Pure Hydrogen Production via PROX over Gold Catalysts on Alumina Supported Y-Doped Ceria: Effect of Support Preparation

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Abstract - Gold catalysts on CeO_2/Al_2O_3 and Y-doped CeO_2/Al_2O_3 supports (20 wt.% CeO_2 and 1 wt.% Y_2O_3) were synthesized. The mixed oxide supports were prepared by impregnation (IM) or by mechanical mixing (MM). The samples were characterised by BET, XRD and HRTEM/HAADF measurements. The catalytic properties in the preferential CO oxidation in hydrogen rich stream (PROX) using gas feed composition: 60% H_2+ 1% CO + 1% O_2 (He as balance) were estimated. The effect of supports preparation on the gold loading and its dispersion, supports features and catalytic performance was commented. The positive effect of yttrium for catalysts stability was evidenced during long run tests in PROX with CO_2 and water addition to gas stream. The obtained results could be useful for the design of catalysts for CO-free hydrogen production with good PROX performance at reasonable price.

Keywords: PROX, Gold catalysts, Alumina supported Y-doped ceria, Impregnation, Mechanical mixing.

1. Introduction

The proton exchange membrane fuel cells (PEMFC) require hydrogen purification from carbon monoxide up to the levels below 10 ppm for Pt anodes and below 100 ppm for CO-tolerant alloy anodes. The preferential CO oxidation in H_2-rich stream (PROX) is a cheap and efficient way to decrease the CO concentration in the stream after the reforming process and the subsequent water gas shift reaction. The effective PROX catalysts must meet some specific requirements: i) high CO oxidation activity but low activity for the unwanted H_2 oxidation in the region of relatively low PEMFC operating temperatures between 80–120 °C; ii) reduced harmful effect of water and especially of CO_2, usually present in the reformate stream. Regarding the latter the improved resistance to CO_2 is characteristic for acidic as compared to the basic supports [1]. In relation to the former requirement many studies were focussed on supported nanosized gold catalysts because at low temperature higher rate of CO oxidation than that of H_2 oxidation was observed [2,3]. It is generally agreed that the catalytic activity of gold-based catalysts strongly depends on the gold particles dispersion. At the same time, the support nature and features, preparation method and catalyst pretreatment are also important factors [1,4]. Ceria has received a special attention among the appropriate supports for gold catalysts because of the well-known enhanced redox transfer $Ce^{4+} \leftrightarrow Ce^{3+}$ and the ability to promote gold dispersion by the presence of surface oxygen vacancies as nucleation sites for small particles [5]. Concerning PROX it has been proposed that the predominant mechanism over gold/ceria catalysts is the Mars–van Krevelen mechanism with the ceria lattice oxygen involvement [6]. Carabineiro et al. evidenced that there is a correlation between CO oxidation activity and lattice oxygen supply by ceria [7]. The modification of ceria by appropriate metal dopants could increase the oxygen vacancies creation leading to higher number of surface sites for gold deposition as well as improving

the support redox properties. A relatively new approach for development of catalytically efficient but also cost-effective gold/ceria catalysts motivated our very recent study of PROX over gold on CeO_2/Al_2O_3 and Y-doped CeO_2/Al_2O_3 supports. The ceria amount was 10, 20 or 30 wt.% and the mixed oxide supports were prepared by impregnation [8]. The addition of yttrium was 1 wt.% Y_2O_3 on the bases of promising results previously obtained in PROX over gold deposited on Y-modified ceria supports [9]. In agreement with literature data [10], the optimal ceria amount established with respect to CO conversion and selectivity was 20 wt.%.

In the present study the gold catalysts for PROX on CeO_2/Al_2O_3 and Y-doped CeO_2/Al_2O_3 (1 wt.% Y_2O_3) supports with 20 wt.% ceria deposition by impregnation or mechanical mixing are compared. The effects of preparation method on: i) gold loading and dispersion; ii) supports features and iii) catalytic activity, selectivity and stability in PROX are discussed.

2. Experimental
2.1. Samples preparation
The alumina supported ceria and Y-modified ceria were prepared by two different methods: wet impregnation (IM) and mechanical mixing (MM). The amount of ceria was 20 wt.%. The Y-doping was 1 wt.% Y_2O_3 in respect of the ceria content. Using the first method, aqueous solution of $Ce(NO_3)_3.6H_2O$ was used for the impregnation of γ-alumina (Sasol) via vigorous stirring for 4 h at room temperature followed by the complete water removal at 70 ^{o}C in a rotary evaporator. The precursor was calcined for 2 h in air at 400 ^{o}C. The same impregnation procedure was repeated for the synthesis of the Y-doped ceria adding aqueous solution of $Y(NO_3)_3.6H_2O$. For the MM method of preparation, cerium hydroxide was previously synthesized by precipitation of $Ce(NO_3)_3·6H_2O$ with K_2CO_3 at 60 ^{o}C and constant pH = 9.0. The precipitate was aged at the same temperature for 1 h, filtered, washed until the removal of NO_3^-ions and dried in vacuum at 80 ^{o}C. Then, a mixture of alumina and the calculated amount of cerium hydroxide was subjected to mechanical mixing for 30 min in a mortar and calcined at 400 ^{o}C for 2 h. The Y-containing support was prepared by the same procedure but the mechanical mixing was performed with addition of the calculated amount of Y_2O_3. The thermal treatment was carried out in air at 400 ^{o}C for 2 h.

Gold (3 wt.%) was loaded by deposition-precipitation method at pH 7.0 and 60 ^{o}C following the procedure already reported in Ref. [9]. The gold catalysts were denoted as Au20CeAlIM and Au20CeAlMM as well as AuY20CeAlIM and AuY20CeAlMM. Gold on ceria and gold on alumina, designated as AuCe and as AuAl respectively, were also synthesized for comparison.

2.2. Samples characterization
The X-ray fluorescence (XRF) analysis for estimation of the actual gold loading (±0.05 wt.%) was performed with MiniPal4 XRF desktop spectrometer from Panalytical. It is energy dispersive spectrometer with SDD detector of 145 eV resolution with Rh anode tube.

The specific surface areas of the catalysts were determined by the BET equation using Quantachrome Instruments NOVA 1200e (USA) at −196 ^{o}C in the pressure range 0.05–0.3 p/p$_o$. The mean pore size diameter was calculated by BJH method applied to the desorption branch. The accuracy of each measured point was 2%. Prior to the measurements, the samples were outgassed at 200 ^{o}C for 90 min under vacuum.

The powder X-ray diffraction (XRD) patterns were measured using D5000 diffractometer from Bruker AXS. As X-ray source a Cu sealed tube charged with 40 kV and 40 mA (stability 0.01% per 8 hours) was used. The X-ray optics formed primary beam of 1 deg divergence in the scattering plane and 5 deg in perpendicular plane in Bragg-Brentano focusing geometry. The intensity was measured every 0.02 deg using 192 diode strip detector (LynxEye from Bruker) in continuous mode covering 2θ angular range of 20-142°. The measurement range covered 15 reflections of ceria fcc lattice. A Williamson-Hall plot type analysis [11,12] attempted in each case to separate peak broadening originating from the lattice strain and the crystal size. The lattice constants were extrapolated following Nelson-Riley scheme and Debye-Waller mean square lattice displacement was estimated from all intensities corrected for peak multiplicity, Lorenz polarization and structure factors.

The high resolution transmission electron microscopy (HRTEM) and high angle annular dark field (HAADF) observations of the gold catalysts were obtained by means of JEM 2010 FasTem analytical microscope provided with a Z-Z-contrast annular detector. The measurements of more than 700 particles on the basis of the Z-contrast observations were were used to establish the gold particle size histograms. The mean size of gold particles (D_{Au}) was calculated by the formula formula $D_{Au}=\sum n_i D_i/\sum n_i$ where n_i is the number of particles with diameter D_i. The standard error related to the accuracy of of the values reported in both the average diameter and the histogram distributions was in the frame 0.03 – 0.08.

2.3. Catalytic activity, selectivity and stability in PROX

The degree of CO conversion and the selectivity toward CO_2 were evaluated in the temperature range 30–180 ºC by means of ABB infrared analyser for CO and CO_2 detection and ABB paramagnetic Magnos206 for O_2 analysing. The test sample (0.05 g) was placed in a U-shaped quartz glass reactor, equipped with a temperature programmed controller. The gas feed with total rate of 50 mL min^{-1} was composed of 60% H_2+ 1% CO + 1% O_2 and He as balance (WHSV of 60 000 mL g^{-1} h^{-1}). Catalytic tests at realistic PROX conditions were also performed adding to the gas feed 10% CO_2 and 10% H_2O. Long term stability tests at these conditions and at 100 ºC (the temperature of the highest CO conversion) were carried within for 24 h. On the basis of preliminary tests following catalyst pretreatment in oxidizing or reductive atmosphere, a reductive catalyst pretreatment before every test was chosen (5% H_2 in He for 30 min at 150 ºC) [9]. In respect to the analysis system and the appropriate calibration, the accuracy of the conversion and selectivity results was within 2-3% of the given value.

3. Results and discussion
3.1. Catalytic measurements

The degree of CO conversion and selectivity in PROX over gold catalysts on alumina, ceria and mixed oxides supports prepared by IM or MM methods are illustrated in Fig. 1.
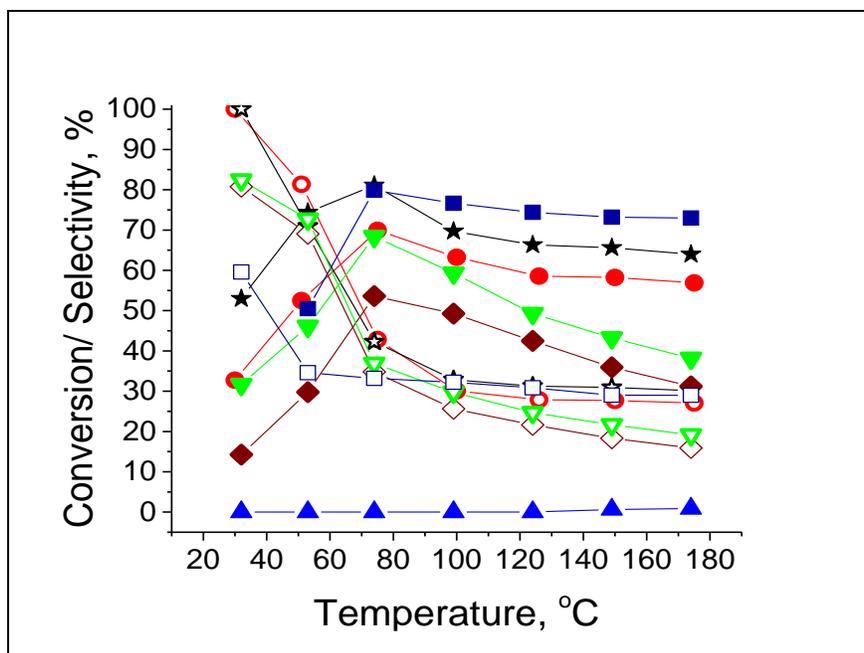

Fig. 1: CO conversion and selectivity of the studied gold catalysts: AuCe (■), AuAl (7), Au20CeAlMM (★), AuY20CeAlMM (●), Au20CeAlIM (◆) and AuY20CeAlIM (▼). The selectivity is illustrated by the corresponding empty symbols.

In all cases no trace of methane as a side product was registered. AuAl sample showed almost zero activity. Generally, the gold catalysts on CeO_2/Al_2O_3 and Y-doped CeO_2/Al_2O_3 supports prepared by MM exhibited better PROX behaviour as

compared to the corresponding supports prepared by IM. These results are in agreement with the study of Carabineiro et al. [13] showing that gold catalysts on supports obtained by simple physical mixture of commercial alumina and different metal oxides (including CeO_2) were much more active in CO oxidation than the gold catalysts on corresponding supports prepared by traditional way of impregnation. The positive effect of yttrium [9] was confirmed by the higher activity of AuY20CeAlIM then that of Au20CeAlIM catalyst. However, the yttrium-free Au20CeAlMM catalyst showed the highest CO conversion, equal to that of AuCe at 80 ºC. The activities of the catalysts at this temperature followed the row: AuCe=Au20CeAlMM>AuY20CeAlMM=AuY20CeAlIM> Au20CeAlIM. The selectivity toward CO_2 at 80 ºC over Au20CeAlMM was even better as compared to AuCe sample. Catalytic test with 10% CO_2 and 10% H_2O addition to the gas feed was carried out over Au20CeAlMM, AuY20CeAlMM and AuY20CeAlIM samples (the Au20CeAlIM catalyst with the lowest CO conversion was not tested). The results are shown in Fig. 2. The drop of PROX activity and selectivity at these conditions can be explained by the well-known detrimental effect, especially of CO_2. It is related to the competitive adsorption between CO and CO_2, the latest led to the carbonate and carboxylate species accumulation and blocking of the active sites [14,15].
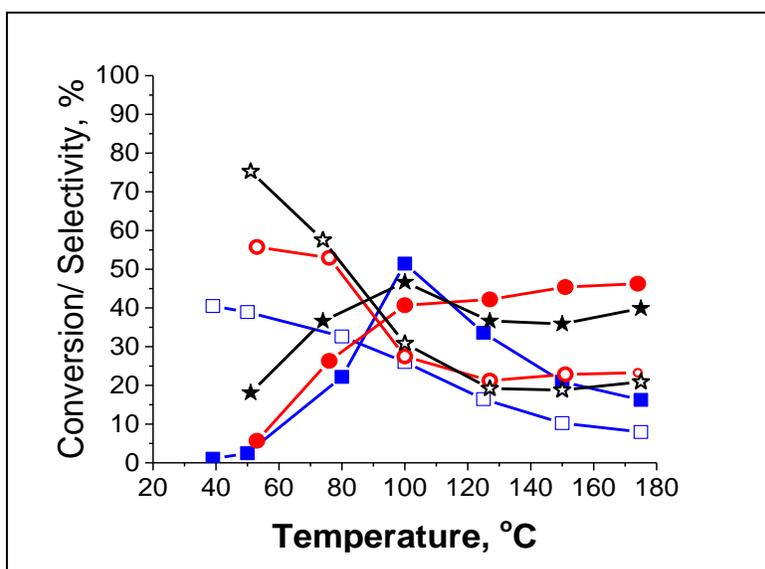

Fig. 2: CO conversion in PROX with CO_2 and water addition over AuY20CeAlIM (■) Au20CeAlMM (★) and AuY20CeAlMM (●) catalysts. The selectivity is illustrated by the corresponding empty symbols.

The best performance in the presence of CO_2 and water was obtained at 100 ºC, following the line of sample activities: AuY20CeAlIM>Au20CeAlMM>AuY20CeAlMM. The long term test during 24 h at this temperature showed more significant decrease with the time of CO conversion and selectivity over Au20CeAlMM catalyst, while Y-containing samples exhibited better stability.

3.2. Catalyst characterization

The actual gold content (C_{Au}), estimated by XRF analysis is given in Table 1. It is seen that the amount of gold on IM supports was closed to the nominal one, while on MM supports the C_{Au} values were almost twice lower. These observations can be explained by the effect of supports preparation on the distribution of the CeO_2 phase with respect to alumina: when applying IM method, the ceria layers covered alumina surface, while by MM ceria phase was randomly distributed and a large part of alumina surface remained free. The lower gold content on MM supports could then be related to the prevailing affinity of gold with ceria during the deposition precipitation procedure. The existence of ceria free alumina areas decreased the gold anchoring probability.
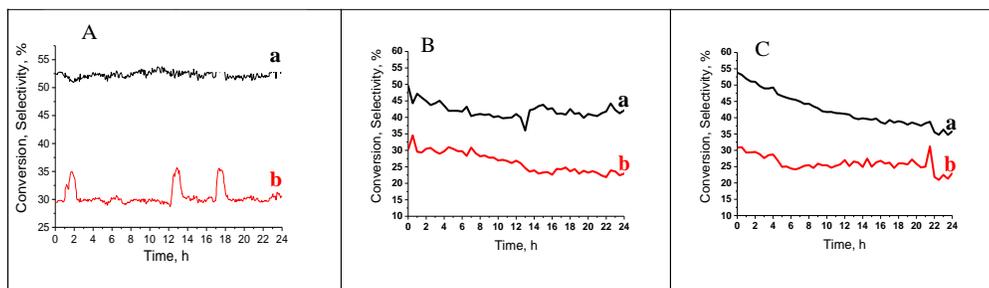
Fig. 3: CO conversion (a) and selectivity (b) in PROX with CO_2 and water addition during the long term test at 100 ºC over: AuY20CeAlIM (A), AuY20CeAlMM (B) and Au20CeAlMM (C).

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The values of specific surface area (S_{BET}), mean pore diameter (d_{pore}) and total pore volume (v_{pore}) of gold catalysts on ceria/alumina and Y-doped ceria/alumina supports prepared by IM and MM are listed in Table 1. The textural characteristics of the supports prepared by MM were similar to the used γ-alumina. A larger decrease of S_{BET} and v_{pore} was observed in the case of the IM supports.

Table 1: BET surface area (S_{BET}), pore volume (v_{pore}), mean pore diameter (d_{pore}), average particles size (D_{ceria}) and lattice parameter (a_{ceria}) of ceria estimated by XRD; actual gold content (C_{Au}) and average size of gold particles (D_{Au}) estimated by HRTEM/HAADF.

Sample	S_{BET} (m²/g)	v_{pore} (cm³/g)	d_{pore} (nm)	D_{ceria} (nm)	a_{ceria} (Å)	C_{Au} (wt.%)	D_{Au} (nm)
γ-Al_2O_3	200	0.53	10.6	-	-	-	-
Au20CeAlIM	149	0.36	9.6	11.4	5.398(1)	2.86	1.9
AuY20CeAlIM	150	0.37	9.3	11.4	5.399(1)	2.88	1.6
Au20CeMM	172	0.45	10.3	6.6	5.409(2)	1.64	2.2
AuY20CeMM	172	0.43	10.1	6.2	5.410(2)	1.66	3.1

The XRD patterns of the studied catalysts showed crystal phases of CeO_2 and γ-Al_2O_3 (not illustrated in a figure). The average size of ceria particles (D_{ceria}) and the lattice parameter (a_{ceria}) are given in Table 1. Significantly smaller (almost half) average crystallite size of ceria was achieved by MM support preparation as compared to the case of impregnation. The values of ceria lattice parameter, obtained for the IM samples, were smaller than the lattice parameter of stoichiometric CeO_2 (5.410 Å) [16,17] or Au/CeO_2 (5.413 Å) [9]. The reason could not be due to the replacement of Ce by Y ions because of the known proximity of the ionic radii (0.97 Å for Ce^{4+} and 1.02 Å for Y^{3+} in eight-fold coordination). In agreement, the a values of undoped and Y-doped samples are quite close for both preparation methods. The BET and XRD results (Table 1) revealed

the influence of preparation method on the textural and structural features of ceria/alumina supports. The smaller ceria particles obtained using MM method entered the pores leading to slight lowering of surface area and pore volume as compared to alumina, while the mean pore diameter remained the same. Differently, ceria particles with average size than the mean alumina pore diameter were obtained using impregnation. The large CeO_2 particles blocked the pores in a decrease of surface area, pore diameter and volume. The clogging pores hindered the access of reagents, causing a reduced reactivity of gold catalysts on IM as compared to MM ceria/alumina supports. These observations explained the better PROX behaviour of Au20CeAlMM and AuY20CeAlMM as compared to the corresponding IM catalysts.
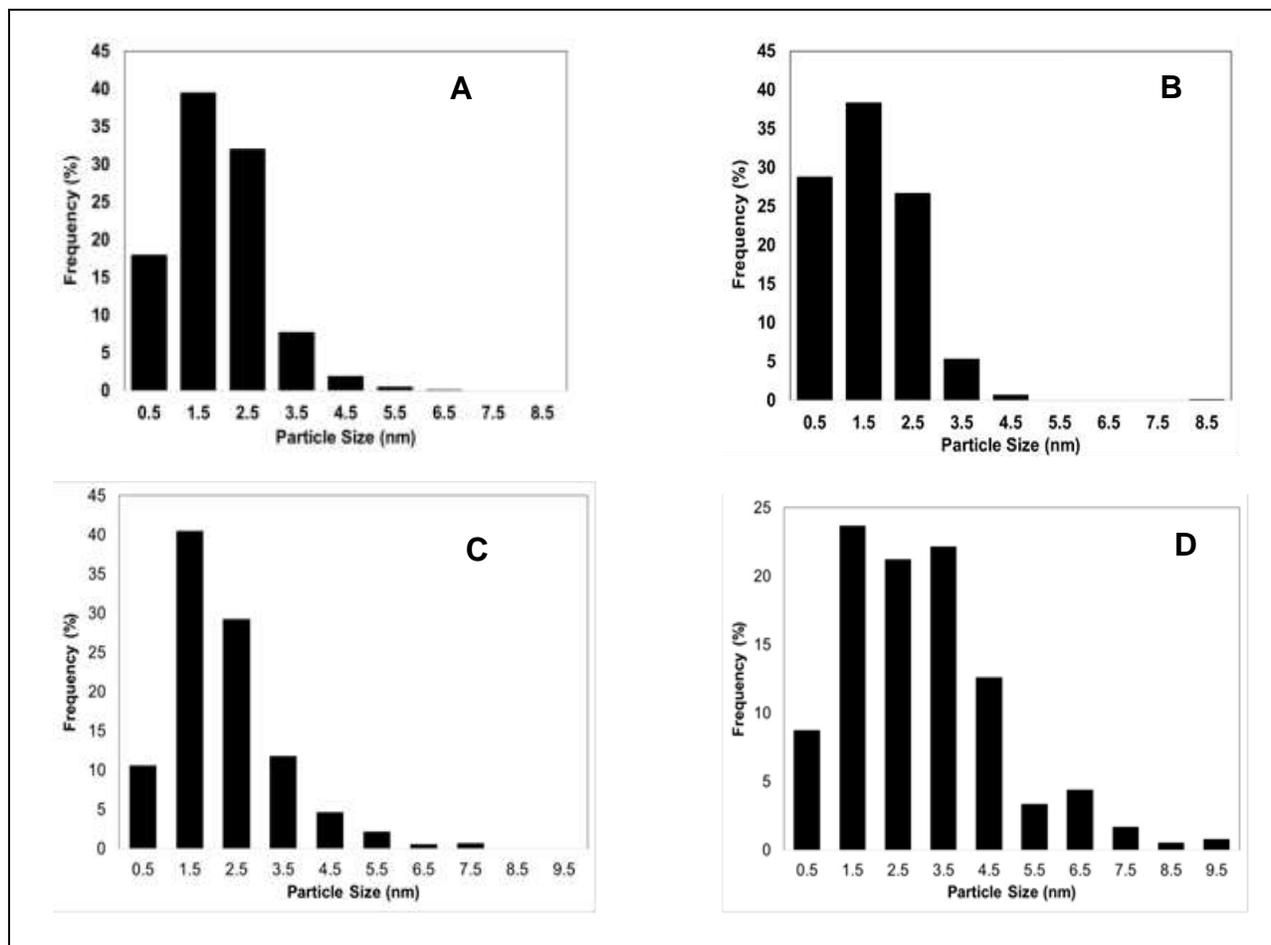

Fig. 4: Size distribution histograms of gold particles for the studied catalysts: Au20CeAlIM (A), AuY20CeAlIM (B), Au20CeAlMM (C) and AuY20CeAlMM (D).

Reflections of gold were registered only for AuAl and the calculated average size of gold particles was 44 nm. This observation was consistent with the extremely low activity in PROX. Reflections of gold and Y_2O_3 phase were not detectable by XRD for the other studied samples. The presence of separate Y_2O_3 crystals in the supports prepared by both methods were evidenced by HRTEM in the respective Fast Fourier transforms images with the interplanar distance of 2.499 Å that corresponds exactly to the distance reported in JCPDS data file 88-1040. Supplementary to the role of Y-modification of ceria, the presence of Au/Y_2O_3 could contribute for higher PROX activity according to the reported conclusion that Y_2O_3, stabilizing Au active species, improved the CO oxidation activity [18]. In this respect, the lower PROX activity of AuY20CeAlMM compared to that of Au20CeAlMM was not expected. The possible reason was

searched in the dispersion of gold as a crucial factor for CO activation. The average size (Table 1) and the size distribution histograms (Fig. 4) of gold particles were determined on the basis of HRTEM and Z contrast (HAADF) images. Small average size of gold particles between 2.0 and 2.4 nm was estimated in all cases except a higher value of 3.1 nm for AuY20CeMM catalyst. The size distribution histogram of this sample represented bigger fractions of particles larger than 2 nm and some particles larger than 10 nm were also registered (0.9 % of the measured particles). Differently, for Au20CeMM catalyst (average size of gold particles 2.2 nm) the percentage of particles from 1 to 1.99 nm was the highest (40%) and no particles larger than 10 nm were observed.

It is known that bigger Au particles adsorb relatively less CO [19]. Moreover, accepting the Mars–van Krevelen mechanism [6], the interface between gold and support is of crucial importance. The HRTEM analyses showed that apparently the gold particles deposited on Al_2O_3 crystals were larger than those deposited on CeO_2. Such results in combination with the already commented lower gold loading on the supports prepared by MM could mean a reduced perimeter length between the gold particles responsible for CO activation and the supplying oxygen active ceria phase in the case of AuY20CeMM as compared to Au20CeMM catalyst. We supposed this as a reason for the unforeseen lower PROX activity over the Y-containing MM sample (Fig. 1).

In the case of CO_2 and water addition, the observed activity at 100 ºC over Au20CeMM was slightly higher than that of AuY20CeMM but at higher temperatures the Y-presence showed a positive effect. The performance of AuY20CeMM catalyst was better above 100 ºC than that of the Au20CeMM one for which the highest CO conversion sharply decreased. The long term tests (Fig. 3) revealed the role of Y-doping for better catalyst stability. It was reported that CeO_2 has stronger basic properties as compared to Y_2O_3 [20]. The higher resistance to CO_2 deactivation could be related to the Y_2O_3 (as commented above a separate Y_2O_3 phase was evidenced by HRTEM) covering ceria and lowering the surface basicity.

4. Conclusion

Gold catalysts on CeO_2/Al_2O_3 and Y-doped CeO_2/Al_2O_3 supports (20 wt.% of CeO_2 and 1 wt.% Y_2O_3) prepared by mechanical mixing exhibited better PROX behaviour as compared to the corresponding samples deposited over supports obtained by impregnation (gas feed composition 60% H_2+ 1% CO + 1% O_2). The explanation was related to the effect of preparation method on the textural and structural properties of the supports. The MM method led to smaller ceria particles which did not clog the pores of alumina. Differently, in case of IM technique the pore blocking by ceria particles with average size bigger than the mean pore diameter of alumina caused difficult access of reagents and therefore a reduced activity. The result of the highest CO conversion at 80 ºC, equal to that of Au/ceria, over the yttrium-free MM catalyst was unexpected. The explanation was found in the key role of the interface between gold, responsible for CO activation, and ceria support supplying active oxygen. The results for actual gold loading and the HRTEM data revealed reduced length of the gold/ceria border for Y-doped MM catalyst. Adding CO_2 and water to the gas stream, this sample exhibited again a slightly lower activity as compared to the undoped one at 100 ºC but at higher temperatures the order of activities changed. The long term test in the presence of CO_2 and water revealed the beneficial role of Y-doping for catalysts stability.

The reported results about gold catalysts deposited on CeO_2/Al_2O_3 supports (with only 20 wt.% of CeO_2) could contribute to the developing of active, selective and cost-efficient catalysts for hydrogen purification in PEMFC devices.

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