

# RHODIUM ON CERIA CATALYSTS FOR WATER-GAS-SHIF REACTION

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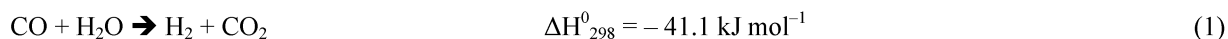
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The present paper deals with the study concerning the CO removal from reforming H<sub>2</sub>-rich gas stream through water gas shift WGS reaction over a 2% Rh-based catalysts supported on CeO<sub>2</sub> carrier. CeO<sub>2</sub> was prepared by Solution Combustion Synthesis; Incipient Wetness Impregnation method was used to deposit the active metal on the carrier. The catalyst activity at the powder level in a fixed bed micro-reactor highlighted that feeding a simulated reformat mixture (5% CO + 20% H<sub>2</sub>O + 11% CO<sub>2</sub> + 40% H<sub>2</sub>, N<sub>2</sub> balance), the equilibrium WGS curve was exceeded, due to the parasite methanation reactions of both CO and CO<sub>2</sub>, favored by the presence of the large hydrogen concentration in the reactor. A quite high CH<sub>4</sub> outlet concentration (max 8.5%) was determined. Then, tests at different weight space velocities WSV were carried out: the best performance was obtained by lowering WSV.

## 1. INTRODUCTION

Future energy generation for stationary, distributed and mobile applications will be based in a large extend upon fuel cell technology. In the majority of current applications, proton exchange membrane fuel cell (PEM-FC) technology is employed (Shukla, 2001; Carette, 2001). PEM-FCs are, regardless of their operating temperature, sensitive to carbon monoxide. Thus, a fuel processor for the H<sub>2</sub>-rich gas production (Ghenciu, 2002) is composed of the reformer itself and the gas purification items which may work catalytically or by membrane separation processes. Catalytic CO clean-up of all kind of fuels requires water-gas shift reactors, whatever the CO tolerance of current PEM-FCs may be. As the FC anodes can be poisoned even by impurities of CO, this gas has to be removed to a concentration below 50 ppm for the state-of-art Pt-Ru anode electro-catalysts (Fujiwara, 2002; Farrell, 2007; Cheng, 2007) and below 10 ppmv for Pt anode electro-catalysts (Divisek, 1998; Passalacqua, 2000; Bowers, 2007) for low temperature LT PEM-FCs, whereas for the high temperature HT PEM-FCs the maximum CO tolerance seems to be 30% (Li, 2003; Cheng, 2007).

The WGS reaction:



is limited by its thermodynamic equilibrium, which may be calculated according to the formula provided below (Newsome, 1980):

$$K_p = \exp\left(\frac{4577.8}{T} - 4.33\right) \quad (2)$$

Since at high temperatures CO conversion is equilibrium limited and at low temperatures is kinetically controlled, normally two steps of WGS are industrially used: a high temperature (HT) WGS step followed by a low temperature (LT) WGS one. Commercially a combination of the two WGS catalysts is used with in between a cooling stage. However, commercial catalysts pose some disadvantages (low activity and some thermodynamic limitations at high temperatures for the HT catalysts; pyrophoricity for the LT ones) that render the catalysts

themselves unsuitable for residential or automotive applications, where fast start-ups, carried out by heating-up the items chain with suitably produced flue gases, dictate the use of reactors with low catalyst volume, and therefore very active, and non-pyrophoric catalysts (Ghenciu, 2002). If more active WGS catalysts are developed, the CO conversion can then approach more favorably the equilibrium limit.

Several literature studies on catalysts for the WGS reaction considered noble metals (Pt, Au, Rh, Pd) on various oxide carriers (ceria, titania, alumina) (Hilaire, 2005; Jacobs, 2003; Jacobs, 2005; Kolb, 2007; Kolb, 2008; Luengnaruemitchai, 2003; Panagiotopoulou, 2004; Sakurai, 2005; Tabakova, 2004; Gurbani, 2010). In this work, a 2% Rh-based catalyst on CeO<sub>2</sub> was prepared: ceria, by means of the Solution Combustion Synthesis SCS method; the active metal was added on the carrier via the Incipient Wetness Impregnation IWI technique. The catalytic activity toward WGS reaction was tested at powder level in a fixed bed micro-reactor.

## **2. EXPERIMENTAL**

CeO<sub>2</sub> was prepared by SCS technique [Patil, 2002; Specchia, 2010]. Rh was deposited with the IWI method by using RhCl<sub>3</sub>·xH<sub>2</sub>O as precursor; the Rh chloride was dissolved in distilled water and the solution was added drop by drop over the support meanwhile thoroughly mixing the whole mass. The wet mass was then placed in an oven at 200 °C to evaporate water. The catalyst powder was calcined in still air for 2 h at 350 °C to remove the chloride ions. The Rh load was 2% in weight.

Firstly, the catalyst was characterized by XRD analysis (Philips PW1710 apparatus equipped with a monochromator for the Cu K $\alpha$  radiation) to verify the effective composition and derive qualitative indications of the presence of comparatively large Rh metal crystallite from its eventually visible peaks. The specific surface area of the Rh-supported catalyst was measured via N<sub>2</sub> by the BET method (Micromeritics ASAP 2020 C apparatus). The morphology of the as prepared catalyst was additionally examined by scanning electron microscopy (SEM FEI Quanta Inspect LV 30 kV apparatus) and field emission scanning electron microscopy (FESEM FEI Quanta Inspect 200 LV apparatus, coupled with EDAX GENESIS SUTW-sapphire detector).

A fixed bed micro-reactor (a quartz tube of 4 mm I.D.), heated up by a PID regulated oven and containing 0.3 g of catalyst in powder, diluted with 0.5 g of SiO<sub>2</sub>, held in place by flocks of quartz wool, was used for the WGS reaction. A K-type thermocouple was inserted into the reactor to measure the temperature of the catalytic bed. The catalyst was firstly reduced into the micro-reactor flowing 50% H<sub>2</sub> in N<sub>2</sub> (100 Nml min<sup>-1</sup>) at 200 °C for 1 h, and then tested between 150 and 550 °C, with different weight space velocity (WSV).

As preliminary screening of the catalyst's performance, the gas fed to the fixed bed micro-reactor had firstly the following composition: 5% CO, 20% H<sub>2</sub>O and N<sub>2</sub> as balance. After that, CO<sub>2</sub> and H<sub>2</sub> were added, initially each alone and then together to the original CO-H<sub>2</sub>O mixture; the four gases mixture was representative of the reformat gas at the outlet of the HT-WGS stage, where the CO concentration was partially reduced.

The outlet gas stream was analyzed through a micro gas-chromatograph (Varian CP-4900) equipped with a thermal conductivity detector (TCD), whose CO detection limit was 2 ppmv.

## **3. RESULTS AND DISCUSSION**

A preliminary characterization of the as-prepared Rh-CeO<sub>2</sub> catalyst was carried out by XRD (see the spectrum in Fig. 1). Only the peaks belonged to CeO<sub>2</sub> were visible, whereas no diffraction peaks belonging to Rh could be detected, indicating that the active metal dispersion over the CeO<sub>2</sub> support occurred presumably without the formation of large clusters.

As determined by multipoint N<sub>2</sub> adsorption/desorption technique, the BET specific surface areas was 24 m<sup>2</sup> g<sup>-1</sup>. SEM and FESEM analyses completed the physical characterization of the catalyst structure. Fig. 2 shows the micrographs of the 2% Rh/CeO<sub>2</sub> catalyst: SEM analysis (Fig. 2A) showed a sample with quite big aggregates, in the order of 200÷400 nm, more evident by FESEM analysis (Fig. 2B). Rh was not visible, or not distinguishable from the carrier, neither with FESEM analysis, sign that presumably Rh was very well distributed and present in nanometric dimensions, possibly visible only via HR-TEM investigations.

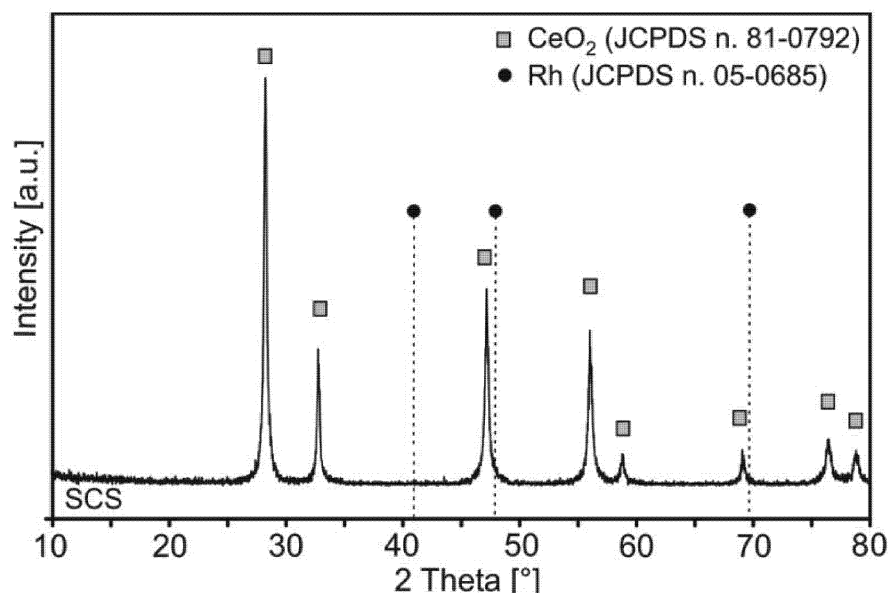


Fig. 1: XRD spectrum for 2%Rh/CeO<sub>2</sub> catalyst.

EXD analysis, carried out during FESEM session, allowed enlightening a quite homogeneous Rh distribution, as evident from the atomic ratios reported on different areas of the FESEM image (Fig. 2B). The SCS synthesis allowed preparing a catalyst with a higher purity degree (Specchia, 2010).

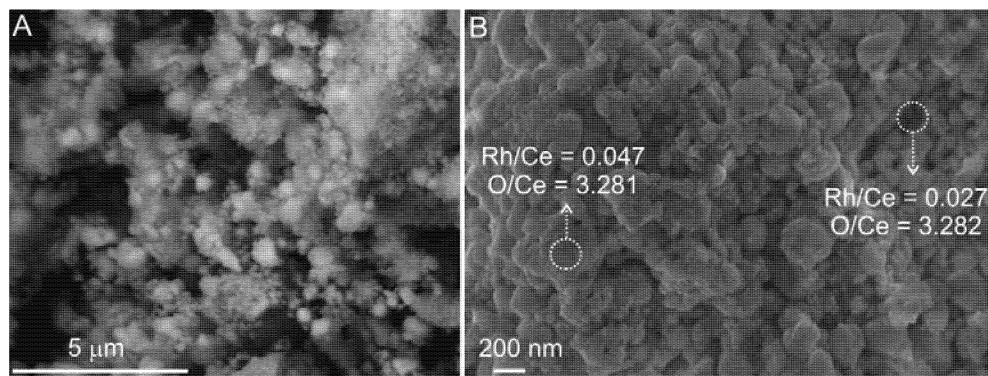


Fig. 2: SEM (A) and FESEM (B) with EDX analysis (in terms of atomic ratios) micrographs for 2%Rh/CeO<sub>2</sub> catalyst.

A preliminary screening of the catalytic performance of the 2% Rh/CeO<sub>2</sub> catalyst, in terms of CO conversion, was then carried out with the fixed bed micro-reactor.

First of all, activity tests by feeding only CO and H<sub>2</sub>O in N<sub>2</sub> (5% of CO, H<sub>2</sub>O/CO equal to 4 and N<sub>2</sub> to balance) were performed with WSV equal to 0.33 Nl min<sup>-1</sup> g<sup>-1</sup>. The obtained results, expressed as CO conversion and methane outlet concentration vs. temperature are shown in Fig. 3. The WGS equilibrium conditions at the various temperatures and gas feeding compositions considered was estimated by using equation (2). The equilibrium curve was reached at about 330 °C. Considering the CH<sub>4</sub> outlet concentration, a value of 0.62% was measured.

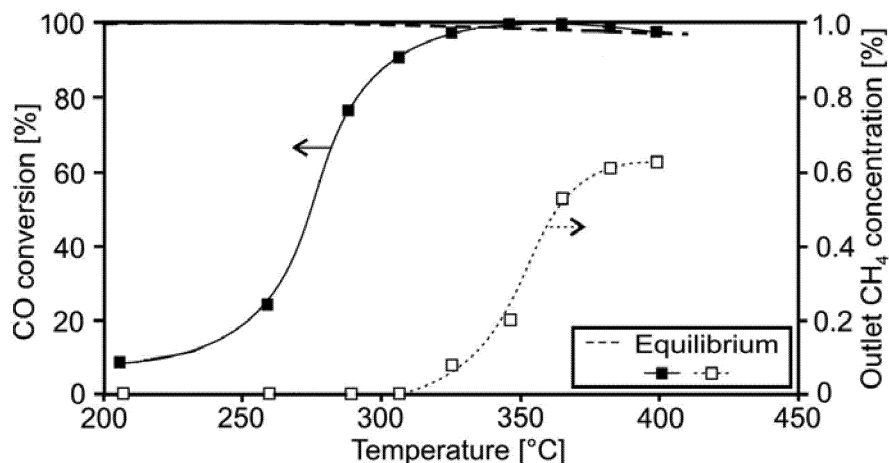


Fig. 3: CO conversion and outlet CH<sub>4</sub> concentration vs. temperature for 2%Rh/CeO<sub>2</sub> catalyst (inlet gas composition: 5% CO + 20% H<sub>2</sub>O, N<sub>2</sub> balance. WSV=0.33 Nl min<sup>-1</sup> g<sup>-1</sup>).

Then, in order to evaluate the effect of the presence in the feed of either each single WGS product or all together, 11% CO<sub>2</sub> (Fig. 4), 40% H<sub>2</sub> (Fig. 5) and finally both the last two gases (standard feed: 5% CO, 20% H<sub>2</sub>O, 11% CO<sub>2</sub>, 40% H<sub>2</sub>, N<sub>2</sub> balance, Fig. 6) were added sequentially. For all the feed compositions, CO conversion and CH<sub>4</sub> outlet concentration were evaluated and plotted vs temperature.

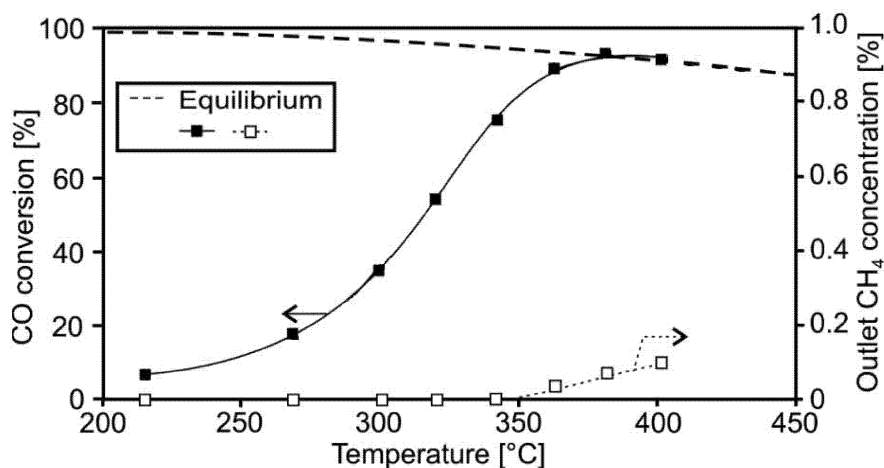


Fig. 4: CO conversion and outlet CH<sub>4</sub> concentration vs. temperature for 2%Rh/CeO<sub>2</sub> catalyst (inlet gas composition: 5% CO + 20% H<sub>2</sub>O + 11% CO<sub>2</sub>, N<sub>2</sub> balance. WSV=0.33 Nl min<sup>-1</sup> g<sup>-1</sup>).

Adding only CO<sub>2</sub> (Fig. 4), no substantial difference were enlighten in CO conversion. By considering the methane outlet concentration, about 6 times lower values (not exceeding 0.1%) were obtained compared to the concentration measured with the previous CO + H<sub>2</sub>O mixture (0.62%).

With the addition of H<sub>2</sub> to the CO+H<sub>2</sub>O mixture (Fig. 5), CO conversion started at slightly lower temperature and the conversion curve exceeded the equilibrium one at 340 °C, reaching also 100% of conversion at 360 °C thanks to the CO methanation reaction, CO-MET. Therefore, in presence of large H<sub>2</sub> concentration, the outlet CH<sub>4</sub> concentration dramatically increased, up to 6%.

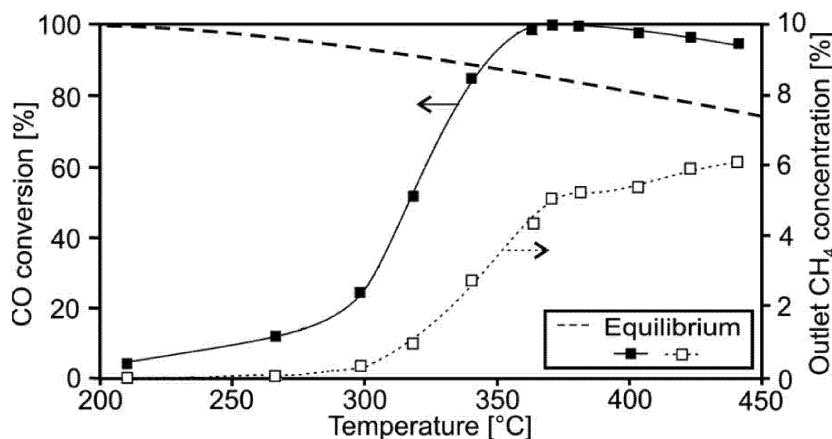


Fig. 5: CO conversion and outlet CH<sub>4</sub> concentration vs. temperature for 2%Rh/CeO<sub>2</sub> catalyst (inlet gas composition: 5% CO + 20% H<sub>2</sub>O + 40% H<sub>2</sub>, N<sub>2</sub> balance. WSV=0.33 Nl min<sup>-1</sup> g<sup>-1</sup>).

Finally, feeding the standard gas composition (5% CO, 20% H<sub>2</sub>O, 11% CO<sub>2</sub>, 40% H<sub>2</sub>, N<sub>2</sub> balance, Fig. 6), the equilibrium curve was exceeded as CO-MET parasite reaction took place consuming part of the residual CO. A higher CH<sub>4</sub> outlet concentration (8.5%) was reached, caused also by CO<sub>2</sub>-MET parasite reaction.

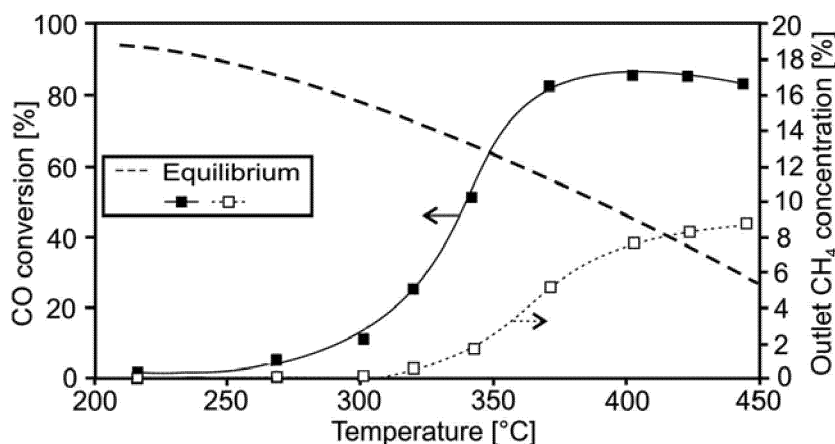


Fig. 6: CO conversion and outlet CH<sub>4</sub> concentration vs. temperature for 2%Rh/CeO<sub>2</sub> catalyst (inlet gas composition: 5% CO + 20% H<sub>2</sub>O + 11% CO<sub>2</sub> + 40% H<sub>2</sub>, N<sub>2</sub> balance. WSV=0.33 Nl min<sup>-1</sup> g<sup>-1</sup>).

Furthermore, in order to determine the best operating conditions, tests at different WSV were carried, feeding only the CO + H<sub>2</sub>O mixture. The results are drawn in Fig. 7. The equilibrium conditions were easily approached at lower temperature by decreasing WSV.

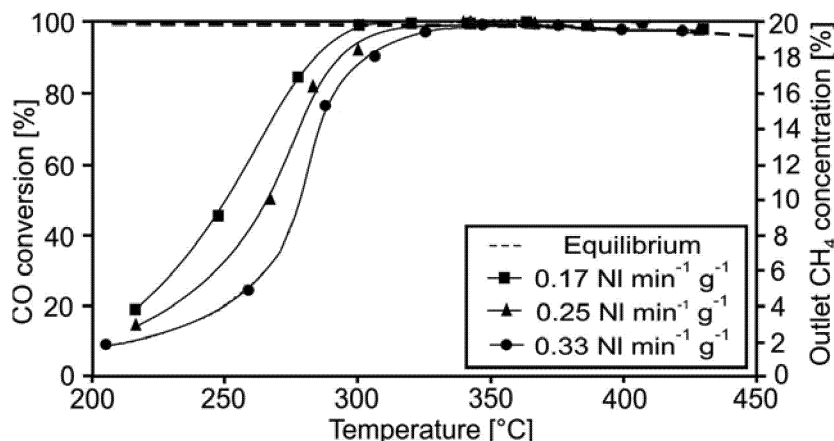


Fig. 7: CO conversion vs. temperature at different WSV values for 2%Rh/CeO<sub>2</sub> catalyst (inlet gas composition: 5% CO + 20% H<sub>2</sub>O, N<sub>2</sub> balance).

#### 4. CONCLUSIONS

Rh active metal (2% load) was deposited by means of the Incipient Wetness Impregnation method on CeO<sub>2</sub> prepared by the Solution Combustion Synthesis. After the catalyst structure characterization, the performance to WGS reaction of the prepared catalytic material at the powder level was carried out in a fixed bed micro-reactor fed with various synthetic gas mixture compositions. By feeding only CO and H<sub>2</sub>O, the equilibrium curve was reached at about 330 °C. Catalytic activity tests performed with a realistic reformat feed (complete mixture containing also H<sub>2</sub> and CO<sub>2</sub>), showed different shape of CO conversion curves: the equilibrium curve was, in fact, exceeded by the Co conversion one. This result was explained considering the CH<sub>4</sub> formation due to the reaction of CO (and probably also CO<sub>2</sub>) with the excess of H<sub>2</sub>, which also consumed CO by pushing to higher conversion values. The catalyst was also tested at different WSV values: the CO conversion reached the WGS thermodynamic equilibrium condition at lower temperatures by decreasing WSV.

#### 5. REFERENCES

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