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Influence of the preparation method on the performance of Rh catalysts on CeO_2 for WGS reaction

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ABSTRACT

The present paper deals with the study concerning the CO removal from reforming H_2-rich gas stream through WGS reaction over Rh-based catalysts supported on CeO_2 carriers. CeO_2 was prepared by two different methods: solution combustion synthesis (SCS) and hard template (HT); incipient wetness impregnation method was used to deposit the active metal on the carriers. The screening at powder level in a fixed bed micro-reactor highlighted that feeding 5% CO and 20% H_2O (N_2 balance) with the HT-prepared catalyst, CO conversion started at slightly lower temperature, but CH_4 outlet concentrations were higher than those of the SCS-prepared one. With a simulated reformate mixture (5% CO + 20% H_2O + 11% CO_2 + 40% H_2, N_2 balance), the equilibrium WGS curve was exceeded for both catalysts (for the HT-prepared catalyst, CO conversion started at lower temperature and reached 100%), due to the parasite methanation reactions of both CO and CO_2, favoured by the presence of a large hydrogen concentration in the reactor. A very high CH_4 outlet concentration (max 18.6%) was measured for the HT-prepared catalyst. Then, tests at different weight space velocities WSV were carried out: with the SCS-prepared catalyst 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 extent upon fuel cell technology. In the majority of current applications, proton exchange membrane fuel cell (PEM-FC) technology is employed [1,2]. PEM-FCs are, regardless of their operating temperature, sensitive to carbon monoxide. Thus, a fuel processor for the H_2-rich gas production [3] 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 [4–6] and below 10 ppmv for Pt anode electro-catalysts [7–9] for LT PEM-FCs, whereas for the HT PEM-PEMs the maximum CO tolerance seems to be 30% [10,11].

The WGS reaction:

$$CO + H_2O \leftrightarrow CO_2 \quad \Delta H^{\circ}_{298} = -41.1 \ \text{kJ mol}^{-1} \tag{1}$$

is limited by its thermodynamic equilibrium, which may be calculated according to the formula provided below [12]:

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

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 (the latter characteristic required for the presence of residual oxygen in the start-up heating medium [3]). If more active WGS catalysts are developed, the CO conversion can then approach more favourably 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) [13–22]. In this work, Rh-based catalysts on CeO_2

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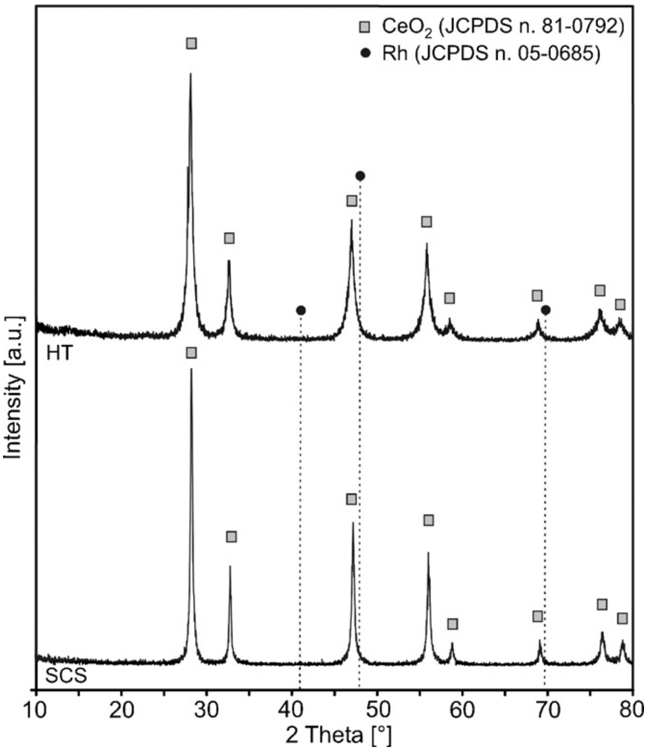

Fig. 1. XRD spectra for 2% Rh/CeO$_2$ prepared by SCS and HT method.

were prepared by means of two different methods: Solution Combustion Synthesis (SCS) and Hard Template (HT). Their catalytic activity was tested at powder level in a fixed bed micro-reactor, to evaluate the influence of the preparation method parameters on the catalytic activity toward WGS reaction.

2. Experimental

Two different preparation procedures were employed to synthesize Rh/CeO$_2$. CeO$_2$ was prepared both by SCS technique [23,24] and HT method with KIT-6 silica acting as a template [25,26].

On CeO$_2$ synthesized by SCS, Rh was deposed with the incipient wetness impregnation method by using $RhCl_3{\cdot}xH_2O$ 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/CeO$_2$ (HT) catalyst was prepared by impregnation of the HT-obtained CeO$_2$ with ethanol–Rh(NO$_3$)$_3$ solution, dried at 60 °C for 3 h and finally calcined at 550 °C for 3 h in air. The Rh load was 2% for both the catalysts.

Firstly, the prepared catalysts were characterized by XRD analysis (Philips PW1710 apparatus equipped with a monochromator for the Cu Kα radiation) to verify their 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 catalysts was measured via N$_2$ by the BET method (Micromeritics ASAP 2020C apparatus). The morphology of the as prepared catalysts 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$_2$, 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 catalysts were firstly reduced into the micro-reactor flowing 50% H$_2$ in N$_2$ (100 Nml min^{-1}) at 200 °C for 1 h, and then

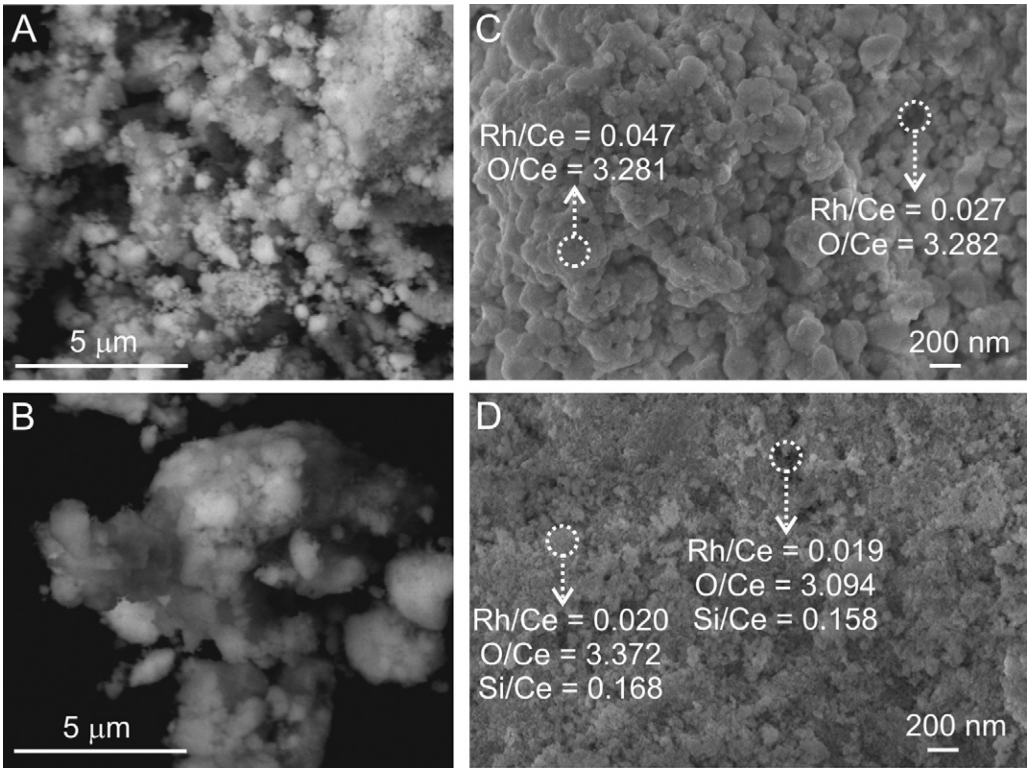

Fig. 2. SEM (A and B) and FESEM (C and D, with EDX analysis in terms of atomic ratios) micrographs for 2% Rh-CeO$_2$ prepared by SCS (A and C) and HT (B and D) method.

tested between 150 and 450 °C, with different weight space velocity (WSV).

As preliminary screening of the catalysts performance, the gas fed to the fixed bed micro-reactor had firstly the following composition: 5% CO, 20% H_2O and N_2 as balance. After that, CO_2 and H_2 were added, initially each alone and then together to the original CO/H_2O mixture; the four gases mixture was representative of the reformate gas at the outlet of the HT-WGS stage, where the CO concentration was partially reduced.

The outlet gas stream was analysed 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-based catalysts was carried out by XRD; the spectra related to the catalysts synthesized by SCS and HT method are shown in Fig. 1. For both the catalysts, only the peaks belonged to CeO_2 were visible, whereas no diffraction peaks belonging to Rh could be detected, indicating that their dispersion over the CeO_2 support occurred presumably without the formation of large clusters.

As determined by multipoint N_2 adsorption/desorption technique, BET specific surface areas were 121 and 24 $m^2\,g^{-1}$ for the two 2% Rh/CeO_2 catalysts, respectively prepared by HT and SCS method.

SEM and FESEM analyses completed the physical characterization of the catalysts structure. Fig. 2 shows the micrographs of the two 2% Rh/CeO_2 catalysts prepared with SCS and HT methods: SEM analysis (Fig. 2A and B) showed different carrier structures. In particular, the SCS sample presented bigger aggregates, in the order of 200–400 nm, more evident by FESEM analysis (Fig. 2C), compared to the HT one (Fig. 2D). In both cases Rh was not visible, or not distinguishable from the carrier, neither with FESEM analysis (Fig. 2C and D), sign that presumably Rh was very well distributed and present in nanometric dimensions possibly visible via HR-TEM investigations. EDX analysis, carried out during FESEM session, allowed enlightening a quite homogeneous Rh distribution on both samples. As evident from the atomic ratios reported on different areas of the FESEM images (Fig. 2C and D, respectively), the catalyst prepared by HT (Fig. 2D) presented a slightly more uniform Rh distribution, compared to the SCS one, but it showed also some residues of the silica used as template in the preparation method. The SCS synthesis allowed preparing a catalyst with a higher purity degree [24].

A preliminary screening of the catalytic performance of Rh-based catalysts, 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_2O in N_2 (5% of CO, H_2O/CO equal to four and N_2 to balance) were performed on the catalysts prepared by HT and SCS method with WSV equal to 0.33 Nl $min^{-1}\,g^{-1}$. 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 were estimated by using Eq. (1). The equilibrium curve was reached with both catalysts at about 330 °C, but CO conversion started at slightly lower temperature with SCS-prepared catalyst. Considering the methane outlet concentration, higher values were obtained with the HT-prepared catalyst (about 0.87% compared to the 0.62% with SCS one).

Then, in order to evaluate the effect of the presence in the feed of either each single WGS product or all together, 11% CO_2 (Fig. 4A), 40% H_2 (Fig. 4B) and finally both the last two gases (standard feed: 5% CO, 20% H_2O, 11% CO_2, 40% H_2, N_2 balance, Fig. 5) were added sequentially. For all the feeds, CO conversion and CH_4 outlet concentration were evaluated and plotted vs. temperature.

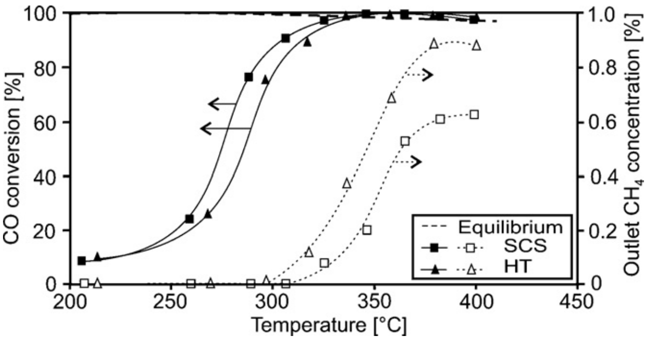

Fig. 3. CO conversion and outlet CH_4 concentration vs. temperature for Rh/CeO_2 catalysts prepared by SCS and HT method (inlet gas composition: 5% CO + 20% H_2O, N_2 balance. WSV = 0.33 Nl $min^{-1}\,g^{-1}$).

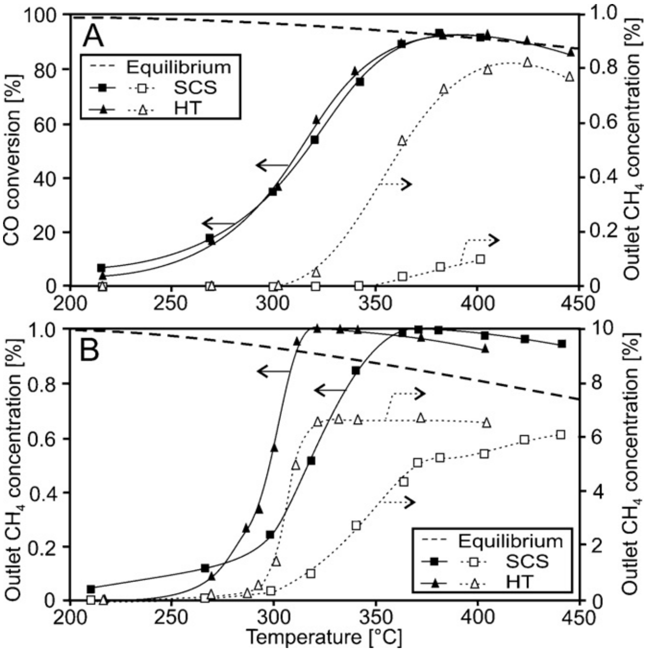

Fig. 4. CO conversion and outlet CH_4 concentration vs. temperature for Rh/CeO_2 catalysts prepared by SCS and HT method (inlet gas composition: A: 5% CO + 20% H_2O + 11% CO_2, N_2 balance; B: 5% CO + 20% H_2O + 40% H_2, N_2 balance; WSV = 0.33 Nl $min^{-1}\,g^{-1}$).

Adding only CO_2 (Fig. 4A), no substantial differences were enlightened in CO conversion. By considering the methane outlet concentration, about six times lower values (not exceeding 0.1%) were obtained with SCS-prepared catalyst compared to the concen-

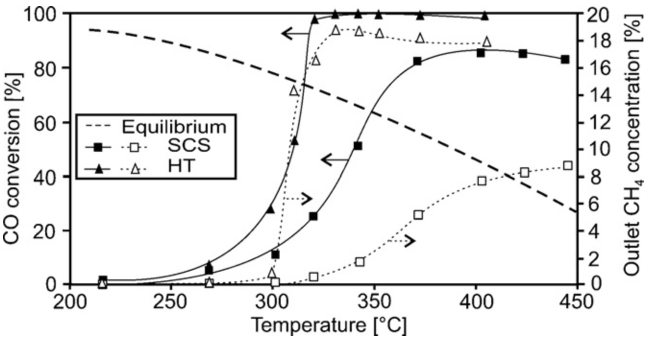

Fig. 5. CO conversion and outlet CH_4 concentration vs. temperature for Rh/CeO_2 catalysts prepared by SCS and HT method (inlet gas composition: 5% CO + 20% H_2O + 11% CO_2 + 40% H_2, N_2 balance; WSV = 0.33 Nl $min^{-1}\,g^{-1}$).

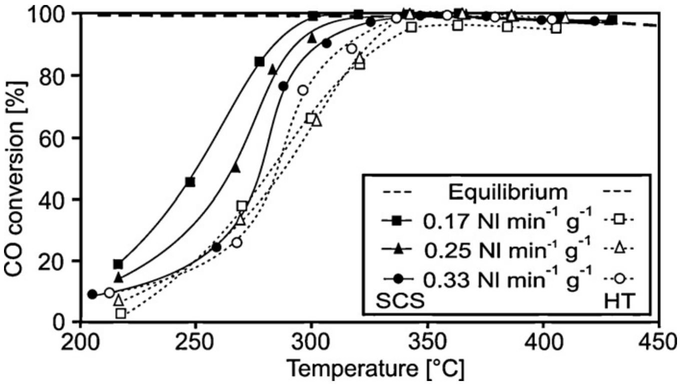

Fig. 6. CO conversion vs. temperature at different WSV values for Rh/CeO_2 catalysts prepared by SCS and HT method (inlet gas composition: 5% CO + 20% H_2O, N_2 balance).

tration measured with CO + H_2O mixture (0.62%), whereas a max concentration of 0.82% was reached for HT-prepared catalyst.

With the addition of only H_2 (Fig. 4B), CO conversion for catalyst synthesized by HT method started at lower temperature and both the conversion curves exceeded the equilibrium one (at 310 and 340 °C, for HT and SCS-prepared catalysts, respectively) reaching also 100% owing the methanation reaction. Therefore, in presence of large hydrogen concentration, the outlet CH_4 concentration dramatically increased, in particular for the HT-prepared catalyst (up to 6.8%).

Finally, feeding the standard gas composition ($CO/H_2O/CO_2/H_2$, Fig. 5), the equilibrium curve was exceeded with both catalysts as CO-MET parasite reaction took place consuming the residual CO. In particular, for the HT-prepared catalyst, CO conversion started at lower temperature and reached 100% of conversion; then, a very high CH_4 outlet concentration (max 18.6%) was reached, caused also by CO_2-MET parasite reaction.

Furthermore, in order to determine the best operating conditions, tests at different WSV were carried out on both the catalysts, feeding only CO–H_2O mixture. The results are drawn in Fig. 6. For SCS-prepared catalyst, the equilibrium conditions were easily approached at lower temperature by decreasing WSV. As concerns the HT-prepared catalyst, there was not an appreciable difference in approaching the equilibrium curve at WSV of 0.25 and 0.33 $\mathrm{Nl\,min^{-1}\,g^{-1}}$, whereas at the lower tested WSV value (0.17 $\mathrm{Nl\,min^{-1}\,g^{-1}}$) the CO conversion curve remained for a small gap beneath the equilibrium line. It could be that increased mass transfer limitations were not balanced by the increased residence time.

4. Conclusions

Rh active metal was deposited by means of a deposition-precipitation method on CeO_2 prepared with two different techniques: the SCS and the HT. After the catalysts structure characterization, a screening of their performance at the powder level as WGS catalytic materials was carried out in a fixed bed micro-reactor fed with various synthetic gas mixture compositions. By feeding only CO and H_2O, the equilibrium curve was reached with both catalysts at about 330 °C, but CO conversion started at slightly lower temperature with SCS-prepared catalyst. Moreover, higher CH_4 outlet concentration was obtained with the HT-prepared catalyst. Catalytic activity tests performed with a realistic reformate feed (containing also H_2 and CO_2), showed different shape of CO conversion curves and with the complete mixture the equilibrium curve was exceeded for both catalysts. These results were explained considering the CH_4 formation, which also consumed CO by pushing to higher conversion values. This was particularly compelling for 2% Rh/CeO_2 HT catalyst, whose very high values of methane concentration were reached probably involving CO_2 methanation, too. The two catalysts were also tested at different WSV values: with the SCS-prepared catalyst, the CO conversion reached lower temperatures by decreasing WSV, whereas the HT-prepared catalyst showed similar performance at higher WSV values (anyway lower than the ones obtained with the SCS-prepared catalyst) and a lower activity when WSV was decreased to the lowest tested value.

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