

# Methane Dry Reforming over Nickel Perovskite Catalysts

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In recent years dry reforming of methane (DRM) has received considerable attention as a promising alternative to steam reforming for synthesis gas (H<sub>2</sub> and CO) production. This process could be industrially advantageous, yielding a syngas with a H<sub>2</sub>/CO ratio close to 1, suitable for Fischer-Tropsch synthesis to liquid hydrocarbons and for production of valuable oxygenated chemicals.

The major drawback of the process is the endothermicity of the reaction that implies the use of a suitable catalyst to work at relatively low temperatures (923 – 1,023 K). Higher temperatures would make the process unaffordable for an industrial development and would increase the risk of undesirable side reactions, such as coke formation, that are the main causes of catalyst deactivation.

In this work the activity of nickel perovskite catalysts were studied and the results were compared with rhodium perovskite. It is well known that rhodium is very active and stable for dry reforming but its high cost makes its utilization limited. The Ni, due to its low cost, is a promising substitute even if it is more susceptible to coking. The perovskite structure allows a high dispersion of the metal into the catalyst increasing the catalytic activity. In this work the Ni perovskite was obtained with two methods (auto-combustion and modified citrate methods). The results pointed out that the Ni perovskite obtained with the auto-combustion method is a promising route for the use of Ni in this process. The experimental tests show that with Ni catalyst very good activity can be achieved from temperature of 973 K.

## 1. Introduction

In recent years CO<sub>2</sub> (dry) reforming of hydrocarbons such as methane (DRM) has received considerable attention as a promising alternative to steam reforming for synthesis gas (H<sub>2</sub> and CO) production (Tungkamani et al., 2013).

This process could be industrially advantageous, yielding a syngas with a H<sub>2</sub>/CO ratio close to 1, suitable for Fischer-Tropsch synthesis to liquid hydrocarbons and for production of valuable oxygenated chemicals. DRM features also some potential environmental implications, utilizing the main greenhouse effect contributors (CH<sub>4</sub> and CO<sub>2</sub>) and transforming them into high added value products.

Furthermore DRM allows the direct utilization as renewable feedstock of biogas from various anaerobic biological waste processes and its valorization as syngas or for hydrogen production (de Caprariis et al., 2014).

The major drawbacks are related to the high endothermicity of the dry reforming reaction (1) and to the concurring side reactions, the most important of which are the reverse water–gas shift reaction (2), the methane cracking reaction (3) and the Boudouard reaction (4)



The extent of these competitive reactions influences the selectivity of the DRM process, modifying the CH<sub>4</sub> and CO<sub>2</sub> equilibrium conversion. Moreover formation of carbon takes place from both reactions (3) and (4), and furthermore it is favoured in the overall usual operative temperature interval, at low temperatures ( $T < 973$  K) due to the reaction (4) and at high temperatures ( $T > 973$  K) for reaction (3). The consequent deactivation of DRM catalysts due to the carbon deposition constitutes a serious limit in the industrial DRM reaction development.

Thus, for achieving industrially relevant conversions at relatively moderate temperatures, the use of a catalyst with high activity and selectivity for the DRM reaction and with good stability towards carbon deposition is required.

Supported metals of groups 8, 9 and 10 are known to be active and stable catalysts for the DRM reaction, the order of activity for these metals is Ru > Rh > Ni ~ Ir > Pt > Pd (Bradford and Vannice, 1999). Despite the high activities and low sensitivities to carbon deposits of the noble metals, costs and limited availability of these metals discourage their widespread industrial applications. Nickel is more promising since Ni-based catalysts are relatively inexpensive. However, nickel is more susceptible to coking and deactivates more rapidly than noble metals.

Perovskite-type oxides (ABO<sub>3</sub>, where A = alkali, alkaline earth or rare-earth elements and B = transition metal) as precursors in the catalytic DRM are receiving growing attention. These oxides show high thermal and hydrothermal stability and when subjected to reduction of the B-sites cations they produce nanometric particles with the transition metal highly dispersed at the surface of a basic support, thus increasing the catalytic activity and stability and providing unfavourable conditions to carbon deposition. Moreover the catalytic performances can be strongly affected by the partial substitution at A and B sites, modifying the transition metal oxidation state, the oxygen mobility within the crystal lattice and the catalyst redox properties (Valderrama et al., 2010).

In this work the activity of a Ni-based perovskite in the form of BaZr<sub>(1-x)</sub>Me<sub>x</sub>O<sub>3</sub> was evaluated and the results were compared with the same perovskite using Rh as active metal. In order to evaluate the influence of the catalyst preparation methods, two different methods were used, the modified citrate (Viparelli et al., 2005) and the auto-combustion ones (Sharma et al., 2014). The catalyst preparation by means of auto-combustion presents some advantages over the modified citrate methods: simple reagents and procedure, formation of high purity products, stabilisation of metastable products, special equipment not required and limited agglomeration of final powder product. Combustion synthesis is a two-step process: formation of precursor and then autoignition. The processing parameters that affect the properties of final product are fuel to oxidizer ratio, type of fuel, amount of fuel percentage, ignition temperature, water content in precursor, pH of the solution. In order to evaluate the influence of the type of fuel, three different fuels were tested, citric acid with ammonia, urea and glycine.

## 2. Experimental section

### 2.1 Experimental set-up

The laboratory set-up, reported in Figure 1, is composed by a quartz tube reactor (id=0.8 cm, h=50 cm) equipped with a quartz frit for the formation of the catalyst bed made of 0.1 g of catalyst diluted in 2 g of silicon dioxide. The reactor was heated by an external cable heater controlled by a K-type thermocouple. The total inlet flow was kept constant for all the performed tests at 0.6 l min<sup>-1</sup>. The operative conditions used in the experimental tests are reported in Table 1.

Table 1: Operative conditions used in the experimental tests.

Operative conditions	
Temperature (K)	873-1023
Contact time (g <sub>cat</sub> min l <sup>-1</sup> )	0.67
CO <sub>2</sub> :CH <sub>4</sub> ratio	1.0
N <sub>2</sub> flow rate (l min <sup>-1</sup> )	0.3

At the reactor exit the water produced with the reverse water gas shift reaction was condensed and then the gas was sent to an online analyzer for the CO, CO<sub>2</sub> and CH<sub>4</sub> species (Simens Ultramat 23). The hydrogen concentration was analyzed with a gas chromatograph (DANI 3800) equipped with TCD using Ar as carrier gas sampling the gas every 10 min.

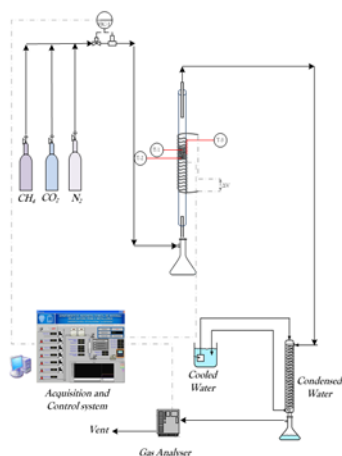


Figure 1: Dry reforming experimental set-up.

## 2.2 Catalyst synthesis

A modified citrate method (Viparelli et al., 2005) was used for the synthesis of the Rh and Ni perovskites, containing respectively a percentage of active metal of 5 % ( $\text{BaZr}_{(1-x)}\text{Rh}_x\text{O}_3$ ) for Rh and 10 % for Ni ( $(\text{BaZr}_{(1-x)}\text{Ni}_x\text{O}_3)$ ). A solution of citric acid was added under continuous stirring to a water suspension of the zirconium precursor (zirconium isopropoxide) and the mixture was kept at its boiling point for 4 hours in order to assure the complete solubilization of zirconium. After cooling, a water solution containing citric acid, the A-site cation precursor (barium oxide) and the active metal precursors (rhodium acetate or nickel nitrate hexahydrate) was added.

The resulting solution was neutralized with concentrated ammonium hydroxide and then slowly evaporated under vacuum to obtain a low density spongy material. The solid citrate precursor was crushed and sieved to obtain particles with dimension ranging from 150 to 300  $\mu\text{m}$ , then the organic part was decomposed in a fixed bed reactor at 673 K with a  $\text{N}_2\text{-O}_2$  mixture containing 2 % of  $\text{O}_2$ , and finally calcined at 1,123 K for 5 h to obtain the mixed oxide.

For what concerns the autocombustion method three Ni-based catalysts were prepared with three different oxidizers. The method consists of adding the oxidizer (glycine, urea and citric acid with ammonia) to an aqueous solution of Ni nitrate to obtain a  $\text{NO}^{-3}/\text{NH}_2$  ratio equal to 1 (Sierra et al., 2009). The resulting solution was slowly evaporated at  $\sim 373$  K until a green gel was obtained. The gel was heated up to around 573 K, a temperature at which the autoignition reaction takes place producing a powdered precursor which still contains carbon residues. Calcination at 1,173 K for 6 h eliminates all the remaining carbon and leads to the formation of the perovskite structure.

To evaluate the formation of the perovskite structure and the degree of crystallinity, X-ray diffraction (XRD) was performed on all the obtained samples. XRD patterns were obtained using an X-ray microdiffractometer, Rigaku D-max-RAPID, using Cu-K $\alpha$  radiation.

## 3. Kinetic model

The kinetic modelling of the process was performed taking into consideration only the dry reforming reaction. Under steady state conditions only one continuity equation is required for completely describing methane conversion: the mass balance for  $\text{CH}_4$ . In these conditions, considering a small volume of catalytic bed, the mass balance can be written as:

$$F_{\text{CH}_4,\text{in}} - F_{\text{CH}_4,\text{out}} = (-r_n) \cdot w \quad (5)$$

Where  $w$  is catalyst weight [g].

Using Eq(5) it is possible to calculate the apparent reaction, or net reaction, rate of methane steam reforming expressed in units of  $\text{mol g}^{-1} \text{s}^{-1}$ .

In absence of significant deactivation and of variations of thermodynamic and transport phenomena, forward reforming rates ( $r_f$ ) can be rigorously obtained by the measured net reaction rates ( $r_n$ ), using the equilibrium approach, by defining the  $\beta$  and  $\eta$  parameters from dry reforming thermodynamic reaction data and the experimental partial pressures  $P_i$  of reactants and products (Maestri et al., 2008):

$$\beta = 1 - \eta \quad (6)$$

where  $\eta$  is the ratio between the dry reforming thermodynamic constant at the operative conditions and at the equilibrium.

$$r_f = \frac{r_n}{\beta} \quad (7)$$

The determination of the dependencies of the forward reaction rate is based on the work of Wei and Iglesia, which have reported that there is no dependence on the  $\text{CO}_2$  (Wei and Iglesia, 2004), therefore,  $\text{CH}_4$  dry reforming rates become simply first order in  $\text{CH}_4$  and zero order in  $\text{CO}_2$ :

$$r_f = KP_{\text{CH}_4} \quad (8)$$

Additional effects due to the concentrations of the products are taken into account in the evaluation of the parameter  $\beta$ .

Kinetic parameters of the dry reforming, activation energy  $E_a$  and pre-exponential factor, can be carried out with the Arrhenius law, linearizing the equation and taking into account data at different temperatures.

## 4. Results and discussion

### 4.1 Catalyst characterization

The results of the X-ray diffraction analysis are reported in Figure 2 for the reference perovskite ( $\text{BaZrO}_3$ ), the perovskite synthesized with the citrate method and the one made by auto-combustion using glycine as oxidizer. The peaks corresponding to the  $\text{BaZrO}_3$  refers to a well-developed perovskite structure (Taglieri et al., 1999). Looking at the perovskite synthesized by auto-combustion, it can be noticed that the structure shows all the peaks of the  $\text{BaZrO}_3$  even if with slightly smaller intensity. Two more peaks are evident and they refer to the Ni in metallic form and the NiO, as highlighted in the plot. This result indicates that not all the Ni is included in the perovskite structure but a part is segregated probably causing a decreased activity of the catalyst with respect to a complete perovskite structure (Courson et al., 2000).

On the other hand, the XRD of the catalyst made with the modified citrate method reveals that the perovskite structure is not formed and that a great part of the Ni is segregated. The peaks referring to the Ni and the NiO have high intensity while the peaks corresponding to the reference perovskite lattice are of small intensity or not present at all.

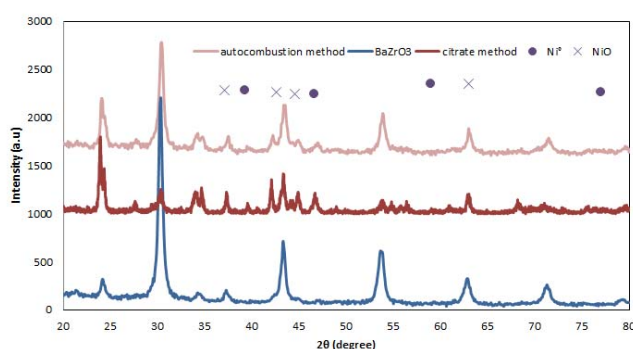


Figure 2: XRD of  $\text{BaZrO}_3$ ,  $\text{BaZr}_{(1-x)}\text{Ni}_x\text{O}_3$  prepared for auto-combustion and  $\text{BaZr}_{(1-x)}\text{Ni}_x\text{O}_3$  prepared with the citrate method.

### 4.2 Methane dry reforming results

Experimental tests at different temperatures were performed in order to study the range of operability of the catalysts. Furthermore different temperature tests are requested for the kinetic study. A long term test, lasting

65 h, was conducted to evaluate the resistance of the Ni catalyst to carbon deposition with respect to the Rh perovskite catalyst that it is known to have a high resistance to this phenomenon (Zeppieri et al., 2010). In the Figure 3 the results of the methane conversion and of the H<sub>2</sub>/CO ratio are reported for the four perovskites with Ni.

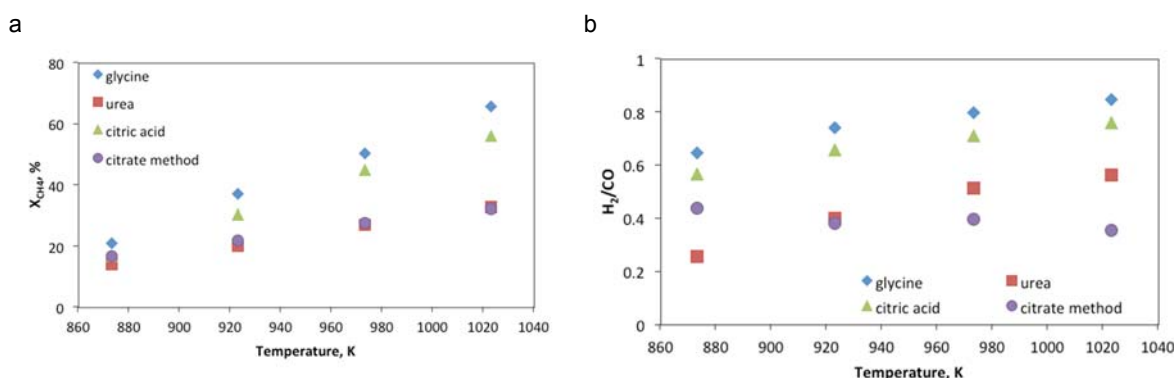


Figure 3: a-CH<sub>4</sub> conversion for the four Ni catalysts; b-H<sub>2</sub>/CO ratio.

The perovskite synthesized by auto-combustion using glycine as oxidizer shows the best performances: the methane conversion at 1073 K is about 65 % with a H<sub>2</sub>/CO ratio of 0.84. Similar results are obtained using citric acid with ammonia. On the other hand, in this range of temperature, the perovskite prepared with urea has a much lower activity: the conversion of methane, indeed, do not reach the 30 % at 1,073 K, which is a very low value.

These results are confirmed by the analysis of the kinetic parameters (Table 3). The perovskites made with glycine and citric acid present almost the same value of kinetic parameters, comparable with literature values (Zeppieri et al., 2010). The kinetic parameter values referring to the catalyst synthesized with urea are very low, probably due to the range of temperatures used in the experimental tests, out of the interval of activity of this catalyst.

Table 3: Kinetic parameters of the three catalysts prepared with the auto-combustion method.

Operative conditions	E <sub>a</sub> (kJ mol <sup>-1</sup> )	K <sub>0</sub> (mol g <sub>cat</sub> <sup>-1</sup> s <sup>-1</sup> atm <sup>-1</sup> )
Glycine	105.2	71969
Citric acid	92.0	65
Urea	59.1	21135

From Figure 3 it can be also that the catalyst prepared with the modified citrate method presents the lowest activity, with a H<sub>2</sub>/CO ratio that never exceeds 36 %. As already noticed the perovskite structure in this case was not formed, almost all the Ni is in metallic or in oxide form, not properly dispersed in the catalyst structure. In fact, when the catalyst is fresh, for the first 10 minutes of the experimental tests, value of methane conversion of about 50 % are reached and suddenly the catalyst deactivates.

The comparison of the methane conversion between the Ni perovskite synthesized with the auto-combustion method using glycine as oxidizer and the Rh perovskite one is reported in Figure 5a, showing that the two catalyst almost the same performances of the Rh catalyst in that temperature range. Even though the higher amount of Ni in the catalyst, 10 % with respect to the 5 % of Rh, the process with Ni is to be preferred due to the lower operational costs. The difference appears when the Ni catalyst is tested for 65 h (Figure 5b). The Rh perovskite does not deactivate at all, while the Ni one does not deactivate for the first 30 h of operation and then presents a decrease of activity of about 25 %.

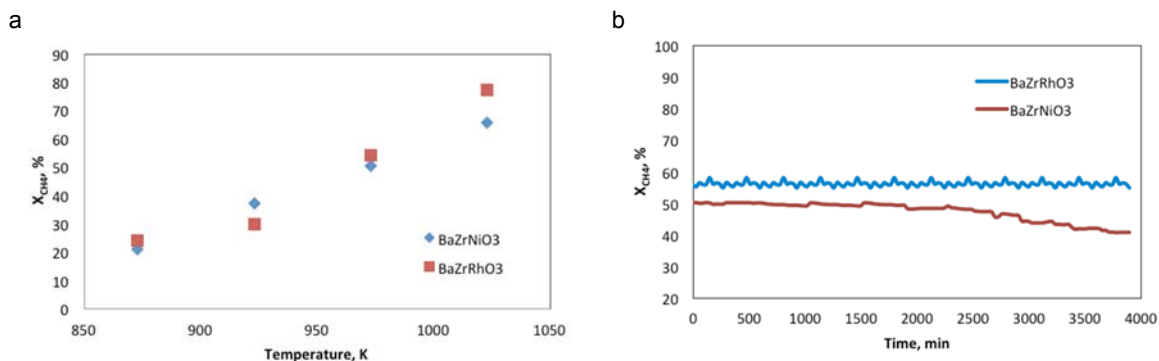


Figure 5: a-comparison of the CH<sub>4</sub> conversion between the BaZr<sub>(1-x)</sub>Rh<sub>x</sub>O<sub>3</sub> and the BaZr<sub>(1-x)</sub>Ni<sub>x</sub>O<sub>3</sub> (glycine) at different temperature; b-comparison of the CH<sub>4</sub> conversion for the BaZr<sub>(1-x)</sub>Rh<sub>x</sub>O<sub>3</sub> and the BaZr<sub>(1-x)</sub>Ni<sub>x</sub>O<sub>3</sub> (glycine) in the long term test performed at 700 °C.

## 5. Conclusions

In this work the performances of BaZr<sub>(1-x)</sub>Ni<sub>x</sub>O<sub>3</sub> perovskites synthesized with two different methods were analysed and compared with the BaZr<sub>(1-x)</sub>Rh<sub>x</sub>O<sub>3</sub> perovskite in the dry reforming process. The modified citrate method does not allow to obtain the typical perovskite structure and the Ni is segregated and is found to be in metallic and oxide form by XRD analysis. This catalyst indeed does not work in the chosen range of temperature. Three similar Ni-perovskites were prepared with the auto-combustion method, changing the used oxidizer: glycine, citric acid with ammonia and urea, respectively. With the first two oxidizers, catalysts with good activity are obtained, the BaZr<sub>(1-x)</sub>Ni<sub>x</sub>O<sub>3</sub> prepared using glycine gives CH<sub>4</sub> conversion of 65 % and H<sub>2</sub>/CO ratio approaching 0.85. The long term test indicates that the Ni included in a perovskite structure is resistant to deactivation due to carbon deposition, in fact the loss of activities is limited, about 25 %.

From the results obtained in this work it can be concluded that Ni could be an interesting alternative to noble metal for methane dry reforming if included in a perovskite structure, allowing to reduce the operative costs. In this way good conversions are obtained at temperature lower than 1073 K and also a quite good resistance to deactivation of the catalyst is obtained

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