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Chemical Engineering Journal 134 (2007) 45–50

Chemical Engineering Journal

www.elsevier.com/locate/cej

Catalytic performance of Au–TiO_2 catalysts prepared by deposition–precipitation for CO preferential oxidation in H_2-rich gases

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Abstract

CO preferential oxidation (CO-PROX) can lead to a reduction of the CO content in the hydrogen-rich gas derived from hydrocarbon reforming down to at least 10 ppmv or below, so as to enable its direct feeding to standard PEM fuel cells. Au-based catalysts supported on titania were prepared and tested as potential applications in CO-PROX operating over a temperature range compatible with PEM FCs (80–100 °C).

Au–TiO_2 catalysts were prepared by means of two deposition–precipitation methods, varying pH (with NaOH) and some other parameters during the preparation procedure. Also the calcinations temperature was a varied parameter to evaluate the most promising catalyst.

Catalyst prepared by deposition–precipitation method, using lower pH and calcined at 300 °C was found to be the most suitable one for the CO-PROX at low temperature: it reduced the inlet CO concentration below 10 ppmv within a temperature range of at least 60–80 °C.

Tests at progressively lower O-to-CO feed ratio (λ) and the same WSV value were carried out for the sake of reducing H_2 consumption and improve CO-PROX selectivity. For 2%Au–TiO_2 the minimum λ value, ensuring a sufficiently wide temperature range of a nearly complete CO conversion at temperatures compatible with PEM FCs operation was found to be equal to 4. Tests doubling WSV were also carried out, but a complete CO conversion was not reached. Finally, CO inlet concentration was reduced to 0.5% (possible CO outlet concentration from WGS stage); parasite RWGS reaction seemed to take place leading to worse performance.

Keywords: Hydrogen gas mixture clean-up; CO preferential oxidation; Au-based catalyst

1. Introduction

Polymer electrolyte membrane fuel cells (PEM FCs) fed with pure hydrogen can provide power to electrically operated vehicles with virtually no pollutants. At present, significant introduction of PEM FC in the automotive field is limited by their cost, the unavailability of a hydrogen mass production and distribution infrastructure and the rather low amounts of hydrogen gas that can be safely stored on board vehicles. A number of European research projects [1–4], however, are aimed at demonstrating both an internal combustion engine (ICE) hydrogen powered for car traction and a FC-based auxiliary power unit (APU) for any other on board truck power requirements. The APU systems are based on a reforming process (either steam or autothermal [5,6]) of hydrocarbon feedstock fuels, integrated with a PEM fuel cell on board vehicles. As extensive infrastructures already exist for gasoline and diesel oil, these sources are the preferred hydrocarbon feedstocks for on board reforming [7]. The H_2 fuel gas for the PEM FC is required to be "nearly CO free" as FC platinum-based anodes get poisoned by traces of CO. The H_2-rich gas produced by catalytic reforming of fossil fuels, such as gasoline or diesel oil, followed by water–gas shift reaction may go through catalytic selective CO oxidation to completely remove its undesired CO content [8,9].

The CO concentration of the syngas from the reformer is at first reduced by means of the water–gas shift (WGS) reaction which also enriches the H_2 concentration in the gas stream:

$$CO + H_2O \leftrightarrow CO_2 + H_2, \qquad \Delta H_{298} = -41.2\,\mathrm{kJ/mol} \quad (1)$$

The WGS reaction is generally operated in two stages (high temperature—HT and low temperature water–gas shift—LT) to minimize the overall amount of catalyst required and the reac-

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doi:10.1016/j.cej.2007.03.055

tion volume. However, the outlet gas from the LT WGS reactor still contains approximately 0.5–1% b.v. (5000–10,000 ppmv) of CO. Tolerable levels of CO concentration for standard-grade PEM fuel cells are 10 ppmv, with peaks of 50 ppmv for a few minutes, and so a further removal of CO from the gas stream has to be performed [10]. Preferential oxidation of carbon monoxide to carbon dioxide (CO-PROX) is a widely studied option to achieve these residual CO levels.

CO-PROX is an exothermic process which involves the oxidation of carbon monoxide in the reformate stream to carbon dioxide over a suitable catalyst using molecular oxygen fed on purpose. The hydrogen in the reformate stream should not be consumed at all to not decrease the efficiency. A reduction in hydrogen concentration results indeed in decrease in power generation. Therefore, both active and very selective catalysts are required to convert carbon monoxide to carbon dioxide while minimizing hydrogen oxidation to water.

Various catalysts have been proposed and tested in the literature for selective CO oxidation in H_2-rich streams, but until the end of the 1980s, only very limited attention was paid to catalysis governed by gold metal because of its electronic configuration of noble metal which is usually accompanied by very low activities [11]. This situation changed in recent years with the discovery of the catalytic activity of gold nanoparticles [12]. Remarkable catalytic properties of supported gold were first obtained for the reaction of CO preferential oxidation at sub-ambient temperature by Haruta et al. [13]. The most studied catalyst for preferential CO oxidation was Au supported on TiO_2 because it demonstrated to be one of the most active catalysts for this reaction at low temperature, allowing thus to operate at temperatures compatible with those of PEM fuel cell (80–100 °C). The optimum gold particle size was found to be 2–3 nm [14–16]. Such particle sizes could be achieved following suitable preparation methods and a careful control of the running conditions during preparation.

Up to now, for the preparation of Au–TiO_2 catalysts, the best method was the deposition–precipitation with NaOH [17], particularly because it allowed the size of the gold particles to be adjusted towards very small values by controlling the pH during the preparation.

As a consequence, in the present work, Au supported catalysts on TiO_2 were firstly prepared by deposition–precipitation method and then tested for potential application in CO-PROX units operating at temperatures compatible with the PEM fuel cells [18].

2. Experimental

2.1. Catalyst preparation and characterization

The metal oxide material (TiO_2) to be used as Au carrier was prepared through the gel combustion method [19]. The supported Au catalysts were prepared following two different deposition–precipitation routes employing $HAuCl_4 \cdot 3H_2O$ (Sigma–Aldrich) as precursor.

In the first procedure, an aqueous solution of $HAuCl_4$ (4.2×10^{-3} M) was adjusted to pH 10.4 by drop wise addition of NaOH, then a suitable amount of TiO_2 particles was dispersed in the solution; the latter was then heated to 70 °C and in the same time the pH lowered till 8.6. Finally the suspension was filtered and the separated particles washed with H_2O.

With the second method, the same aqueous solution of $HAuCl_4$ (4.2×10^{-3} M) was firstly heated up to 80 °C, then its pH was adjusted to 7 by drop wise addition of NaOH (1 M). A suitable amount of TiO_2 was dispersed in the solution and the pH was readjusted to 7 with NaOH. The suspension maintained at 80 °C was vigorously stirred for 2 h, then filtered and the separated particles washed with H_2O. After preparation, all the Au–TiO_2 catalysts were calcined in air at 200 and 300 °C for 2 h in order to create an homogeneous powder. The catalyst powder was pressed at 125 MPa into tablets which were then crushed in an agate mortar and sieved to separate granules of 0.25–0.42 mm in size; the latter were used in a fixed bed micro-reactor for the activity tests. The Au concentration in all the prepared catalysts was equal to 2% by weight.

The obtained Au-based catalysts were analyzed by high-resolution transmission electron microscopy (HRTEM, Jeol JEM 2010 apparatus) to investigate the metal dispersion on the supports. They were also examined by scanning electron microscopy and energy dispersion spectroscopy (SEM–EDS, LEO Supra 35) to evaluate their morphology and elemental distribution.

2.2. Reactor system and analytical methods

A fixed bed micro-reactor (a quartz tube of 4 mm i.d.) heated up by a PID regulated oven and containing 0.15 g of catalyst particles held in place by flocks of quartz wool was used for the CO oxidation reaction. A K-type thermocouple was inserted into the reactor to measure the temperature of the catalytic bed. The inlet gas was fed at a flow rate of 100 ml/min and with the following b.v. composition: 37% H_2, 5% H_2O, 18% CO_2, 0.5–1% CO, 1–2% O_2 and helium as balance. This composition (helium apart) is representative of that at the outlet of a LT WGS reactor following a gasoline autothermal reformer [1]. Mass flow controllers (Brooks) were used to regulate the feed flow rate of each component; a pressure transducer (VIKA) was employed to monitor the pressure at the bed inlet to check its possible clogging.

The outlet gas stream was analyzed through a gas-chromatograph (Varian CP-3800) equipped with a thermal conductivity detector (TCD), a "Poraplot Q" column (0.53 mm diameter, 30 m length) to separate CO_2 and H_2O, and a "Molsieve 5A" column (0.53 mm diameter, 25 m length) to separate CO, H_2 and O_2. The two columns, connected in series by a six-way valve were kept at 70 °C; the sample injection was accomplished using helium as carrier gas at a flow rate of about 2.8 ml/min. The CO detection limit was 10 ppmv.

The experimental tests were carried out in the temperature range of 40–180 °C, at different O to CO feed ratio (λ) and with different weight space velocities. The various measures were carried out with a step temperature increase of about 10 °C; the outlet concentrations were recorded when a steady-state situation was attained.

The conversion of CO (ξ_{CO}) and O_2 (ξ_{O_2}), as well as the oxygen selectivity to CO oxidation (σ, assuming no CO formation by reverse water–gas shift-RWGS) were calculated as follows:

$$\xi_{CO} = 1 - \frac{[CO]_{out}}{[CO]_{in}} \tag{1}$$

$$\xi_{O_2} = 1 - \frac{[O_2]_{out}}{[O_2]_{in}} \tag{2}$$

and

$$\sigma = \frac{1}{2}\frac{[CO]_{in} - [CO]_{out}}{[O_2]_{in} - [O_2]_{out}} \tag{3}$$

Then, maintaining the same CO inlet concentration, the influence of O_2 concentration in the micro-reactor feed gas stream on the catalytic performance of 2%Au–TiO_2 catalyst was determined by reducing the O_2 concentration from 2 down to 1 vol.%.

3. Results and discussion

A first comparison was performed on catalysts prepared through the first route and calcined at two different temperatures: 200 and 300 °C (2%Au–TiO_2-1-200, 2%Au–TiO_2-1-300), working at a weight space velocity WSV = 0.66 Nl/(min g_{cat}); the obtained results are shown in Fig. 1.

The complete CO conversion (10 ppm of residual CO) was reached in the range 40–45 °C with sample calcined at 300 °C, whereas the minimum CO residual amount for the catalyst calcined at 200 °C was 150 ppm at about 60 °C. However, the complete conversion with 2%Au–TiO_2-1-300 was obtained at too low temperature, as the operating temperature of PEM FC is in the range 80–100 °C.

Moreau et al. [20] studied Au–TiO_2 catalyst prepared through a method similar to the first procedure we employed, but with a lower gold load (1.4% versus 2%). In contrast with their results, our 2%Au–TiO_2-1 catalyst calcined at 300 °C reached the complete CO conversion and this was probably due to the little bit higher Au load deposited on titania. On the other hand, Moreau et al. catalyst calcined at 200 °C reached complete CO conversion but at about 60 °C, a too low temperature for the required application. Then, there is a discrepancy in performances between Moreau et al. and our Au–TiO_2 catalysts.

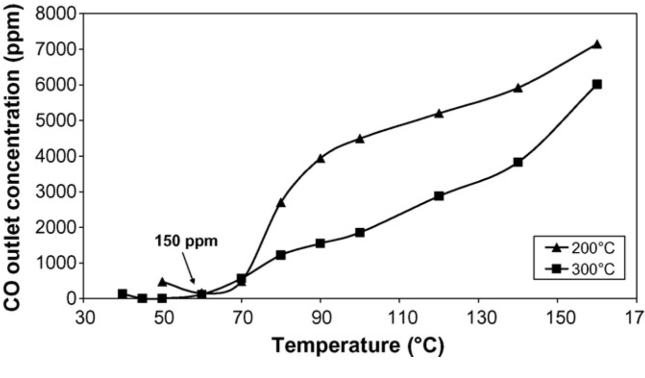

Fig. 1. CO outlet concentration vs. temperature for 2%Au–TiO_2-1 catalysts at different calcination temperatures, with standard feed gas composition, λ = 4, WSV = 0.66 Nl/(min g_{cat}).

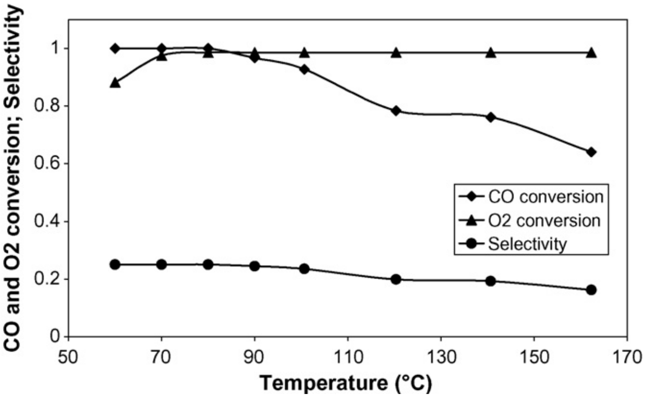

Fig. 2. CO and O_2 conversion and O_2 selectivity vs. temperature for 2%Au–TiO_2-2-300, with standard feed gas composition, λ = 4, WSV = 0.66 Nl/(min g_{cat}).

Therefore, the second preparation method, as indicated above, was used and catalytic activity tests were carried out on the catalyst calcined at 300 °C, identified as 2%Au–TiO_2-2-300. The obtained results are shown in Fig. 2.

A good performance was obtained with 2%Au–TiO_2-2-300: complete conversion of CO with a residual CO concentration below 10 ppmv was observed from 60 to 80 °C, a temperature range enough in agreement with the operating PEM fuel cells range (80–100 °C).

The better performance for the catalyst prepared by the second technique could be explained considering Au cluster size in the two catalysts: 2%Au–TiO_2-2 catalyst presented smaller Au particles compared to 2%Au–TiO_2-1 (few nanometers versus 20–30 nm), as shown in SEM micrographs (Fig. 3A and B).

This is in agreement with literature [20]: high catalytic activity requires the metal particles size to be very small ($\leq$10 nm).

As shown in Fig. 2, at temperature higher than 100–120 °C, CO conversion rapidly decreased; in contrast the O_2 conversion was complete in a wider temperature range (80–160 °C). Therefore, oxygen was consumed in the oxidation reactions of both carbon monoxide ($CO + (1/2)O_2 \rightarrow CO_2$) and hydrogen ($H_2 + (1/2)O_2 \rightarrow H_2O$) with a certain decrease in power generation capability.

In addition, the above decrease could be related to the reverse water–gas shift reaction RWGS ($CO_2 + H_2 \rightarrow CO + H_2O$) which limits the CO conversion at higher temperature [7].

Then, on this promising catalyst, the research activity was deepened varying some parameters, as λ, the weight space velocity and the inlet CO concentration.

As mentioned above, in order to improve the oxygen selectivity to CO oxidation with the lowest possible H_2 parasitic oxidation (the previous tests were carried out with λ = 4 and O_2/CO = 2) the oxygen concentration in the feed gas was decreased. The obtained results are shown in Fig. 4.

With 2% O_2 concentration (λ = 4), as mentioned above, the complete CO conversion was observed in the temperature range 60–80 °C. By decreasing O_2 concentration to 1.5% (λ = 3), the residual CO concentration reached a value equal to 10 ppm only

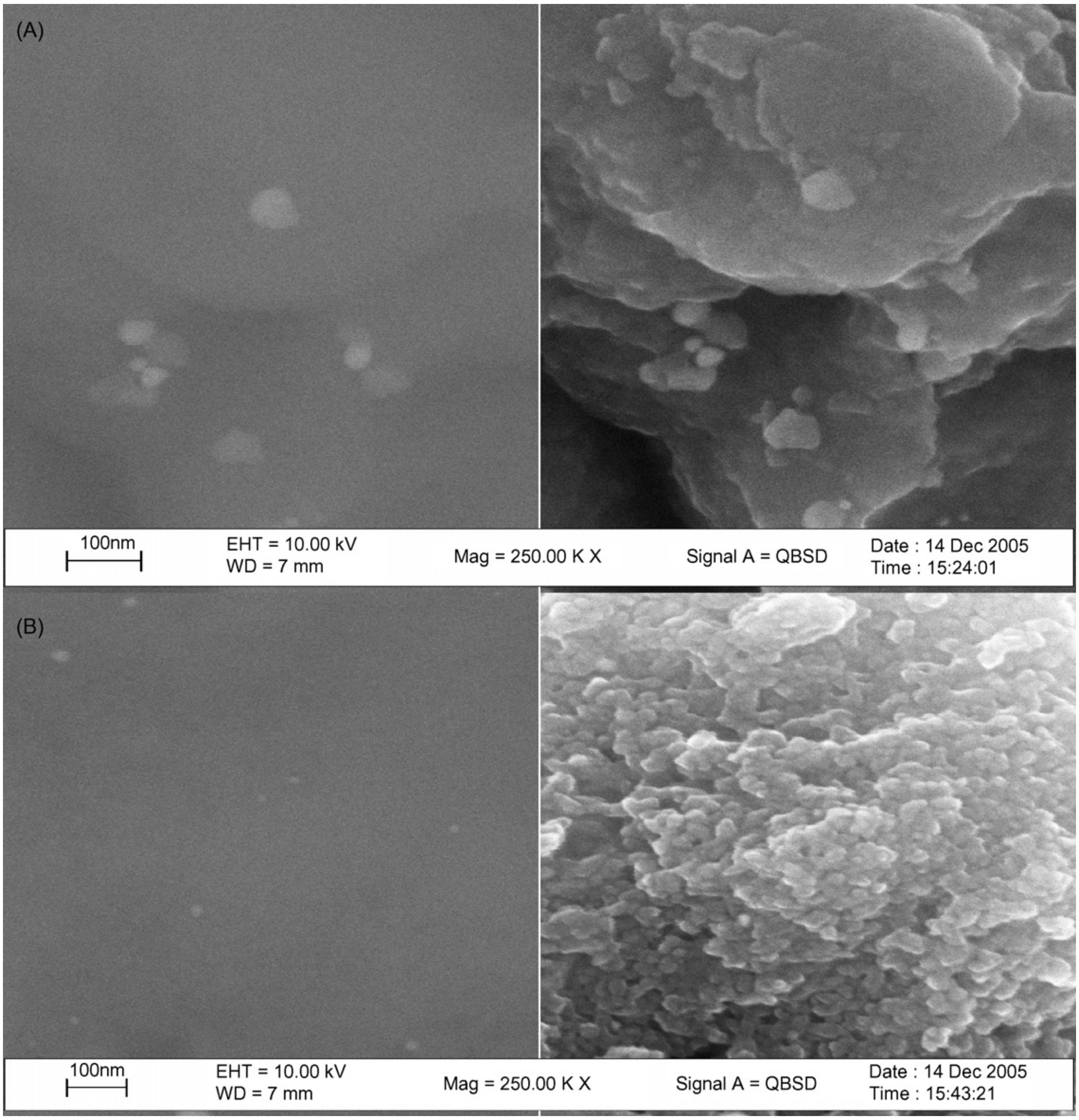

Fig. 3. SEM micrographs of Au-catalysts: (A) 2%Au–TiO_2-1 and (B) 2%Au–TiO_2-2.

at 60 °C, and, moreover, at a temperature a little bit low for PEM applications.

Taking into account the possibility to achieve complete CO conversion at temperature range compatible with PEM FC and as large as possible for a satisfactory PROX reactor controllability, the feed O_2 concentration of 2 vol.% ($\lambda = 4$) was considered as the best one.

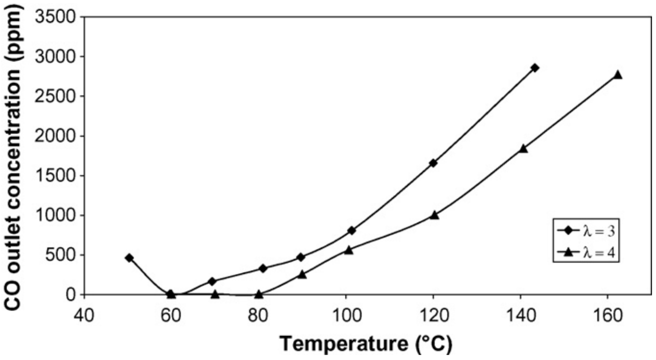

Fig. 4. CO outlet concentration vs. temperature for 2%Au–TiO_2-2-300 at different λ values and WSV = 0.66 Nl/(min g_{cat}).

In sight of reducing the reactor volume for industrial applications, weight space velocity was doubled to 1.32 Nl/(min g_{cat}); unfortunately, the complete CO conversion was not yet achieved and the minimum residual CO concentration was 600 ppm at 70 °C. A comparison of the 2%Au–TiO_2-2-300 catalyst performance at different WSV is shown in Fig. 5.

As CO-PROX unit is downstream the LT-WGS stage, also a gas flow with a lower CO concentration (0.5%) outgoing from the latter was fed through the catalytic bed, with WSV = 0.66 Nl/(min g_{cat}) and at two different λ values. The results obtained with the 2%Au–TiO_2-2-300 catalyst are shown in Fig. 6.

By decreasing the inlet CO concentration, the complete CO conversion was not yet reached; in particular, with λ value equal to 4 the minimum residual CO concentration was about 450 ppm at 80 °C, and it increased to 1000 ppm with $\lambda = 3$, at about 90 °C.

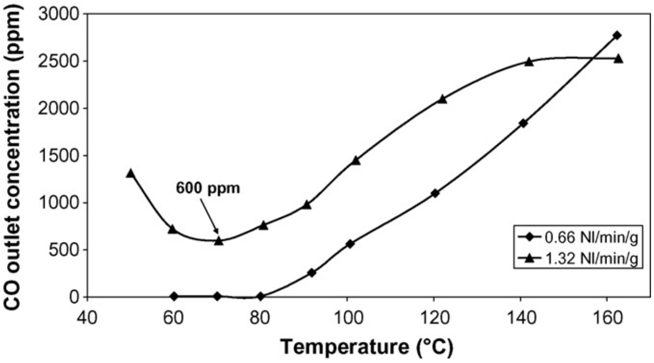

Fig. 5. CO outlet concentration vs. temperature for 2%Au–TiO_2-2-300 at two different WSV values and λ = 4.

The different inlet CO concentration could be responsible for the above results: with lower CO concentration the parasite RWGS reaction ($CO_2 + H_2 \rightarrow CO + H_2O$) could be more favoured, then decreasing CO conversion. Moreover, by decreasing λ value, CO conversion was further reduced and maximum conversion temperature slightly increased.

Therefore, the 2%Au–TiO_2-2-300 catalyst (calcined at 300 °C) could potentially be used for low temperature CO-PROX applications working with λ = 4: the catalyst showed, in fact, to be able to reduce the inlet CO concentration from 1% to below 10 ppm in the temperature range of 60–80 °C.

In order to have an idea of the 2%Au–TiO_2-2-300 catalyst stability, a performance test on this promising catalyst was carried out for several hours of operation at WSV = 0.66 Nl/(min g_{cat}) and λ = 4. As shown in Fig. 7, the fresh catalyst reached the complete conversion in a range of 20 °C and the temperature range was reduced after 20 and 30 h to about 17 and 8 °C, respectively. The complete CO conversion was not reach after 40 h of work: in fact, the residual CO concentration was about 150 ppm.

Therefore, by increasing the operating time, the temperature window of the complete CO conversion was reduced, but the complete CO oxidation was guarantee at least for about 30 h of operation. The width decrease of the temperature window could be explained with slow variations of catalyst surface, probably caused by blocked pores and crystal growth or by the presence of impurities in reactants stream.

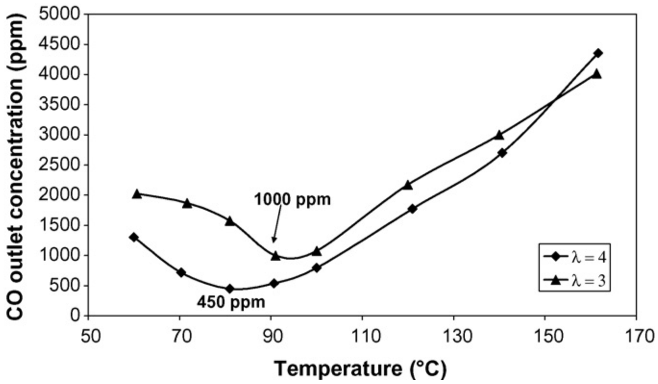

Fig. 6. CO outlet concentration vs. temperature for 2%Au–TiO_2-2-300 at different λ values; with WSV = 0.66 Nl/(min g_{cat}) and inlet CO = 0.5%.

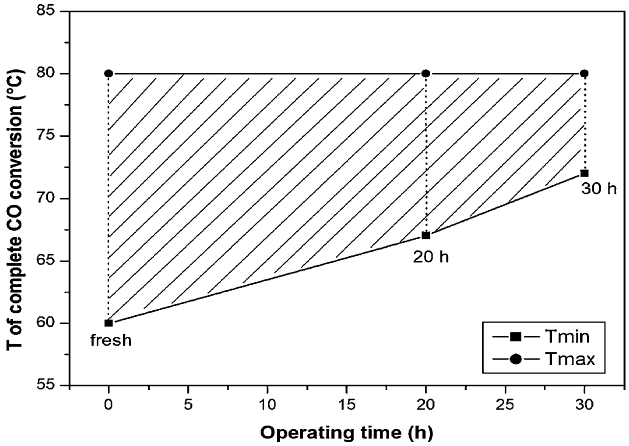

Fig. 7. Range of complete CO conversion by increasing the 2%Au–TiO_2-2-300 catalyst stage.

Our best catalyst, 2%Au–TiO_2 was, however, that prepared by means of a second procedure, previously used by Zanella et al. [21]. The 2%Au–TiO_2-2-300 catalyst, although, characterized by lower gold load, showed a superior catalytic activity in comparison with the 3%Au–TiO_2 analyzed by Zanella et al. Moreover, their stability test suggested a short time of maximum activity; in fact, after 3–4 h, catalyst performance notably worsened. On the contrary, as discussed above, our catalyst maintained a complete CO conversion over 30 h. These better results were probably due to the gold size and its widespread distribution on titania, also favoured by the nanosized structure of this oxide as employed in our study.

Then, for an industrial application, where stability is a basic requirement, our catalyst seems to be more promising and, probably, less expensive owing the lower Au load.

4. Conclusions

CO-PROX tests carried out under realistic conditions with Au catalysts supported on titania indicated as the most suitable catalyst for application in CO-PROX operating at a temperature range compatible with a PEM fuel cell (80–100 °C) the 2%Au–TiO_2-2-300 calcined at 300 °C. The latter was able to reduce the CO concentration under the test conditions (WSV = 0.66 Nl/(min g_{cat})) to below 10 ppmv within a temperature range of at least 60–80 °C with λ = 4.

In order to increase the oxygen selectivity of this catalyst, tests with reduced O_2/CO ratio (λ) were carried out. Unfortunately, with the 2%Au–TiO_2-2-300 catalyst, the λ value of 3 was found to give a complete CO conversion only at 60 °C.

In sight of reducing the reactor volume for industrial applications, the weight space velocity was doubled from 0.66 to 1.32 Nl/(min g_{cat}); however, the complete CO conversion was not yet achieved with the higher tested WSV value.

Moreover, as the outlet CO concentration from the LT WGS step could be lower than 1%, tests were carried out with a feeding CO concentration of about 0.5%. Conversely, the residual outlet CO concentration resulted much higher than 10 ppm; this worse performance was probably due to the increased influence of parasite RWGS reaction (reduced amount of CO shifted equilibrium toward CO formation).

Finally, a first stability test at 0.66 Nl/(min g_{cat}) and $\lambda = 4$ was carried out on the most promising catalyst. Complete CO conversion was still reached for more than 30 h of operation showing anyway a certain stability level for the catalyst.

Therefore, the 2%Au–TiO_2-2-300 catalyst (calcined at 300 °C) operating at $\lambda = 4$ could potentially be used for CO-PROX applications at temperatures compatible with the working ones of the PEM fuel cells: freshly prepared, it was, in fact, able to reduce the inlet CO concentration below 10 ppmv within a temperature range of 60–80 °C.

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