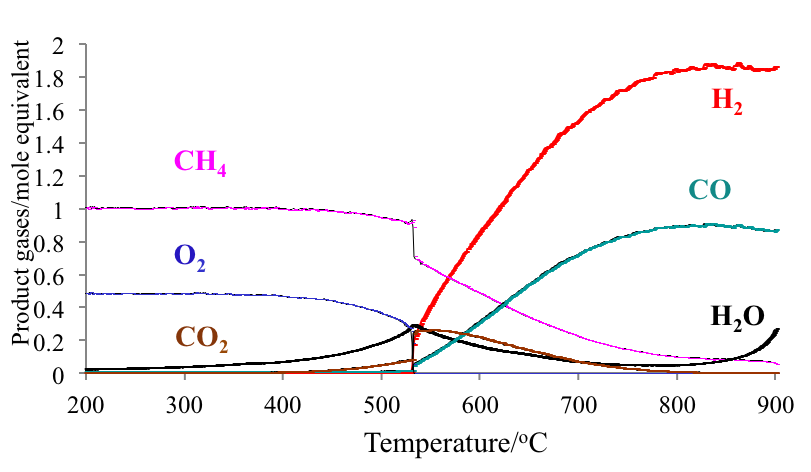
**Table 1.** Averagemethane conversion for three types of reforming at different temperatures after 20 hours of reaction.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | %CH4/CO2conversion for 10%Ni/Al2O3 | | %CH4/CO2conversion for Ni-Fe doped SrZrO3 | |
| Reforming type | **800 °C** | **900 °C** | **800 °C** | **900 °C** |
| Partial oxidation | 95 | 99 | 87 | 90 |
| Dry reforming | 93/94 | 96/99 | 92/94 | 94/97 |
| Biogas reforming | 44/93 | 46/97 | 48/96 | 51/99 |

**Figure 1.** Powder X-ray diffraction patterns of as-prepared Ni-Fe doped SrZrO3 (top), Ni doped SrZrO3 (middle) and SrZrO3 (bottom).

**Figure 2.** Reduction profiles of (1) calcined 10%Ni/Al2O3 (2) as-prepared Ni-Fe doped SrZrO3.

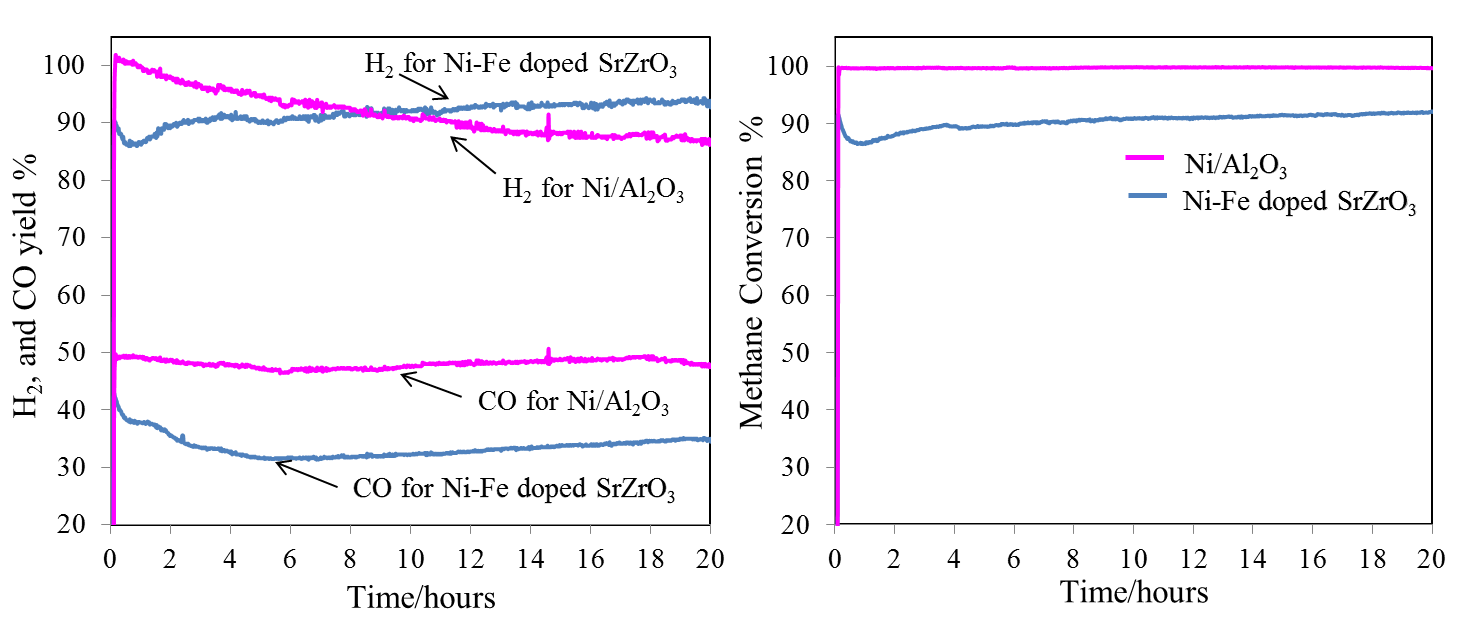
**Figure 3.** XRD pattern of Ni-Fe doped SrZrO3 perovskite after reaction, \* indicates ZrO2.



(a)

(b)

**Figure 4.** Reaction profile for a mixture of (1:0.5) CH4: O2 over (a) 10%Ni/Al2O3 and (b) Ni-Fe doped SrZrO3.

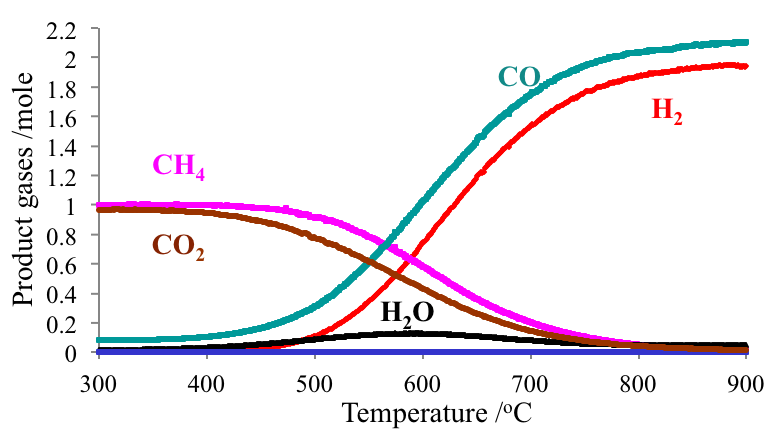
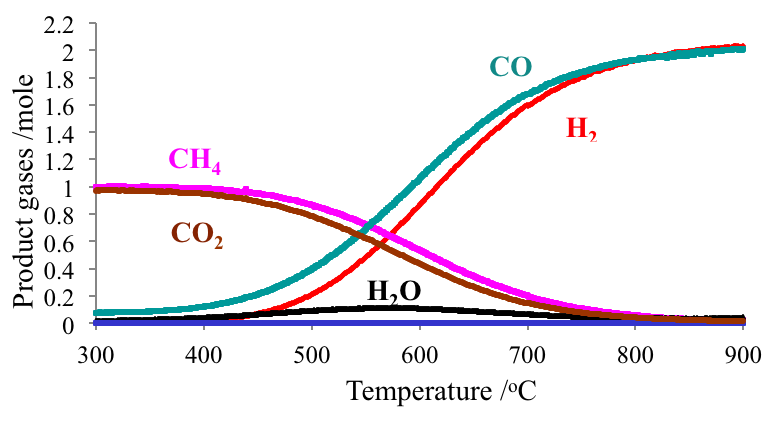


(a)

(b)

**Figure 5.** Percentage of (a) H2 and CO yield and (b) CH4 conversion profiles of (1:0.5) CH4: O2 mixture over 10%Ni/Al2O3 and Ni-Fe doped SrZrO3 at 900°C for 20 hours.

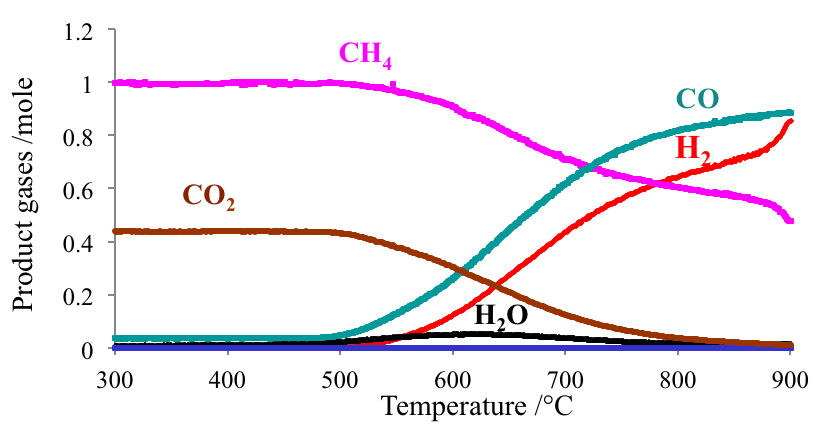
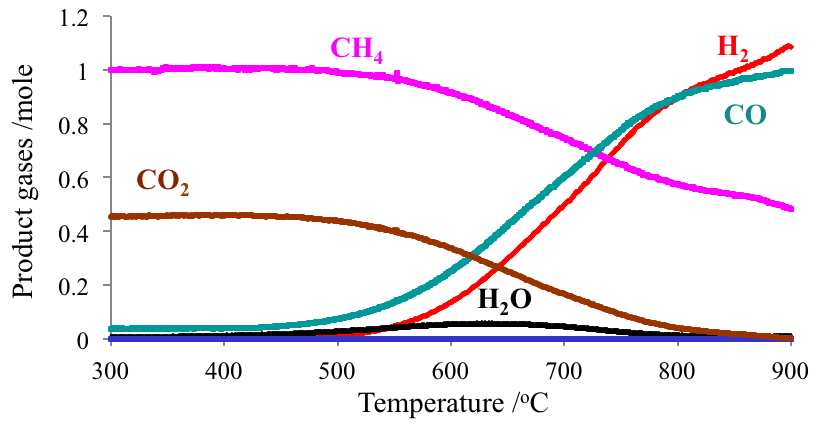
**Figure 6.** TPO profile for (1) Ni-Fe doped SrZrO3 and (2) 10% Ni/Al2O3 following a POM temperature programmed reaction over the temperature range of 100 to 900 °C.



(a)

(b)

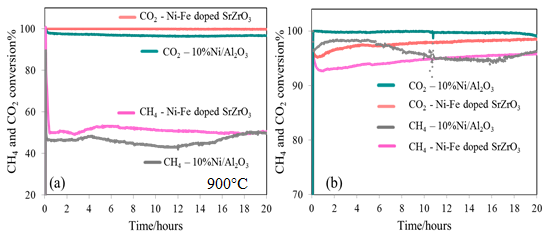
**Figure 7.** Reaction profile for a 1:1 mixture of CH4:CO2 over (a) 10%Ni/Al2O3 and (b) Ni-Fe doped SrZrO3 catalysts.

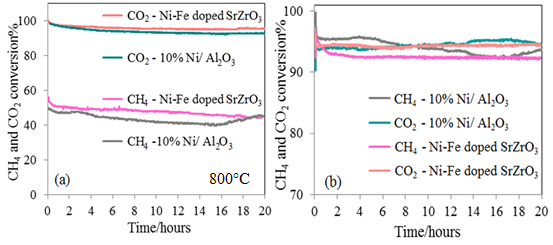


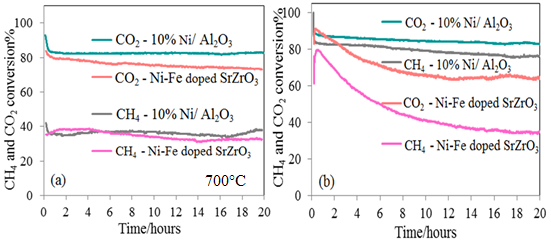
(a)

(b)

**Figure 8.** Reaction profile for a mixture of 2CH4:CO2 over (a) 10%Ni/Al2O3 and (b) Ni-Fe doped SrZrO3 catalysts.







**Figure 9.** CH4 and CO2 conversion profiles of (a) 2:1 ratio of CH4:CO2 and (b) 1:1 ratio of CH4:CO2 mixture over two catalysts for 20 hours at temperatures of 700°C, 800°C and 900°C.

**Figure 10.** Effect of temperature and reforming reaction type on carbon deposition during reforming of methane for 20 hours in mg of carbon/gram of catalysts.