



ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he

H₂ purification through preferential oxidation of CO over ceria supported bimetallic Au-based catalysts

Roberto Fiorenza, Carmelo Crisafulli, Salvatore Scirè*

Dipartimento di Scienze Chimiche, Università di Catania, Viale A. Doria 6, 95125, Catania Italy

ARTICLE INFO

Article history:

Received 8 February 2016

Received in revised form

13 May 2016

Accepted 13 May 2016

Available online xxx

Keywords:

PROX

Bimetallic catalysts

Cerium oxide

PEM fuel cells

Deposition-precipitation

ABSTRACT

CeO₂ supported mono and bimetallic Au catalysts (Au–Ag, Au–Cu, Au–Pd, Au–Ru), prepared by deposition-precipitation, were tested in the preferential oxidation of CO in the excess of H₂ (PROX). Activity data showed that the PROX performances of Au/CeO₂ are boosted by addition of Ag and to a minor extent Cu, whereas Ru and Pd have a negative effect. For both Au–Ag and Au–Cu systems the deposition order did not affect the catalytic performance whereas 1wt%/1wt% was found as the optimal Au/second metal ratio. On the basis of characterization data (H₂-TPR, TG-DTA, DRIFT, Surface Area measurements) it was proposed that the addition of Ag and Cu to Au/CeO₂ leads to a higher reactivity of surface ceria oxygen involved in the PROX reaction through a Mars-van Krevelen mechanism. The higher activity of the Au–Ag/CeO₂ system was attributed to the occurrence of a strong mutual interaction between gold and silver that positively affects the PROX performance in terms of yields to CO₂ and stability under reaction conditions.

© 2016 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

Low temperature proton exchange membrane fuel cells (PEMFC) promise to be a cleaner and more efficient alternative to fuel combustion for power generation in stationary and mobile applications [1]. This technology has been extensively studied during the last two decades due to low operation temperature (around 80 °C), high efficiency and environmentally benign nature. The H₂ used in the PEMFC is usually obtained by steam reforming or partial oxidation of hydrocarbons followed by the water gas shift (WGS) reaction. However, the H₂-rich stream coming from the WGS still exhibits 1–2 vol% of CO, not tolerated by the PEMFC anode [2]. Therefore it is necessary to reduce the CO content in the hydrogen stream with the minimum H₂ consumption. For this purpose, several methods have been reported [3],

selective oxidation of CO (known as PROX reaction, PReferential OXidation) being one of the most promising [4].

Gold-based catalysts for PROX reaction still attracts the attention of researchers [5]. In fact, compared to other systems, as Pt-based or CuO/CeO₂, gold catalysts are more active in the low temperature range, matching the PEMFC operating temperature. It is well established that the catalytic performances of supported gold catalysts strongly depend on the preparation method, gold particles size and metal-support interaction [6]. In the last years CeO₂ has been largely employed as support in oxidation reactions due its high oxygen storage capacity (OSC), namely the ability to take up oxygen under oxidizing conditions and releasing it under reducing ones. In particular gold supported on ceria has been reported among the most active systems for volatile organic compounds combustion [7], low temperature WGS reaction [8] and PROX [7,9].

* Corresponding author. Tel.: +39 0957385112; fax: +39 095580138.

E-mail address: sscire@unict.it (S. Scirè).

<http://dx.doi.org/10.1016/j.ijhydene.2016.05.114>

0360-3199/© 2016 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

Gold performance can be improved by alloying gold with another metal. Various bimetallic systems were investigated for the PROX and CO oxidation as Au–Mn, Au–Ce, Au–Pt, Au–Rh, Au–Cu and Au–Ag [10–17]. Recently we investigated CeO₂ supported Au–Ag and Au–Cu catalysts for both VOC combustion and PROX, pointing out a positive role of small amounts of the second metal [18]. We here compared the results of addition of different metals (Ag, Cu, Pd, Ru) to Au/CeO₂, with the aim to find the best bimetallic system for the PROX reaction, in particular focussing on the role of the second metal content and the order of deposition.

Experimental

Catalysts preparation

The cerium oxide support was prepared by precipitation with KOH (0.1 M) from water solution of Ce(NO₃)₃·6H₂O, and subsequent filtration and calcination in air at 450 °C for 4 h of the obtained solid. CeO₂ supported metal catalysts were prepared by deposition-precipitation using KOH as precipitating agent and HAuCl₄, AgNO₃, Cu(NO₃)₂·6H₂O, RuCl₃ or PdCl₂ as precursors. For the monometallic samples after the pH of the aqueous solutions of the metal precursor was adjusted to the value of 8 with KOH (0.1 M), cerium oxide was added under stirring to the solution, keeping the slurry at 70 °C for 3 h, then kept digesting for 24 h, filtering, washing until disappearance of nitrates and chlorides and then drying at 110 °C. The same procedure was used for the bimetallic samples with the difference that the solution of the second metal was added 30 min after the addition of CeO₂ at the solution of the first metal. Samples were coded with the element symbol preceded by the number indicating the weight % of the metal. The order of the element symbols reflects their deposition order in bimetallic samples.

Catalysts characterization

TG/DTA measurements were carried out on a Linseis STA PT 1600 instrument. Samples were heated in an aluminium sample boat up to 500 °C at 20 °C min⁻¹ under N₂. The analysis was performed on sample powders pre-calcined in air at 200 °C for 1 h and then reduced in H₂ at 150 °C for 1 h, as in the catalytic tests.

Diffuse reflectance IR spectra were recorded in the range 4000–600 cm⁻¹ with a Perkin–Elmer FT-IR System 2000, KBr being employed to obtain the background spectrum.

Temperature programmed reduction (H₂-TPR) was carried out in a conventional flow apparatus with a TCD detector at heating rate of 10 °C min⁻¹ using 5 vol% H₂ in Ar. Before TPR experiments samples were calcined in air at 200 °C for 1 h. CuO powder was used to calibrate the detector signal, in order to estimate the quantitative consumption of hydrogen.

Surface area measurements were carried out with the BET nitrogen adsorption method using a Sorptomatic series 1990 (Thermo Quest). Before tests samples were outgassed (10⁻³ Torr) at 120 °C.

Catalytic activity tests

Catalytic activity tests were carried out in the gas phase at atmospheric pressure and different temperatures in a continuous-flow microreactor filled with catalyst (50 mg, 80–140 mesh) diluted with inert glass powder. Preliminary runs at different flow-rates showed the absence of external diffusion limitations. The absence of internal diffusion was verified by experiments with different grain size powders. The gas composition (total flow rate: 80 ml/min) was 1% CO, 1% O₂, the rest being H₂. A space velocity (GHSV) of 3.92 × 10⁻² mol CO h⁻¹g_{cat}⁻¹ was used. The effluent gases were analysed by an online gas chromatograph with packed column (Carboxen1000) and TCD detector. Before PROX activity tests samples were calcined in air at 200 °C for 1 h and then reduced in H₂ at 150 °C for 1 h.

CO and O₂ conversions, selectivity (defined as the ratio of O₂ consumption for the CO oxidation over the total O₂ consumption) and CO₂ yield were calculated by the following equations:

$$\text{CO conversion (\%)} = ([\text{CO}_2]_{\text{out}}/[\text{CO}]_{\text{in}}) \times 100$$

$$\text{O}_2 \text{ conversion (\%)} = (([\text{O}_2]_{\text{in}} - [\text{O}_2]_{\text{out}})/[\text{O}_2]_{\text{in}}) \times 100$$

$$\text{Selectivity (\%)} = (0.5 \times [\text{CO}_2]_{\text{out}}/([\text{O}_2]_{\text{in}} - [\text{O}_2]_{\text{out}})) \times 100$$

$$\text{CO}_2 \text{ yield (\%)} = (\text{CO conversion} \times \text{Selectivity})/100$$

Results and discussion

Screening of PROX activity of different gold-based bimetallic catalysts

Fig. 1 shows catalytic activity results, in terms of conversion of CO (Fig. 1A), selectivity towards CO oxidation (Fig. 1B), and yield to CO₂ (Fig. 1C) over gold-based bimetallic catalysts having 1wt%/1wt% Au/second metal ratio. No CO and O₂ conversions were observed up to 180 °C on the bare ceria and no CH₄ was detected in all experiments. On all samples CO conversion (Fig. 1A) increased with increasing reaction temperature reaching a maximum of 70% for 1Au at 60 °C, 85% for 1Au1Cu at 80 °C, 95% for 1Au1Ag at 85 °C, 65% for 1Au1Ru at 90 °C and 55% for 1Au1Pd at 60 °C. These results show that the CO oxidation activity is influenced by the catalyst used, with higher CO conversions at low temperature (60–100 °C) over the 1Au1Ag sample. Selectivity towards CO oxidation (Fig. 1B), defined as the ratio of O₂ consumption for the CO oxidation to the total O₂ consumption, always decreased on increasing reaction temperature. This behaviour agrees with literature results and it was attributed to the sensibly higher activation energy of H₂ oxidation compared to that of CO oxidation [7,15,16,18].

Download English Version:

<https://daneshyari.com/en/article/5147189>

Download Persian Version:

<https://daneshyari.com/article/5147189>

[Daneshyari.com](https://daneshyari.com)