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Overcoming carbon deactivation in biogas reforming using a hydrothermally synthesised nickel perovskite catalyst†

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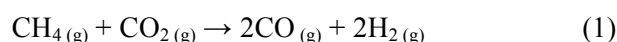
† A patent application based on the results presented here has been filed through Keele University.

Abstract

A hydrothermally synthesised nickel-strontium zirconate perovskite is shown to have excellent selectivity towards biogas reforming without suffering from deactivation due to carbon formation. Experiments reveal that this material is capable of very efficiently converting methane and carbon dioxide to synthesis gas, a mixture of hydrogen and carbon monoxide, at relatively low temperatures and, particularly importantly, high methane contents. Under these conditions we find that carbon production is extremely low and more importantly shows no increase over time, even after 10 days of continuous reforming activity. This conversion of a renewable product, using a catalyst prepared by low temperature hydrothermal methods, provides a route to future sustainable hydrogen, and oxygenate and higher hydrocarbon, production whilst lowering some greenhouse gas emissions.

Introduction

Catalytic reforming of biogas provides a clean and renewable method for the production of synthesis gas, which is widely used for hydrogen production, hydroformylation and Fischer-Tropsch reactions and as a fuel for solid oxide fuel cells (SOFCs).¹⁻⁵ Biogas is produced by the anaerobic bacterial digestion of biomass and consists predominantly of methane and carbon dioxide, typically in a 2:1 ratio. Methane and carbon dioxide can be reacted to form synthesis gas by the reaction shown in (1).⁶



Anthropogenic sources of biogas include sewage treatment and landfill sites,⁷⁻⁹ where currently much of this gas is vented wastefully into the atmosphere, significantly increasing greenhouse gas emissions. The catalytic conversion of biogas into synthesis gas has been the subject of much recent interest as it would provide a method of turning waste greenhouse gases into usable chemical feedstocks.¹⁰ Many of these studies have focussed on the use of supported metal catalysts, which suffer from deactivation due to carbon deposition from methane decomposition and sulphur poisoning from sulfur containing compounds present in biogas.¹¹⁻¹⁴

Previous studies on the reforming of biogas and dry reforming of methane-rich mixtures over supported nickel catalysts have suffered from numerous side reactions that can lead to significant carbon deposition, which eventually poisons the nickel surface or blocks the flow of reactive gases causing catalyst deactivation. Of particular concern are methane pyrolysis (2) when the rate of oxidation of the resulting carbon species is too low, and the Boudouard reaction (3).^{12, 15}



Although several Ru and Rh based catalysts have been shown to have high reforming rates for dry reforming with low carbon formation, although not for non-stoichiometric methane-rich mixtures, these are prohibitively expensive and a somewhat scarce resource.¹⁶⁻¹⁹ Previous

attempts to overcome these issues using perovskite materials have led to catalysts with low activities and/or poor selectivity or materials that phase separate under reaction conditions.²⁰

Mixed oxide catalysts for dry reforming have traditionally been prepared by various solid state synthesis methods requiring moderate to high temperature calcining, often in excess of 800 °C. These methods typically yield low surface area products that can often contain multiple unwanted phases. Recent work on hydrothermal synthesis has shown that mixed metal oxide materials can be readily prepared with single phase products at temperatures between 120 and 240 °C and that require no high temperature calcination/annealing steps.²¹⁻²⁴

Here we describe a phase pure nickel-strontium zirconate perovskite produced by hydrothermal synthesis which shows excellent selectivity towards biogas reforming without suffering from deactivation due to carbon formation observed for other dry-reforming catalysts despite having high methane contents.

Experimental Section

Synthesis of $\text{Ni}_{0.2}\text{Sr}_{0.8}\text{ZrO}_3$ catalyst

Strontium nitrate and nickel nitrate hexahydrate were dissolved in deionised water. Zirconium oxychloride octahydrate was then added, followed by sodium hydroxide. The mixture was stirred by hand to produce a thick gel, with the molar ratio $1\text{ZrOCl}_2 : 0.8\text{Sr}(\text{NO}_3)_2 : 0.2\text{Ni}(\text{NO}_3)_2 : 8\text{NaOH}$, before being transferred to a 23 mL Teflon-lined stainless steel autoclave and heated in a forced air oven at 180 °C. After 72 hours the autoclave was removed and allowed to cool to room temperature. The resulting product was subjected to three cycles of centrifuging (5000 rpm) and washing with deionised water before being dried at 60 °C overnight before use.

Catalyst characterisation

Powder X-ray diffraction patterns were collected using a Bruker D8 Advance diffractometer using a Cu $K\alpha$ source and a flat disc sample holder. Elemental analysis data were collected

using a Hitachi TM3000 scanning electron microscope equipped with a Bruker Quantax 70 EDS system. Surface area measurements were performed using a Quantachrome Autosorb-1-C with N₂ gas.

Catalytic reforming

For each reaction 20 ±0.5 mg of catalyst was placed in a quartz reactor tube and held in place with quartz wool. The reactor tube was heated in a Eurotherm controlled electric furnace and the temperature measured using a K-type thermocouple. The product gases were delivered to a quadrupolar mass spectrometer to give continuous real-time analysis of up to 12 pre-selected product masses.

Before each reaction the catalysts were reduced using a mixture of hydrogen and helium gases with flow rates of 2 mL min⁻¹ and 18 mL min⁻¹ respectively. The temperature of the catalysts was increased from room temperature to 850 °C at a rate of 10 °C min⁻¹, before cooling to the desired reaction temperature under an inert helium flow.

Reforming reactions were performed using a methane-rich (2:1) CH₄/CO₂ mixture at a variety of temperatures using flow rates of 1 mL min⁻¹ CH₄, 0.5 mL min⁻¹ CO₂ and 18.5 mL min⁻¹ He. For the partial oxidation experiments 18 mL min⁻¹ He, 2 mL min⁻¹ CH₄ and 1 mL min⁻¹ O₂ were used and for the steam reforming 18 mL min⁻¹ He, 1 mL min⁻¹ H₂O and 1 mL min⁻¹ CH₄. After each reaction the catalyst samples were cooled to room temperature under a flow of helium gas before carrying out a temperature programmed oxidation experiment. The samples were heated at 10 °C min⁻¹ up to 900 °C under a mixture of 2 mL min⁻¹ oxygen and 18 mL min⁻¹ helium and the resulting CO₂ desorption monitored and integrated to give the mass of carbon deposited during reaction, as well as some insight into the nature of the carbon deposited. The upper quantification limit for the amount of carbon present in the sample was approximately 40 mg.

Results and discussion

The nickel doped strontium zirconium perovskite synthesised by hydrothermal methods presented here is shown by powder X-ray diffraction to be a highly crystalline phase pure material with no presence of NiO or any other crystalline phases being present (Figure 1) and with a surface area of $37 \pm 2 \text{ m}^2 \text{ g}^{-1}$ for the dried material. Previous work on a SrTiO_3 perovskite showed that nickel could only be doped in to the structure up to a maximum of 1 mol% and attempts to increase the doping levels led to impurities of nickel oxide and strontium carbonate.²⁵ Figure 1 clearly shows no presence of either of these impurities and determination of the lattice parameters in the Pbnm spacegroup gave a unit cell of $a= 5.8112 \text{ \AA}$, $b=5.8014 \text{ \AA}$ and $c=8.2037 \text{ \AA}$. X-ray elemental analysis confirmed that the catalysts contained the expected 4.0 mol% of nickel and that no additional elements were present. To confirm that the Ni had been fully incorporated in to the perovskite structure and was not just present as NiO or Ni(OH)_2 , X-ray elemental analysis was performed on samples that had been further washed using 1M nitric acid. These results showed no alteration in the composition and this was confirmed by no observable changes between the powder X-ray diffraction patterns before and after washing. In order to show that the nickel was firmly bound within the perovskite structure and not prone to separation under reaction conditions, powder X-ray diffraction was performed on a reduced sample and the pattern showed no change from that in figure 1, indicating that no phase separation or crystallisation of new phases is occurring. Further analysis was performed post reaction and this also shows no observable peaks that could be attributed to nickel oxide. A more in-depth discussion of the structure and mechanism of the catalyst will be presented elsewhere.

Figure 2 shows the temperature programmed reaction profile and exit gas composition of a 2:1 methane/ CO_2 mixture over 4.0 mol% nickel doped SrZrO_3 . Reaction initially begins at approximately $425 \text{ }^\circ\text{C}$ and by $750 \text{ }^\circ\text{C}$ the catalyst is performing well as indicated by the steady production of carbon monoxide and hydrogen. The ratio of hydrogen to carbon monoxide from $850 \text{ }^\circ\text{C}$ upwards is approximately 1:1 possibly indicating that very little excess methane

decomposition is occurring. This is further confirmed by studying the overall methane conversion, which under the harsh conditions of a $\text{CH}_4:\text{CO}_2$ ratio of 2:1 will have a stoichiometric maximum of 50% conversion with the remaining 50% methane left unreacted or thermally decomposed.

Table 1 clearly shows that the methane conversions over 4.0 mol% nickel doped SrZrO_3 are very close to the maximum theoretical value of 50% and together with the $\text{H}_2:\text{CO}$ ratio, show that below 900 °C there is no indication of any excess methane decomposition. These results are confirmed through the analysis of the carbon residues deposited on the reacted catalyst samples by temperature programmed oxidation (TPO). Although similar carbon deposition values have been previously reported for other catalytic materials, these studies have all used significantly milder conditions ($\text{CH}_4:\text{CO}_2$ ratio of 1:1) where the expected carbon deposition should be substantially less due to the vastly reduced quantity of methane available for pyrolysis to occur.^{20, 26-28} Table 1 shows the quantity of deposited carbon for 4.0 mol% nickel doped SrZrO_3 as a function of temperature with a 2:1 mixture of methane/ CO_2 . It can be seen that at all temperatures the carbon deposition is consistent with the levels of methane decomposition observed. A more remarkable contrast between this new nickel doped SrZrO_3 and many other dry reforming catalysts is its behaviour over time. Figure 3 shows the results of a series of reactions at 850 °C for 4.0 mol% nickel doped SrZrO_3 for varying lengths of time. The results clearly show that the quantity of deposited carbon is unaffected by reaction time, and it is likely that the very small quantity of carbon that is observed (~3 mg) is deposited transiently within the first few minutes of reaction. These results show that 4.0 mol% nickel doped SrZrO_3 is promoting the dry reforming of methane within the methane-rich mixture without promoting the thermal decomposition of the excess methane whilst also still showing no signs of the Boudouard reaction. Further work to investigate the mechanism of these observations is currently in progress.

This material has also been shown to be active for steam reforming and partial oxidation. Figure 4 shows the temperature profile for these types of methane reforming which can be used as an adjunct to biogas reforming in order to convert the remaining methane to synthesis gas. Figure 4a shows the reaction with methane and oxygen (partial oxidation) where a steady increase in synthesis gas

production from around 530 °C is observed with only limited formation of the total oxidation products water and carbon dioxide. Figure 4b shows the steam reforming of methane; again a steadily increasing production of synthesis gas is observed from around 450 °C until total conversion of methane is achieved at around 800 °C. There is some evidence of the water gas shift reaction occurring from around 470 °C but this starts to decline from just 600 °C and is not observed above 800 °C.

Conclusions

The present wasteful venting of anthropogenic biogas needs to be addressed both in terms of wasting a hydrocarbon resource and reducing greenhouse gas emissions. One way of doing so is to catalytically convert the biogas to more commercially useful products such as synthesis gas. We have shown that a phase pure hydrothermally synthesised nickel doped strontium zirconate perovskite is highly effective for the conversion of a 2:1 CH₄:CO₂ mixture to synthesis gas without suffering from the effects of unwanted carbon deposition that can typically occur during dry reforming over conventional supported nickel catalysts particularly for methane-rich mixtures. In addition the catalyst has been shown to be active for both the steam reforming and the partial oxidation of methane from around 600 °C. The limited carbon deposition characteristics, flexible performance and minimal nickel contents of these catalysts should expedite the viable utilisation of biogas.

Acknowledgements

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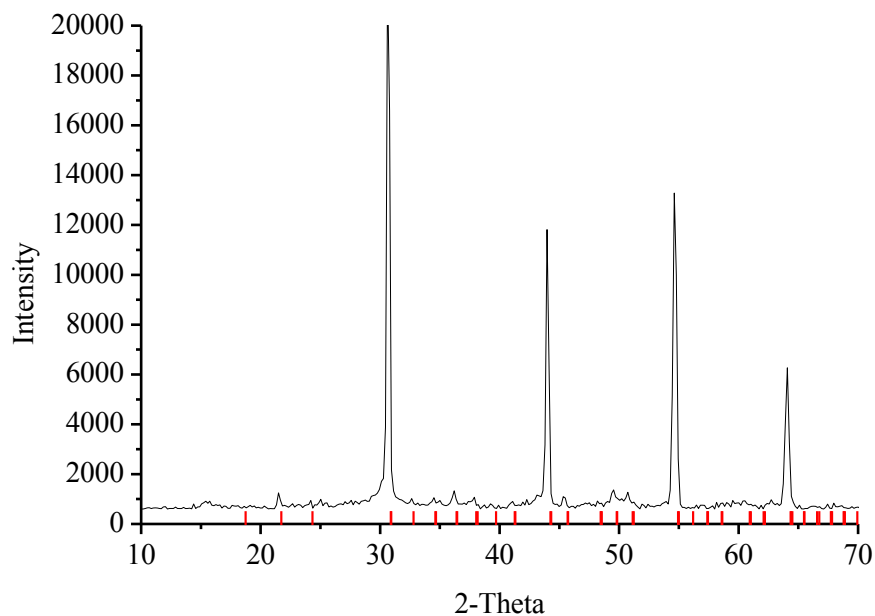


Fig. 1 Powder X-ray diffraction pattern of the dried as-synthesised 4.0 mol% nickel doped SrZrO₃ and corresponding tick marks for orthorhombic SrZrO₃ (Pbnm).

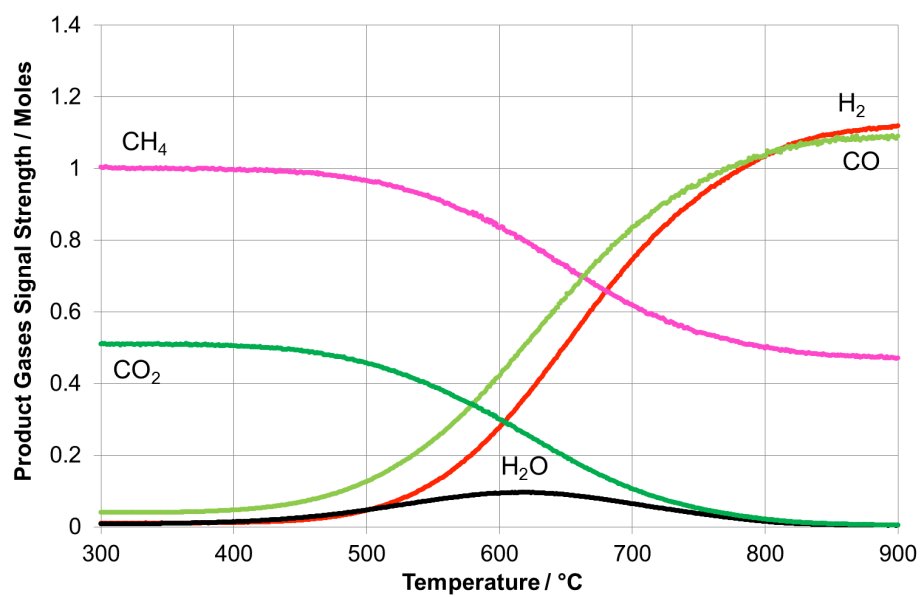


Fig. 2 Temperature-programmed profile (10°C) for the reaction of methane and carbon dioxide in a 2:1 ratio over 4.0 mol% nickel doped SrZrO₃.

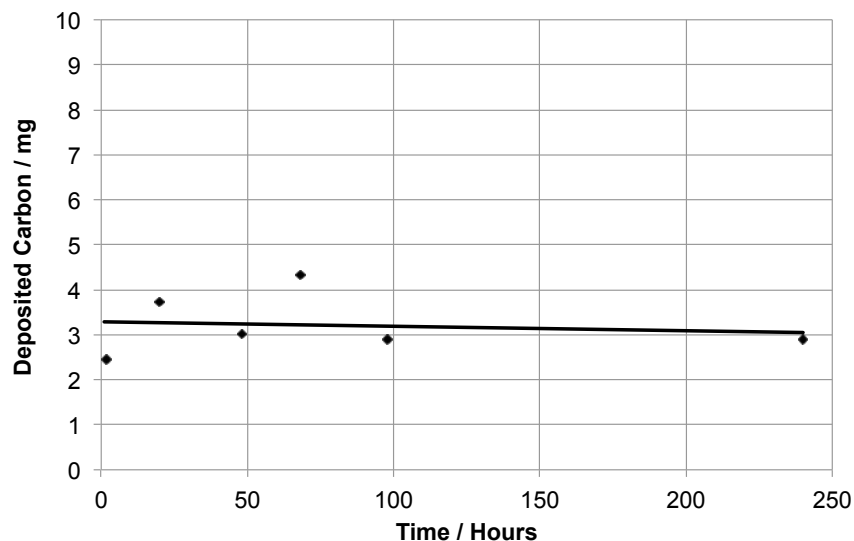


Fig. 3 Carbon deposition over time for simulated biogas reforming over 4.0 mol% nickel doped SrZrO_3 at 850 °C.

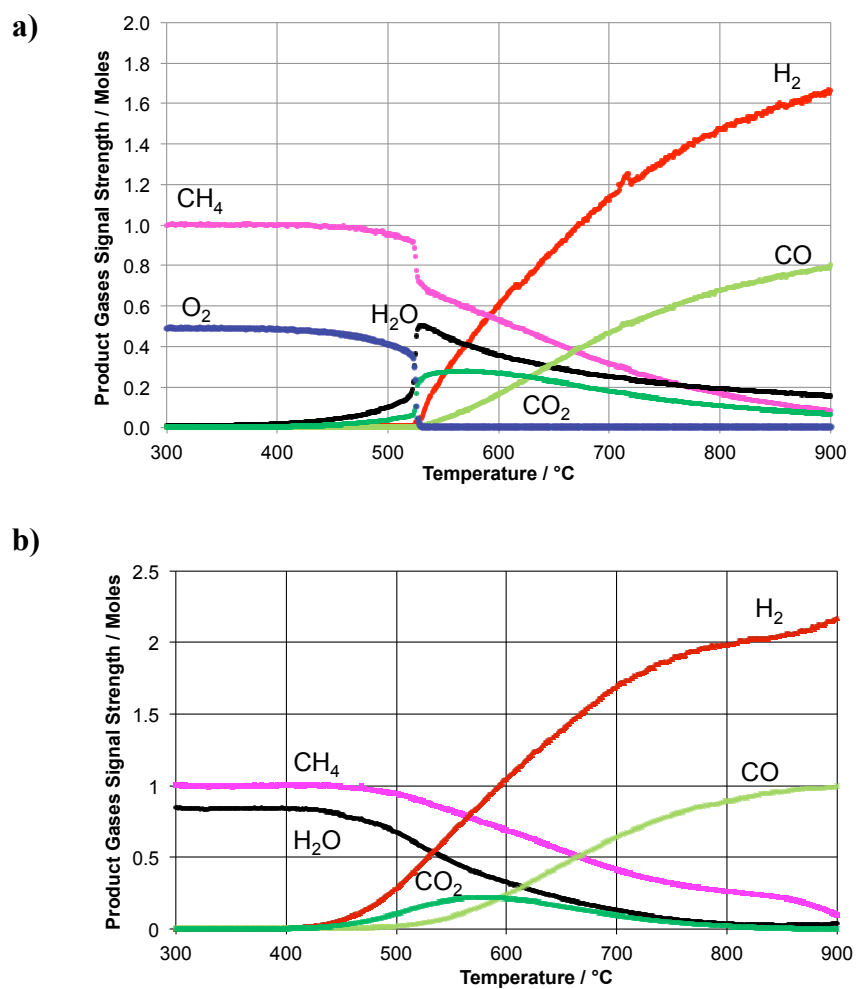
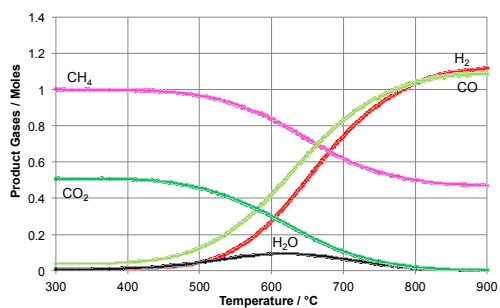


Fig. 4 Temperature profiles for (a) the oxidative and (b) the steam reforming of methane over 4.0 mol% nickel doped SrZrO_3 perovskite.

Table 1 Comparison of the CH₄ and CO₂ conversions and carbon deposition over 20 mg of 4.0 mol% nickel doped SrZrO₃ at 700, 800 and 900 °C and the theoretical maximum values.

Reforming Temperature / °C	% CH ₄ Conversion	% CO ₂ Conversion	Deposited Carbon / mg
700	42.6	86.3	1.1
800	44.0	89.7	1.6
900	55.0	99.0	2.6



A hydrothermally synthesised nickel-doped perovskite catalyst is demonstrated to have excellent selectivity for biogas reforming without suffering from deactivation by carbon formation.