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ARTICLE

A NOVEL PEROVSKITE BASED CATALYST WITH HIGH SELECTIVITY AND ACTIVITY FOR PARTIAL OXIDATION OF METHANE FOR FUEL CELL APPLICATIONS

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Solid oxide fuel cells (SOFCs) have the potential to revolutionise the present fuel economy due to their higher fuel conversion efficiency compared with standard heat engines and the possibility of utilizing the heat produced in a combined heat and power system. One of the reasons they have yet to fulfil this potential is that the conventional anode material of choice, a nickel/yttria-stabilised zirconia cermet, requires a high temperature production process and under operating conditions is susceptible to carbon and sulphur poisoning. Perovskite-based materials have been proposed as potential anode materials for SOFCs due to their potentially high electronic conductivity and catalytic properties. One of the problems in realizing this potential has been their low catalytic activity towards methane reforming compared to conventional nickel based cermet materials. A nickel doped strontium zirconate material produced by low temperature hydrothermal synthesis is described which has high activity for methane reforming and high selectivity towards partial oxidation of methane as opposed to total oxidation products. Initial studies show a very low level of carbon formation which does not increase over time.

Introduction

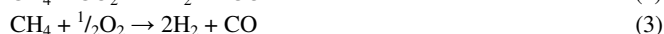
Despite their greater efficiency in converting fuel into electricity¹ fuel cells have so far only found niche applications. This is due to many factors but for most types of fuel cell a major stumbling block to commercialization has been the need to use hydrogen as a fuel². Solid oxide fuel cells (SOFCs) overcome this difficulty and are able to utilize a wide variety of carbon based fuels³⁻⁶. Unfortunately the high operating temperatures of SOFCs, whilst allowing for internal fuel reforming, means that they have a propensity to suffer from deleterious carbon deposition^{7,8}. Carbon deposition can result in either direct poisoning of the catalytic process within the fuel cell

through blocking of active nickel sites or mechanical blocking of the gas flow in the system. The present anode of choice is a nickel/yttria-stabilised zirconia (YSZ) cermet^{9,10}, which shows high conductivity and catalytic activity, but is also catalytically active for the carbon forming reactions. The need to reduce the carbon-forming activity has led to the search for suitable replacement anode materials¹¹⁻¹³.

Due to their potential for electronic and ionic conduction as well as their catalytic properties, perovskites have attracted considerable interest for use as alternative anode materials for use within solid oxide fuel cells¹⁴⁻¹⁶. Perovskites have the general formula ABO_3 ,

with A and B being cations whose charges must sum to +6 to offset the -6 from the three oxygens within the structure¹⁷. This gives a wide range of almost limitless possibilities especially when taking account of the fact that the A and B sites can be occupied by a variety of cations with multiple valencies. The challenge is to find a perovskite with the right properties for use as an anode material, which is catalytically active and selective for methane reforming but with limited catalytic activity towards the carbon forming reactions.

The initial step in utilizing a carbon based fuel such as methane within a fuel cell is to reform the fuel into a mixture of hydrogen and carbon monoxide (syn-gas) by the use of an oxidant such as steam (steam reforming)¹⁸ (1), carbon dioxide (dry reforming)¹⁹ (2) or limited oxygen (partial oxidation)²⁰ (3).



Due to its exothermic nature the least energy intensive of these reforming processes is partial oxidation(3), but a perennial problem with this approach is the tendency to go to complete or total oxidation²¹ (4) or deposit carbon through methane decomposition (5).



In order to make partial oxidation a viable process a catalyst needs to show a significantly higher selectivity towards carbon monoxide and hydrogen than towards carbon dioxide and water.

Previous studies have shown that nickel based catalysts can demonstrate high selectivity to partial oxidation over total oxidation^{22,23}, although carbon deposition through methane decomposition (5) and CO disproportionation can be problematic. In order to utilize this ability to catalyse partial oxidation several attempts have been made to incorporate nickel into a perovskite based catalyst^{24,25}. Unfortunately it has proved to be problematic to successfully incorporate nickel into the perovskite structure, and so in practice examples have simply been perovskite supported nickel based catalysts^{26,27}, which have often suffered from the same problems as more traditional nickel supported catalysts. Hydrothermal synthesis has been used extensively in the preparation of nanoporous framework materials such as zeolites, and more recently for the synthesis of mixed metal oxides. The method has been shown to offer several benefits over traditional solid state synthesis techniques including lower synthesis temperatures, single step process, control of oxidation states and isolation of metastable phases.

In this paper we describe the incorporation of nickel into a strontium zirconate using a hydrothermal synthesis method²⁸⁻³⁰ producing a high purity perovskite³¹ with high activity and selectivity for the partial oxidation of methane. The doped nickel is contained within

the structure isolating the nickel and so limiting any ensemble characteristics, which could lead to carbon formation. The nickel doped strontium zirconate perovskite also shows stability under reaction conditions and is still phase pure after a reaction cycle of four days.

Results and discussion

For comparison purposes a standard commercially available catalytic perovskite was chosen, in this case lanthanum strontium iron cobaltite. The temperature programmed reaction of a 2:1 methane/oxygen mixture over this perovskite is shown in figure 1.

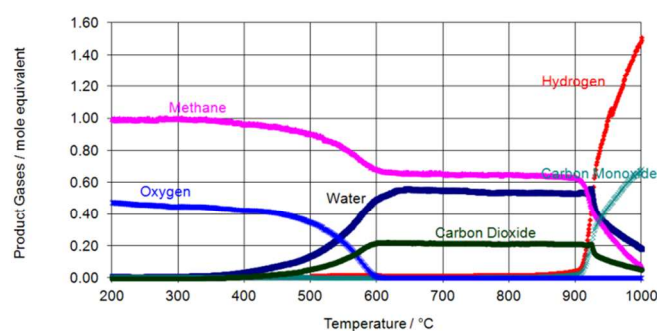


Figure 1. Temperature programmed reaction profile of methane and limited oxygen ($\text{CH}_4:\text{O}_2 = 2$) over lanthanum strontium iron cobaltite.

It can be seen that total oxidation dominates at all temperatures with only limited partial oxidation products, hydrogen and carbon monoxide, starting to become evident at temperatures in excess of 800°C. In contrast, the reaction of limited oxygen with methane for a 90:10 Ni/YSZ anode cermet, figure 2, shows some total oxidation as well as partial oxidation at lower temperatures but with partial oxidation predominating at temperatures above 650°C.

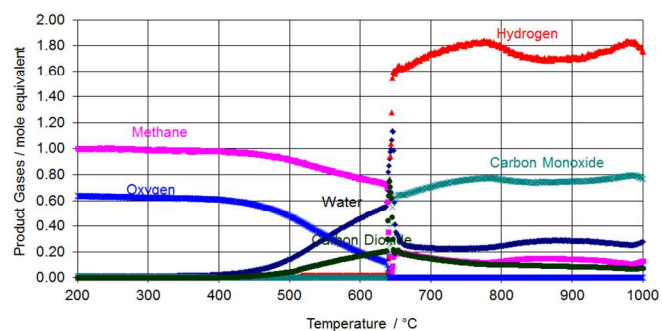


Figure 2. Temperature programmed reaction profile of methane and limited oxygen ($\text{CH}_4:\text{O}_2 = 2$) over a 90:10 Ni/YSZ anode cermet.

The reaction profile shows a sudden change from total oxidation products to partial oxidation, this could be due to conditioning of the catalyst or that the catalyst has partially re-oxidised at the lower temperatures leading to a surface more suitable for total oxidation. In order to investigate this further a reverse temperature programme was ran from 900°C downwards. The results of this are shown in figure 3.

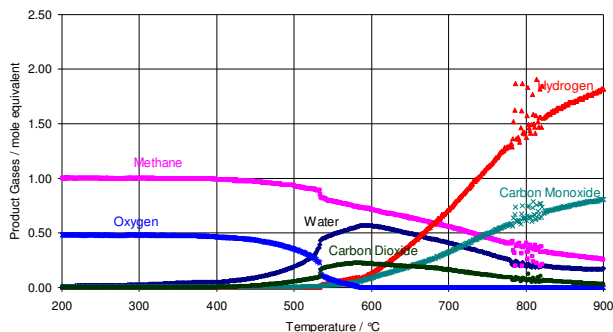


Figure 3. Reverse temperature programmed reaction profile of methane and limited oxygen ($\text{CH}_4:\text{O}_2 = 2$) over a 90:10 Ni/YSZ anode cermet.

The reverse programme shows a steady change over from partial to total oxidation and a falling off in catalyst activity at lower temperatures. Thus a definite hysteresis is observed between the forward and reverse reaction over 90:10 Ni/YSZ. This suggests the catalyst surface had undergone partial re-oxidation prior to reaction creating a surface with a propensity to total oxidation, once sufficient hydrogen is available the surface remains reduced and in a state to promote partial oxidation.

The hydrothermally synthesized $\text{Sr}_{0.8}\text{Ni}_{0.2}\text{ZrO}_3$, shows a similar forward profile to 90:10 Ni/YSZ with initial total oxidation products followed by a sudden change to partial oxidation at around 700°C, as shown in figure 4.

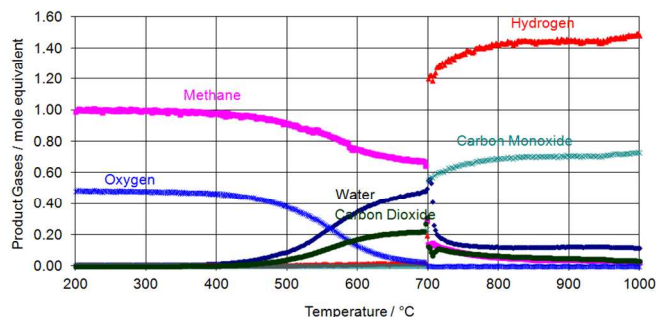


Figure 4. Temperature programmed reaction profile of methane and limited oxygen ($\text{CH}_4:\text{O}_2 = 2$) over $\text{Sr}_{0.8}\text{Ni}_{0.2}\text{ZrO}_3$.

Again the reverse temperature programmed reaction shows a steady conversion from partial oxidation to total oxidation products but in this case partial oxidation is more predominant and deactivation is more immediate once partial oxidation is effectively finished, see figure 5.

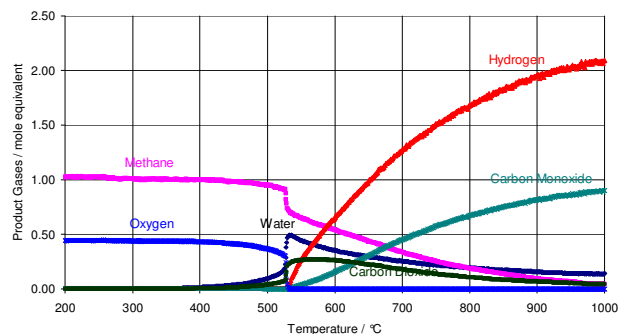


Figure 5. Reverse temperature programmed reaction profile of methane and limited oxygen ($\text{CH}_4:\text{O}_2 = 2$) over $\text{Sr}_{0.8}\text{Ni}_{0.2}\text{ZrO}_3$

In order to confirm that the catalytically active component in this perovskite was related to the nickel incorporation into the material, pure strontium zirconate, SrZrO_3 , was also tested. Undoped strontium zirconate shows limited catalytic activity at higher temperatures (figure 6), which is almost entirely confined to total oxidation products.

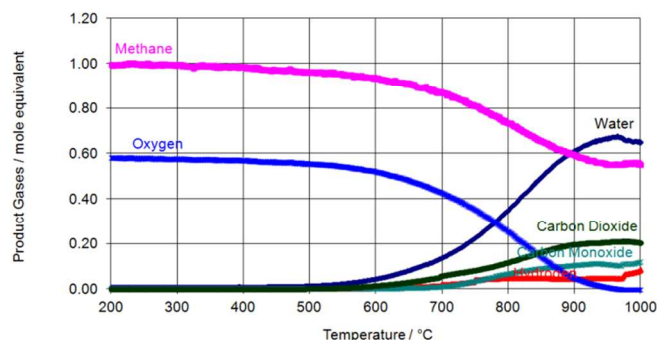


Figure 6. Temperature programmed reaction profile of methane and limited oxygen ($\text{CH}_4:\text{O}_2 = 2$) over SrZrO_3 .

Exchanging the zirconium for hafnium or exchanging the strontium for barium has only minimal effect on the partial oxidation performance of the perovskite (figures 7 and 8, both showing reverse temperature programme profiles to mitigate the hysteresis effect). Both display good activity at comparably low reaction temperatures, and high selectivity towards synthesis gas formation above $\sim 750^\circ\text{C}$, suggesting that the major effect is that of the incorporated nickel.

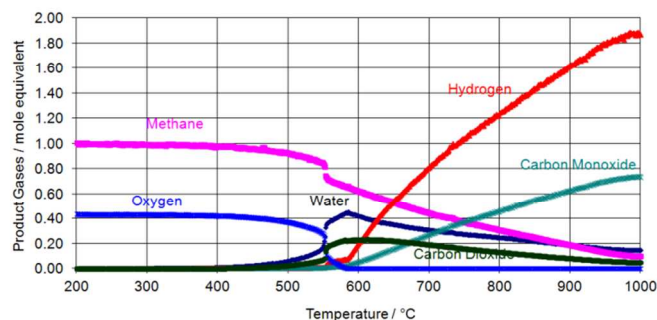


Figure 7. Reverse temperature programmed reaction profile of methane and limited oxygen ($\text{CH}_4:\text{O}_2 = 2$) over $\text{Sr}_{0.8}\text{Ni}_{0.2}\text{HfO}_3$.

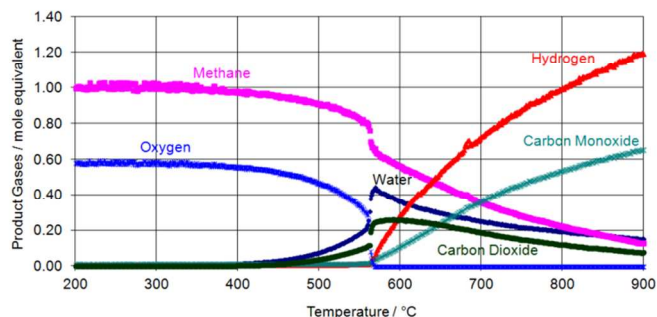


Figure 8. Reverse temperature programmed reaction profile of methane and limited oxygen ($\text{CH}_4:\text{O}_2 = 2$) over $\text{Ba}_{0.8}\text{Ni}_{0.2}\text{ZrO}_3$.

Reaction measurements were carried out at 700°C , 800°C and 900°C in order to investigate the stability and longevity of the $\text{Sr}_{0.8}\text{Ni}_{0.2}\text{ZrO}_3$ perovskite catalyst and to determine the profile of any carbon deposition with reaction time. The methane conversions, shown in figure 9, show a slow decline in conversion over time during reaction at 900°C and 800°C . No such decrease in activity over time is observed at 700°C , which could be due to slight sintering of the material resulting in a loss of surface area at higher reaction temperatures.

Temperature / °C	Time / hrs		
	20	42	70
700	0.5	5.95	2.45
800	1.15	0.3	1.7
900	0.2	8.75	0.10

Table 1. Effect of temperature and reaction time on carbon deposition during reaction of methane and limited oxygen ($\text{CH}_4:\text{O}_2 = 2$) over $\text{Sr}_{0.8}\text{Ni}_{0.2}\text{ZrO}_3$, given in mg of carbon per gram of catalyst.

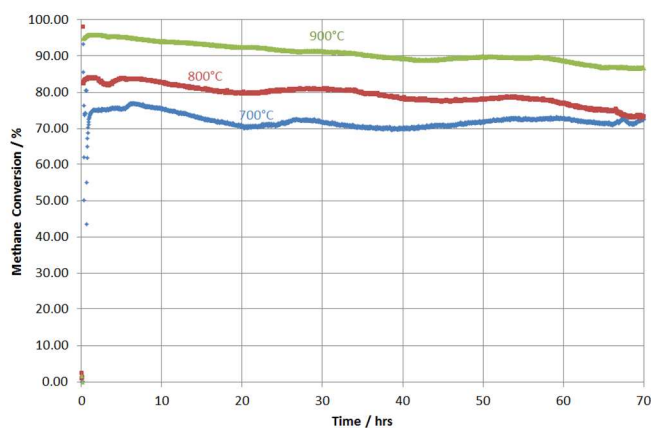


Figure 9. Methane conversion during reaction of methane and limited oxygen ($\text{CH}_4:\text{O}_2 = 2$) over $\text{Sr}_{0.8}\text{Ni}_{0.2}\text{ZrO}_3$ at different reaction temperatures.

Carbon deposition during reaction was investigated by post-reaction temperature programmed oxidation after 20, 42 and 70 hours. The results are summarized in table 1. It can be seen that there is little or no correlation between the amount of carbon deposited and time on stream or temperature. The amount of carbon deposited is extremely low. Even if there was some build-up of carbon over time it would take a considerable amount of time before this becomes an issue.

In order to investigate further the stability of the nickel doped strontium zirconate several reaction cycles were undertaken at 900°C the results of which in terms of methane conversion are shown in figure 10. The reaction cycles consisted of a pre-reduction, followed by isothermal reaction for 20 hours and a post reaction TPO.

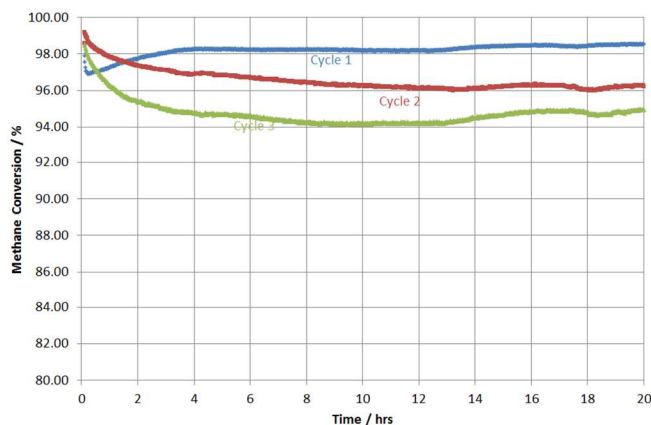


Figure 10. Methane conversion during reaction of methane and limited oxygen ($\text{CH}_4:\text{O}_2 = 2$) over $\text{Sr}_{0.8}\text{Ni}_{0.2}\text{ZrO}_3$ for different cycles at a reaction temperature of 900°C .

These results show a loss of activity of about 2% for each cycle undertaken. Further investigations are presently being undertaken to see if this loss of activity continues or if a stable rate of conversion is eventually achieved.

The phase purity and stability of the nickel doped strontium perovskite was investigated by powder x-ray diffraction (XRD) before and after a four day isothermal partial oxidation reaction at 900°C . The initial XRD pattern, figure 11, shows a phase pure sample with no sign of nickel oxide impurities suggesting that the available nickel is incorporated in the structure and not just supported on strontium zirconate.

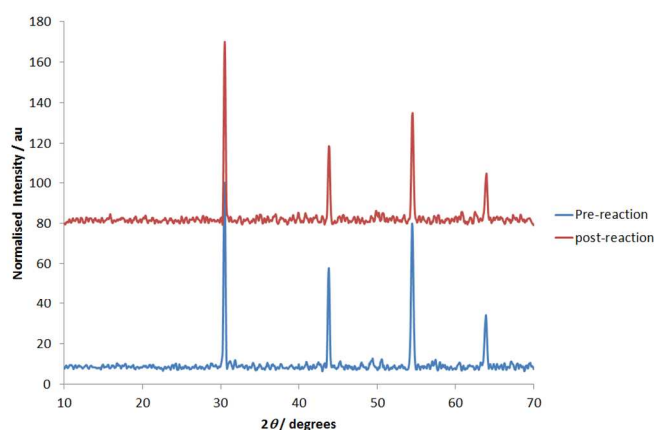


Figure 11. XRD pattern of $\text{Sr}_{0.8}\text{Ni}_{0.2}\text{ZrO}_3$ post 4 days isothermal reaction of methane and limited oxygen at 900°C , compared to pre-reaction profile.

After reaction no change was observed in the XRD pattern, figure 11, with no discernable nickel oxide peaks at around 37, 43 and 63 degrees 2θ , showing a good stability under reaction conditions.

Experimental

For comparison purposes several catalysts were prepared by varying methods. A physically mixed 90 wt.% nickel/yttria-stabilised zirconia (YSZ) anode cermet was produced by mixing nickel oxide and YSZ in a trichloroethene / methanol based solvent, milled for 3 hours and then sintered at 1300°C ³¹. This material was chosen to mimic the outer component of a dual layer SOFC anode. A commercially available lanthanum strontium iron cobaltite (Praxair) was used.

A hydrothermally synthesised nickel doped perovskite based around the formula $\text{Sr}_{0.8}\text{Ni}_{0.2}\text{ZrO}_3$ was prepared. The nickel doped perovskite was prepared by combining $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (Alfa Aesar, 98%),

Sr(NO₃)₂ (Alfa Aesar, 99%), Ni(NO₃)₂·6H₂O (Aldrich, 99%, NaOH (Aldrich) >97%) and ultra-pure water within the Teflon liner of a stainless steel autoclave and stirred to form a homogenous gel. The liner was sealed within the autoclave and heated in an oven at 180°C for 72 hours. The product was then removed, washed with ultra-pure water and recovered using several cycles of centrifuging at 4000 rpm. The sample was then dried and ground to form a powder used for catalytic testing³². For the barium A site perovskite, Ba(NO₃)₂ (Alfa Aesar, 99%) replaced Sr(NO₃)₂, and for the hafnium B site perovskite HfOCl₂·8H₂O (Alfa Aesar 98+%) replaced ZrOCl₂·8H₂O.

Catalyst testing was performed by placing 20 mg ± 0.5 mg of catalytic material between two pieces of quartz wool in a quartz tube of 7 mm external diameter and 4.5 mm internal diameter. This was placed in a furnace controlled by a Eurotherm 818 controller with a K-type thermocouple. A gas manifold delivered reactant gases to the furnace all independently controlled by mass flow controllers (Unit 7300). The exhaust gases were directly fed into a quadrupole mass spectrometer (MKS minilab), capable of simultaneously following up to 12 mass fragments in essentially real time³³.

Experiments were essentially of two types, temperature programmed reaction and isothermal. The temperature programmed experiments could be followed both in the 'up' cycle of increasing temperature and the 'down' cycle of decreasing temperature, to elucidate any hysteresis effects. Isothermal experiments were carried out to study long term stability of the catalyst, behaviour over time and to quantify carbon deposition with time. For all experiments reported here the reaction mixture consisted of a 2:1 methane:oxygen mixture, 2 ml min⁻¹ CH₄, and 1 ml min⁻¹ O₂, diluted in 18 ml min⁻¹ He.

Prior to reaction the catalyst samples were reduced in hydrogen, 2 ml min⁻¹ diluted in 18 ml min⁻¹ helium as a carrier gas. This was done by a temperature programme to 850°C at a rate of 10°C min⁻¹ to ensure complete reduction of the sample.

Post-reaction the sample was analysed for carbon deposition by temperature programmed oxidation. A flow of 2 ml min⁻¹ oxygen in 18 ml min⁻¹ helium was passed over the sample, which was then linearly heated from room temperature to 900°C at a rate of 10°C min⁻¹. The carbon dioxide and carbon monoxide evolved from the oxidation of the carbon deposited on the catalyst surface was followed continuously by mass spectrometry, and the carbon mass determined by integration and reference to a standard curve.

The nickel doped strontium zirconate catalyst was characterised by powder x-ray diffraction using a Bruker D8 Advance powder X-ray diffractometer using CuKα radiation.

Conclusions

The novel nickel containing perovskite, Sr_{0.8}Ni_{0.2}ZrO₃, is shown to have excellent activity and selectivity for the partial oxidation of

methane. At 900°C there is some degradation of performance with time but this is not observed at 700°C. Carbon deposition is minimal and shows no propensity to increase with time. It is suggested that this material will make an excellent reformer for the fuel cell industry due to possessing good catalytic properties, being synthesizable at lower temperatures than current materials and being resistant to characteristic carbon buildup that results in a short lifetime for cermet materials.

The flexibility of this new suite of materials resides in the ability to fine tune the active nickel catalyst by changing the cations in the A and B sites³⁴. This will enable the ability to select characteristics depending on the reforming application. Supported nickel catalysts possess inherent difficulties, such as susceptibility to sintering and ensemble variability, which is not the case for a perovskite with the active nickel bound in. These factors should result in a greater scope for flexible, focused catalyst production and application.

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Notes and references

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The introduction of nickel into a strontium zirconate perovskite converts the reforming characteristics from one of limited activity and total oxidation to one of high activity and selectivity for partial oxidation.

