

Catalytic properties of new anode materials for solid oxide fuel cells operated under methane at intermediary temperature

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Abstract

The recent trend in solid oxide fuel cell concerns the use of natural gas as fuel. Steam reforming of methane is a well-established process for producing hydrogen directly at the anode side. In order to develop new anode materials, the catalytic activities of several oxides for the steam reforming of methane were characterized by gas chromatography. We studied the catalytic activity as a function of steam/carbon ratios r . The methane and the steam content were varied between 5 and 30% and between 1.5 and 3.5%, respectively, corresponding to r -values between 0.07 and 0.7. Catalyst (ruthenium and vanadium)-doped lanthanum chromites substituted with strontium, gadolinium-doped ceria ($\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_2$) referred as to CeGdO_2 , praseodymium oxide, molybdenum oxide and copper oxide were tested. The working temperature was fixed at 850°C, except for 5% ruthenium-doped $\text{La}_{1-x}\text{Sr}_x\text{CrO}_3$ where the temperature was varied between 700 and 850°C. Two types of behavior were observed as a function of the activity of the catalyst. The higher steam reforming efficiency was observed with 5% of ruthenium above 750°C. © 2001 Elsevier Science B.V. All rights reserved.

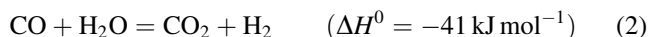
Keywords: Steam reforming; Solid oxide; Fuel cell; Catalytic activity; Internal reforming

1. Introduction

Methane is the major component of natural gas, an inexpensive and abundant natural resource used in energy production. In SOFC, the preferential reaction used to produce synthesis gas from methane is steam reforming (1):

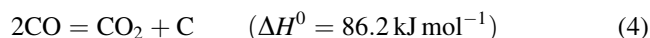
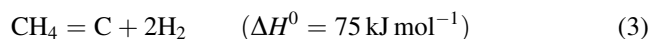


The reforming reaction is generally associated with the gas shift reaction (2):



Steam reforming of methane is highly endothermic and is normally carried out at a temperature above 500°C, typically around 700–800°C in the presence of a suitable catalyst. Two concepts of reforming have been developed: external and internal reforming [1]. In the first case, the reaction takes place in a separate reactor, which consists of a package of outside-fired tubes filled with nickel or noble metal catalysts. For high methane conversion and to avoid carbon

deposition, by methane cracking (3) or by the Boudouard reaction (4), steam is introduced in an exceeding ratio:



In the case of internal reforming, the reaction takes place directly at the anode side. A system efficiency of 70% can be attained. This process allows a better heat exchange between the endothermic reforming reaction and the exothermic electrochemical reaction within the stack. Its main drawbacks are, first, the tendency of carbon deposition, which gradually blocks the electrode electrocatalytic activity and, secondly, temperature gradients that result from the high endothermicity of the steam reforming reaction. A new concept has been proposed, referred to as gradual internal methane reforming [2]. It is based on a local coupling between the steam reforming and the electrochemical oxidation of hydrogen. The steam reforming produces hydrogen, which is electrochemically oxidized to produce water; this is used to reform methane. Thus, the reaction is distributed over the entire anodic surface. With gradual reforming, only a small initial concentration of steam has to be added and the temperature gradients in the anodic side are reduced.

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The material chosen for the SOFC anode must be chemically stable not only in the fuel inlet conditions, but also in the more oxidizing fuel outlet conditions. The low oxygen partial pressure in the anode compartment allows the use of metal as anode material. Because of its low cost and its high activity for the electrochemical oxidation of hydrogen, the Ni/YSZ cermet is the most common anode. Nevertheless, to obtain a high electrical conductivity, the nickel content in the cermet should be above 30%. For this composition, the thermal expansion coefficient does not closely match that of the YSZ electrolyte, which may lead to excessive thermal stresses. Moreover, with methane, a steam/carbon ratio above 2 is required [3] to avoid carbon deposition. One solution is to decrease the nickel catalytic activity. Doping the nickel/zirconia anode with small quantities of molybdenum leads to a substantial reduction in the amount of carbon deposition [4]. In the same way, Miromoto and Shimotsu [5] have proposed to decrease the catalytic activity of the Ni/YSZ cermet by masking with a Fe/YSZ cermet. The Fe/YSZ cermet has a high electrical conductivity but a low catalytic activity for the steam reforming reaction.

Some alternative cermet anodes have been developed. For example, Tokyo gas [6] has reported significant improvement in $V-I$ curves by doping Ni/YSZ electrolyte with 10% of ceria.

Other metals promote the reforming reaction, such as cobalt and some noble metals, such as Pt, Rh and especially Ru. Ruthenium is particularly attractive since it exhibits a low activity dealing with the carbon formation reactions. Suzuki et al. [7] have studied the Ru/YSZ cermet. Ruthenium has high steam reforming reaction activity. More recently, Vernoux et al. [8] measured the reforming activity of Ru/TiO₂, Ru/LaCrO₃ and Ru/YSZ. The YSZ cermet gave the worst performance at low steam/methane ratios at 700°C. For example, with a carbon/steam ratio around 2.5, the water conversion was 81% with Ru/YSZ instead of 100% with Ru/TiO₂ or Ru/LaCrO₃. At 800°C, these materials were found to be inert for methane cocking over periods of weeks.

The development of a new anodic material, which has catalytic activity and electrocatalytic activity, could be of interest for the SOFC with internal steam reforming of methane. For this purpose, we have studied new powders, which could have catalytic activity for the steam reforming

at intermediary temperature and with low initial steam content. The temperature was first fixed at 850°C. The steam/methane ratio was always lower than 1, between 0.07 and 0.7. Different oxides were studied, such as ceria doped with gadolinium, copper oxide, molybdenum oxide, praseodymium oxide. We also tested vanadium- and ruthenium-doped lanthanum chromite.

Lanthanum chromites have been intensively studied as promising interconnect materials for SOFC. The perovskite phase is stable at high temperature (1000°C) and across the P_{O_2} range (1–10⁻²⁹ bars) [9]. Pure LaCrO₃ is a p-type conductor and shows a low electrical conductivity of approximately around 0.6 S cm⁻¹ at 1000°C in air. AE (Mg, Sr and Ca) doping enhances the electrical conductivity by two orders of magnitude. Under hydrogen, Sr-doped LaCrO₃ exhibit the highest conductivity [10]. Moreover, La_{1-x}Sr_xCrO₃ is mechanically and chemically stable under reducing atmosphere for 1000 h [11]. Vernoux [12] have shown that strontium-doped lanthanum chromites presented interesting activity for hydrogen electrochemical oxidation.

2. Experimental

2.1. Catalysts

All the powders, except ruthenium-doped La_{1-x}Sr_xCrO₃ were commercial. The different characteristics of the investigated materials are summarized in Table 1. The particle sizes were measured by laser-granulometry. The specific areas were determined by the Brunauer–Emmett–Teller (BET) method with nitrogen at 77 K. The ruthenium-doped La_{1-x}Sr_xCrO₃ powders were synthesized by spray-pyrolysis technique [13]. The precursor was a solution of lanthanum, chromite, strontium and ruthenium nitrates in stoichiometric proportion.

A high frequency ultrasonic mist generator with piezoelectric ceramic transducers (1.7 MHz) atomized the solution (5 × 10⁻² mol l⁻¹). A gas mixture (reconstituted air) carried the aerosol with a flow rate of 6 l min⁻¹ through a tubular furnace heated at 800°C. After synthesis, these powders were fired at 1100°C for 1 h in air allows one to obtain high purity powders with an efficiency of 90%.

Table 1
Main characteristics of the studied powders

| Catalysts | Provided by | Grain size (μm) | Specific area (m ² g ⁻¹) | Symbols |
|--|---|-----------------|---|--------------------------------|
| La _{0.8} Sr _{0.2} Cr _{0.98} Ru _{0.02} O ₃ | Synthesized using pyrosol technique (this work) | 1–10 | 2 | LS20Ru2 |
| La _{0.8} Sr _{0.2} Cr _{0.95} Ru _{0.05} O ₃ | Synthesized using pyrosol technique (this work) | 1–10 | 2 | LS20Ru5 |
| La _{0.7} Sr _{0.3} Cr _{0.95} Ru _{0.05} O ₃ | Synthesized using pyrosol technique (this work) | 1–10 | 2 | LS30Ru4 |
| Cu ₂ O | Chimie Plus | 1–10 | – | CuO |
| La _{0.8} Sr _{0.2} Cr _{0.97} V _{0.03} O ₃ | Risø National Laboratory | 5–10 | 2 | LS20V3 |
| Ce _{0.9} Ge _{0.1} O ₂ | Rhône Poulenc | 1–10 | – | CeGdO ₂ |
| Pr ₂ O ₃ | Chimie Plus | 10–20 | – | Pr ₂ O ₃ |
| MoO ₃ | Ventron | 20–30 | – | MoO ₃ |

Table 2
Ionic radii of cations

| | La ³⁺ | Sr ²⁺ | Cr ³⁺ | Cr ⁴⁺ | Ru ³⁺ | Ru ⁴⁺ |
|--------------|------------------|------------------|------------------|------------------|------------------|------------------|
| <i>r</i> (Å) | 1.032 | 1.18 | 0.615 | 0.55 | 0.68 | 0.62 |

The ruthenium ion is substituted for chromium ion as indicated by the ionic radii, summarized in Table 2. The powder was referred to as La_{1-x}Sr_xCr_{1-y}Ru_yO₃. We have synthesized several ruthenium-doped strontium–lanthanum chromites. The ruthenium and strontium contents were between 0.02 and 0.05 and between 0.2 and 0.4, respectively.

In Fig. 1 the X-ray spectra of La_{0.7}Sr_{0.3}Cr_{0.95}Ru_{0.05}O₃ and of La_{0.7}Sr_{0.3}CrO₃ are compared. No intermediary phase containing ruthenium was detected. Later on, La_{0.8}Sr_{0.2}Cr_{0.95}Ru_{0.05}O₃ will be referred to as LS20Ru5 and La_{0.8}Sr_{0.2}Cr_{0.97}V_{0.03}O₃ as LS20V3. The LSCRu particle size was in the same order of magnitude as those of LS20V3, around 1 μm with agglomerate of 10 μm.

2.2. Catalytic measurement — equipment

A bench was used to evaluate the catalytic properties of these powders. It consisted of a gas analyzer and a reactor which is a conventional quartz unit with a porous disk (about 30% of porosity), 20 mm diameter. It has previously been described in detail [2]. The amount of catalyst was typically in the range of 200–500 mg. The reactor was heated by a furnace (Pekly JF 12) with a 200 mm hot zone. The reaction gases were mixtures of CH₄ (Air Liquide, 99.995% purity) and helium (Air Gaz, 99.995% purity) which was used as gas vector. The gas mixture flew in a thermostated bath where it was saturated by water. The overall gas flow rate was fixed at 100 ml min⁻¹. The contact time between the gas mixture and the powder was estimated at 1 ms. The reactor was

heated at 850°C under air. The reactor was then isolated under helium and the gas was analyzed by chromatography to determine the initial steam content. The gas mixture was then flown through the reactor.

Chromatography analyses were carried out at regular time intervals. The methane and steam contents were varied between 5 and 30% and between 1.5 and 3.5%, respectively.

After each study, a carbon deposition test was carried out. The reactor was flushed by pure helium for 20 min and then by a gas mixture (50% O₂–50% He). The chromatography analysis was focused on the carbon monoxide or carbon dioxide detection, which results from possible carbon deposit oxidation. The carbon detection sensitivity was of the order of 1 μg.

3. Results and discussion

The following parameters were used to characterize the catalytic activity, i.e. the methane conversion (5), the steam conversion (6) and the carbon monoxide selectivity (7):

$$C_{\text{CH}_4} = 100 \times \left(1 - \frac{(P_{\text{CH}_4})_f}{(P_{\text{CH}_4})_i} \right) \quad (5)$$

$$C_{\text{H}_2\text{O}} = 100 \times \left(1 - \frac{(P_{\text{H}_2\text{O}})_f}{(P_{\text{H}_2\text{O}})_i} \right) \quad (6)$$

$$S_{\text{CO}} = 100 \times \left(\frac{P_{\text{CO}}}{P_{\text{CO}} + P_{\text{CO}_2}} \right) \quad (7)$$

It should be pointed out that in all the experiments, we used steam content lower than methane content. The steam was the limiting factor of the methane-reforming rate. Four different reactions should be considered to analyze the catalytic activity of the powders studied: steam reforming (1) and the gas shift reaction (2), which decreases the carbon

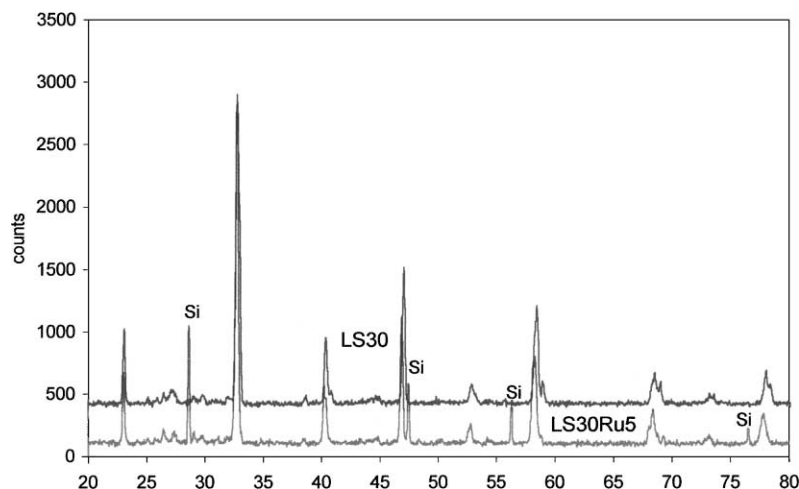


Fig. 1. Comparison of X-ray spectra obtained for LS30 and for LS30Ru5.

Table 3
Results of catalytic experiments with LS30Ru5 powder

| Initial conditions | $r = P_{\text{H}_2\text{O}}/P_{\text{CH}_4}$ | CH ₄ (%) | H ₂ (%) | H ₂ O (%) | CO ₂ (%) | CO (%) |
|---|--|---------------------|--------------------|----------------------|---------------------|--------|
| 20% CH ₄ ; 3.5% H ₂ O | 0.175 | 15.8 | 8.8 | 0 | 0 | 2.7 |
| 20% CH ₄ ; 3% H ₂ O | 0.15 | 16.0 | 8.6 | 0 | 0 | 2.3 |
| 20% CH ₄ ; 2.2% H ₂ O | 0.11 | 16.7 | 8.0 | 0 | 0 | 2.3 |
| 20% CH ₄ ; 1.5% H ₂ O | 0.075 | 17.6 | 6.8 | 0 | 0 | 1.5 |
| 20% CH ₄ ; 3.5% H ₂ O | 0.175 | 15.8 | 8.0 | 0 | 0 | 2.5 |
| 15% CH ₄ ; 3.5% H ₂ O | 0.233 | 11.3 | 8.9 | 0 | 0 | 2.4 |
| 10% CH ₄ ; 3.5% H ₂ O | 0.35 | 7.0 | 9.4 | 0 | 0 | 2.8 |
| 5% CH ₄ ; 3.5% H ₂ O | 0.7 | 2.8 | 9.2 | 0 | 0 | 2.9 |
| 25% CH ₄ ; 3.5% H ₂ O | 0.14 | 20.0 | 8.7 | 0 | 0 | 2.6 |
| 30% CH ₄ ; 3.5% H ₂ O; 2 h | 0.116 | 24.0 | 11.0 | 0 | 0 | 2.8 |
| 30% CH ₄ ; 3.5% H ₂ O; 24 h | 0.116 | 27.5 | 7.2 | 0 | 0 | 1.5 |

monoxide selectivity. If carbon deposition is observed, it results from methane cracking (3) or from the Boudouard reaction (4).

3.1. Strontium-based lanthanum chromite catalysts

Two components based on strontium-doped lanthanum chromites were studied, LS20V3 and La_{1-x}Sr_xCr_{1-y}Ru_yO₃ with $x = 0.2$ – 0.4 and $y = 0.02$ – 0.05 .

Table 3 summarizes the results obtained with LS30Ru5 in different experimental conditions. For all the steam/carbon ratios studied, the steam conversion and the carbon monoxide selectivity were equal to 100%, i.e. the steam reforming reaction was complete and the gas shift reaction did not occur.

Figs. 2–4 compare the results obtained with the different perovskite powders. The strontium content has no influence on the catalytic activity of LSCRu.

For steam/carbon ratio $r < 0.2$, the steam conversion and the carbon monoxide selectivity were equal to 100% and the methane conversion was around 18%, for all the studied powders. However, for ratios higher than 0.2, the powder activity depends on the catalyst content. With LS20Ru2 and LS20V3, the methane conversion, the steam conversion and the carbon monoxide decreased as a function of r . As an example, for $r = 0.35$, the steam conversion was around 75% with LS20Ru2 and 50% with LS20V3 instead of 100% with LS20Ru5. LS20V3 has the lowest catalytic activity. The carbon monoxide selectivity was around 90% for $r = 0.1$ with LS20Ru2 and LS20V3 and only 58 and 30% at $r = 0.7$, respectively, that corresponds to the occurrence of partial gas shift reaction. The methane conversion also decreases with LS20Ru2 and LS20V3: for $r = 0.1$ methane conversion was around 16% with LS20Ru2 and LS20V3, whereas for $r = 0.7$ methane conversion was around 10%. On the contrary, methane conversion increases

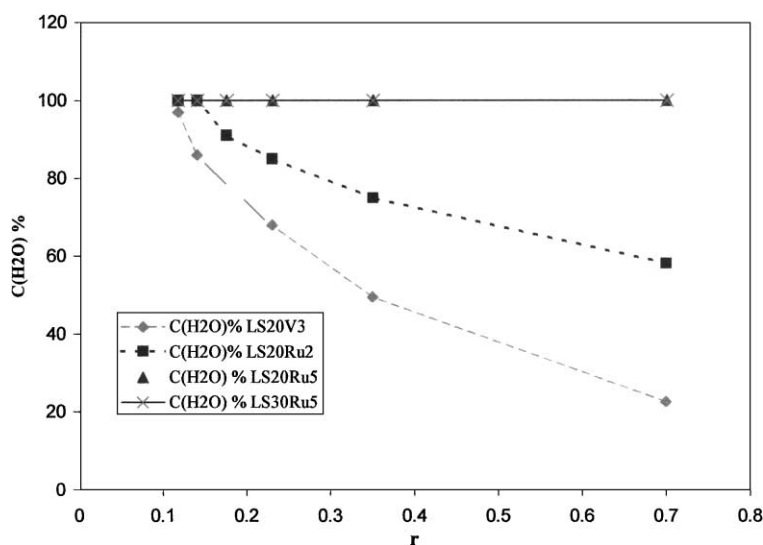


Fig. 2. Steam conversion as a function of r at $T = 850^\circ\text{C}$.

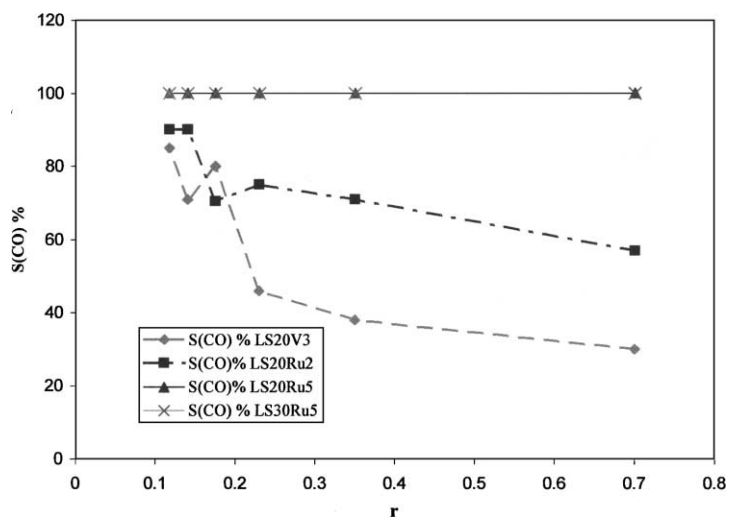


Fig. 3. Carbon monoxide selectivity as a function of r at $T = 850^\circ\text{C}$.

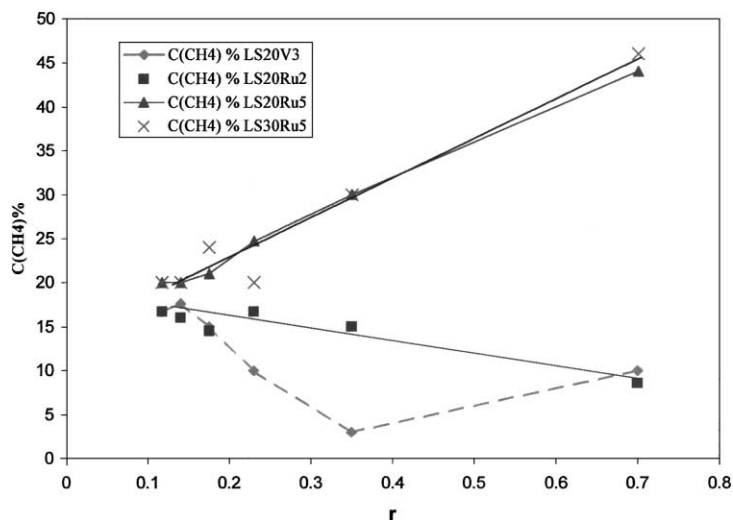


Fig. 4. Methane conversion as a function of r at $T = 850^\circ\text{C}$.

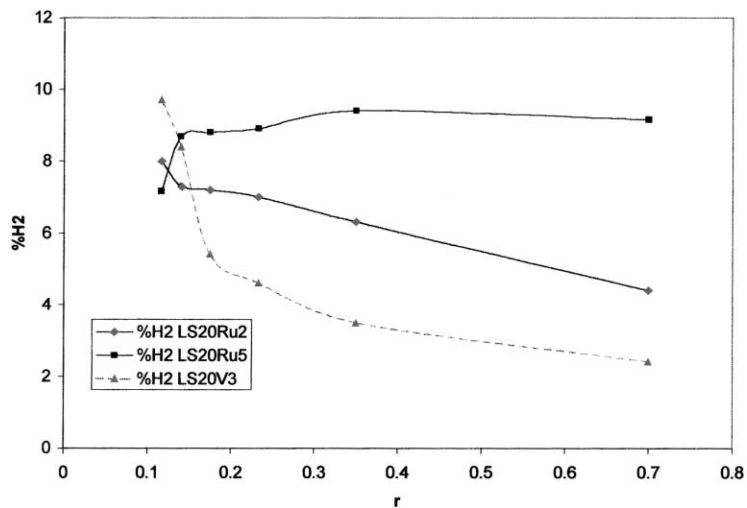


Fig. 5. Percentage of hydrogen produced as a function of r at $T = 850^\circ\text{C}$.

with 5% ruthenium-doped chromite, i.e. 20% conversion for $r = 0.1$ and 45% for $r = 0.7$.

Fig. 5 represents the hydrogen percentage variation as a function of r . The hydrogen content produced decreased with LS20Ru2 and LS20V3 when r increased. The contrary was obtained with LS20Ru5. For example, at $r = 0.35$, the percentage of hydrogen produced with LS20Ru5 was around 10, that is three times the initial steam content (3.5%). This is in agreement with the reforming reaction (1).

With LS20Ru2 or LS20V3, the percentage of hydrogen measured was ca. 6.5 and 3.5, respectively, for $r = 0.35$. The contents of hydrogen produced were less than the percentage foreseen according to Eq. (1) (i.e. 10%).

With 2% of ruthenium or 3% of vanadium, when the r -value increases, reforming reaction rate and the carbon monoxide selectivity decrease. The carbon content is lower and the steam content higher, so the gas shift reaction is favored, say, with low catalyst content, to obtain a steam reforming efficiency superior to initial gas mixture should contain a steam over methane ratio below 0.3.

With 5% of ruthenium, the efficiency of the steam reforming reaction is 100% for all the r -values studied. The steam reforming reaction is total. In this case, the steam reforming is limited by steam content.

It should be pointed out that with all these powders, no carbon deposition was observed and the catalytic activity was stable for more than 200 h under operating conditions.

3.2. Influence of the temperature on the LS30Ru5 catalytic activity

As was previously mentioned, with 5% of ruthenium, the efficiency of the steam reforming was 100% at 850°C. We studied the reforming efficiency versus temperature. Table 4 summarizes the different characteristic parameters as a

Table 4

Results of catalytic experiments with LS30Ru5 as a function of temperature ($r = 0.175$)

| T (°C) | Conversion (%) | | Selectivity of CO (%) |
|----------|------------------|-----------------|-----------------------|
| | H ₂ O | CH ₄ | |
| 700 | 60 | 9.0 | 60 |
| 750 | 100 | 16.3 | 100 |
| 800 | 100 | 15.6 | 100 |
| 850 | 100 | 19.0 | 100 |

function of temperature under 20% CH₄, 3.5% H₂O and 76.5% He. Above 750°C, the steam reforming reaction occurred with an efficiency of 100%. Moreover, no carbon deposition was observed.

3.3. Other catalysts

With MoO₃ and Mo, a very high carbon deposition occurred immediately. In Figs. 6 and 7, are shown the results obtained with the different oxides. Similar behavior can be observed between oxide powders, such as CeGdO₂, CuO and Pr₂O₃.

For $r > 0.25$, as shown in Figs. 8 and 9, the methane conversion and the hydrogen percentage are constant for all the powders tested. CeGdO₂ has the highest catalytic activity, the methane conversion was around 10%, whereas it was only 2% with CuO.

For $r < 0.25$, the methane conversion, the percentage of hydrogen and the carbon monoxide selectivity increased. At the lowest r -values, the catalytic activity of CuO was higher than that of CeGdO₂. As r is lowered, simultaneously, the kinetics of the gas shift reaction decreases and that of the steam reforming reaction increases.

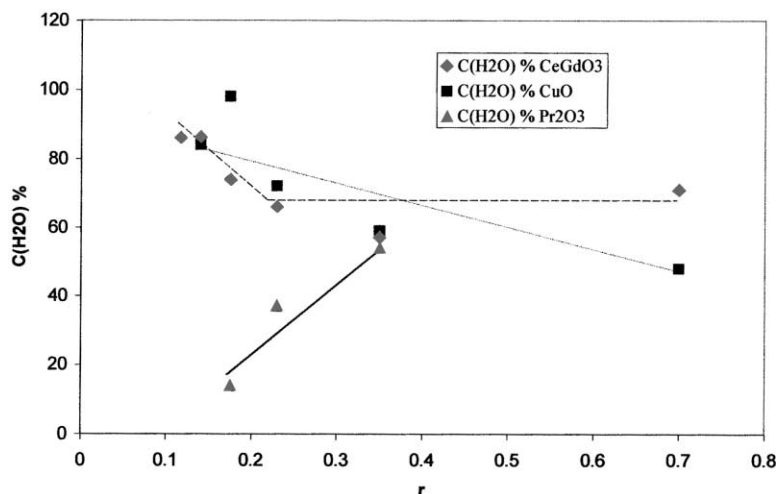


Fig. 6. Steam conversion as a function of r at $T = 850^\circ\text{C}$.

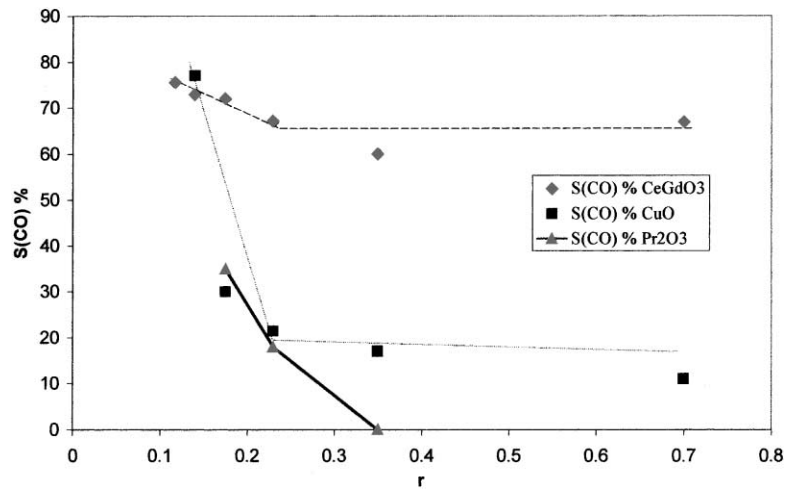


Fig. 7. Carbon monoxide selectivity as a function of r at $T = 850^\circ\text{C}$.

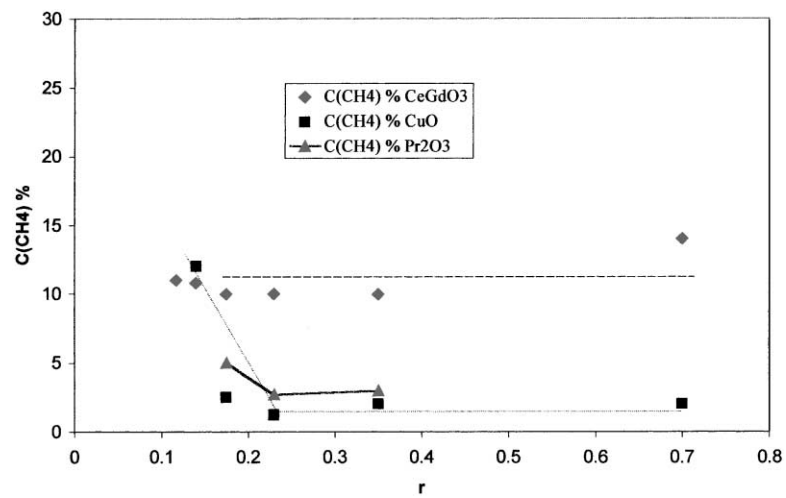


Fig. 8. Methane conversion as a function of r at $T = 850^\circ\text{C}$.

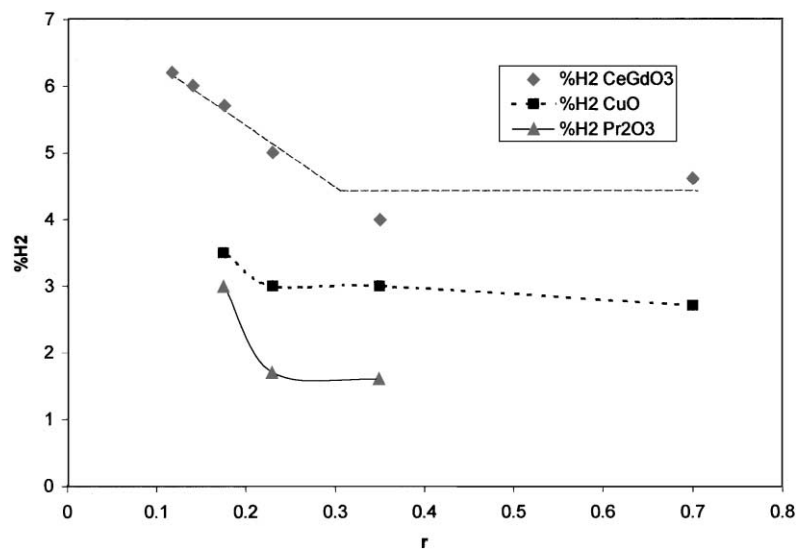


Fig. 9. Percentage of hydrogen produced as a function of r at $T = 850^\circ\text{C}$.

For CeGdO₂, a small carbon deposit was detected during the carbon deposition test. This means that with this powder, the value of r should be carefully controlled.

The results obtained with these three oxides were similar to those of LS20Ru2 and LS20V3. It seems that with a weak catalyst, the steam reforming reaction is favored as r is lowered, as long as no cracking reaction occurs.

4. Conclusion

Carbon deposition was observed with MoO₃, Mo and with CeGdO₂. The quantity of carbon was very great with molybdenum. Thus, the molybdenum cannot be used for steam reforming of methane in our experimental conditions. It should be pointed out, that with CeGdO₂, the r -value should be carefully controlled to avoid carbon deposition.

Pr₂O₃ and CuO have a weak catalytic activity for steam reforming in our conditions. However, no carbon deposition was observed. The catalytic activity of these powders could be sufficient for the gradual internal steam reforming. The activity is very sensitive to r -values for $r < 0.2$.

With the LSC powder doped with ruthenium or vanadium, the catalytic activity depends on the catalyst content. With 2 and 3% of ruthenium and vanadium, respectively, the catalytic activity is moderate. The steam reforming is favored at low ratio r . This result is very interesting. With 5% of ruthenium, the efficiency of the steam conversion is 100% down to 750°C and this reaction is favored at high ratio r . In all the cases, no carbon deposition was detected and no degradation of the catalytic activity was observed after more than 200 h under operating conditions.

We observed two different kinds of behavior as a function of the activity of the catalyst. With a low efficient catalyst, the steam reforming is favored at low ratio r , whereas with a catalyst, which has a high activity, the steam reforming is favored at high ratio r .

The LSRu5 has very interesting catalytic properties. It seems to be a promising catalyst for the SOFC operated under methane at intermediary temperature.

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