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Gold catalysts supported on Y-modified ceria for CO-free hydrogen production *via* PROX

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ABSTRACT

The preferential CO oxidation in the presence of excess hydrogen (PROX) was studied over gold catalysts on yttrium-modified ceria supports synthesized by impregnation (IM) and co-precipitation (CP) methods. In order to avoid oxygen vacancies ordering by heavily yttrium doping, a low extent Y-modification of ceria (up to 7.5 wt.% Y_2O_3, *i.e.*, 11 at.% Y) was investigated. The samples were characterized by XRD, HRTEM/HAADF, Raman and XP spectroscopy and TPR measurements. At the operating temperature of the fuel cells (80–120 °C) the selectivity of the Y-doped gold catalysts was larger than that of Au/CeO_2. However, at these temperatures all studied catalysts exhibited quite similar PROX activity and selectivity. This was explained by the similarity in relatively small average size of gold particles (estimated by HRTEM in the 2.1–3.5 nm range) and the reducibility of ceria surface layers. Raman spectroscopy showed a higher extent of bulk defects, O vacancies and interstitials with increasing Y-doping in the supports made by the CP method and-based on sequential spectra obtained under oxidizing and reducing conditions- enabled the assignment of a band at ~605 cm^{-1} to a vibrational mode within the anionic (oxygen) sub-lattice that involve mobile (detachable) oxygen atoms that can be delivered by the support under suitable conditions. The absence of correlation between CO conversion and yttrium loading could suggest a preferential role played by the surface modification and surface oxygen mobility in PROX. Although under ideal conditions there was not substantial dependence of the behavior in PROX on the preparation method of doped supports, the IM method was more appropriate than the CP method for PROX with CO_2 and water addition to the gas feed. The improved tolerance to CO_2 could be explained by the lowering of ceria surface basicity due to the nanosized Y_2O_3, covering ceria grains.

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1. Introduction

Hydrogen utilization in the proton exchange membrane (PEM) fuel cells to transform the chemical energy into electricity with zero harmful emissions is a topical issue. Hydrogen is mainly produced by hydrocarbons (from fossil or from renewable sources) reforming followed by water gas shift reaction (WGSR) to enhance the production of H_2 and lower the CO concentration in the reformate stream down to 1–2%. However, to prevent the poisoning of fuel cell anodes, the CO amount must be below 10 ppm for Pt anodes and below 100 ppm for CO-tolerant alloy anodes. One of the most effective and economic ways for CO cleanup is its preferential oxidation in the presence of excess hydrogen (PROX). The key issues for PROX catalysts are: (i) control of the undesirable hydrogen oxidation reaction; (ii) in order to avoid the heat changes, the temperature range of high catalytic activity and selectivity in PROX must be the fuel cells operating temperature interval 80–120 °C. This is in line with the catalytic behavior of oxide-supported gold catalysts, exhibiting a satisfactory balance of high activity and selectivity at relatively low temperatures due to the lower energy barrier for CO oxidation as compared to H_2 oxidation [1]. A recent survey [2 and

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references therein] has been focused on the developments of gold-based PROX catalysts and reviewed the effects of the nature of the support (composition, size and morphology), the influence of promoters and the characteristics of gold on the catalytic performance in PROX. Other aspects of the catalysts' behavior in performance grounds, such as (i) high CO conversion with excellent selectivity toward CO_2, (ii) good resistance against the effects of H_2O and CO_2 (in the real reaction stream the usual CO_2 concentration is about 20% and the H_2O amount is about 10%), (iii) stable and reproducible catalytic behavior are far from being well understood. To this end, studies of nanosized gold catalysts for CO-free hydrogen production are of high priority and relevance.

Ceria is an appropriate support for gold catalysts in PROX [3–6] due to its well-known high oxygen storage capacity (OSC). Besides, the intimate interaction between gold and ceria leads to small gold particles stabilization. Doping foreign cations into the ceria lattice is known to improve the redox properties of ceria because of the induced structural and electronic changes. The use of different dopants and various preparation methods could influence not only the OSC of ceria-based supports but the gold dispersion as well.

PROX over gold catalysts on ceria modified with rare earths was investigated in several studies [7–9]. In a recent study by Ilieva et al. [10] praseodymium was chosen as a modifier of ceria. The own redox behavior ($Pr^{4+} \leftrightarrow Pr^{3+}$) was expected to enhance the oxygen supplying by the support. However, a lower CO conversion of gold catalysts on Pr-doped with respect to the undoped ceria was established and the results were attributed to the Pr presence, hindering the surface re-oxidation. The efforts for selection of ceria based gold catalysts with high activity, CO_2 selectivity and long-term stability in PROX at real feed conditions (presence of CO_2 and water) continue in the present study using yttrium as ceria modifier. The yttrium supply is abundant and the Y-doped CeO_2 systems encountered a special interest among doped CeO_2 materials. In a previous study it has been shown that the gold catalyst on Y-modified ceria, prepared by co-precipitation, exhibited the highest PROX activity and selectivity as compared to gold catalysts supported on ceria modified by other rare earths as La, Sm and Gd [9]. However, the results obtained by Jardim et al. [11] pointed out that the Y doping of ceria did not improve the PROX activity and the stability of the gold catalyst, which was less resistant to the thermal treatment as compared to gold on bare ceria. The explanation was related to the large dopant segregation at the surface, leading to higher mobility and sintering of the gold nanoparticles, because the study was carried out with high amount of Y-doping (30 wt.% Y_2O_3). The review of the literature leads to the conclusion that the oxygen ion conductivity (related to OSC) is a function of dopant concentration and that heavily yttrium doped ceria (*i.e.*, above 10–15 at.% [12–14 and references therein]) causes its lowering because of oxygen vacancy ordering. Atribak et al. [15] have studied $Ce_{1-x}Y_xO_2$ catalysts for soot oxidation in air and they concluded that the high yttrium loading ($x = 0.12$) is less effective than low dosage ($x = 0.01$). The results obtained by She et al. revealed that catalytic activity in WGSR first increased with increasing Y amount, but then decreased with further increase in the Y content; CuO/CeO_2 catalyst doped with 2 wt.% of Y_2O_3 showed the highest catalytic activity and thermal stability [16].

The motivation for studying gold catalysts supported on Y_2O_3-doped CeO_2 at low/moderate extent of Y-doping for CO—free hydrogen production *via* PROX comes as straightforward consequence of the aforementioned results. The effect of various Y amounts and different support preparation methods on the gold particles size and supports features was studied by means of XRD, HRTEM/HAADF, high temperature Raman and XP spectroscopy and TPR measurements. The impact of moisture and CO_2 on the catalytic activity and selectivity in PROX over selected catalysts was examined as well.

2. Experimental

2.1. Sample preparation

Two series of yttrium-modified ceria supports were prepared by impregnation (IM) and by co-precipitation (CP) methods. Different Y-dopant amounts were chosen: 1, 2.5, 5 and 7.5 wt.% of Y_2O_3 or correspondingly 1.5, 3.8, 7.4 and 11.0 at.% of Y. Aqueous solutions of $Y(NO_3)_3 \cdot 6H_2O$ were used for the impregnation of ceria that was carried out by vigorous stirring at room temperature for 4 h. Then, the suspension was evaporated under vacuum at 70 °C in a rotary evaporator until water was completely removed. Ceria was prepared by precipitation of aqueous solution of $Ce(NO_3)_3 \cdot 6H_2O$ with K_2CO_3 at constant pH = 9.0 and at a temperature of 60 °C. Using the second technique (CP), the supports were prepared from a solution of the corresponding Y and Ce nitrates in appropriate ratio, coprecipitated with a solution of K_2CO_3 at constant pH 9.0 and temperature 60 °C. The precipitates were aged at the same temperature for 1 h, then filtered and washed until removal of NO_3^- ions. All resulting precursors were dried in vacuum at 80 °C and calcined in air at 400 °C for 2 h. The mixed supports were denoted as *x*YCeIM and *x*YCeCP, correspondingly ($x = 1$, 2.5, 5 and 7.5, denoting the wt.% amount of Y_2O_3).

Gold (3 wt.%) was loaded by the deposition-precipitation method. It was deposited onto mixed oxides thoroughly suspended in water *via* chemical interaction between $HAuCl_4 \cdot 3H_2O$ and K_2CO_3, under vigorous stirring, while keeping constant pH = 7.0. The precipitation was carried out using the 'Contalab' system (Switzerland) under full control of all parameters of preparation (pH, temperature, stirring speed, reactant feed flow rates, etc.). After filtering and careful washing, the precursors were dried under vacuum and calcined in air at 400 °C for 2 h. A careful inspection of XP spectra of the gold catalysts showed that no peaks related to the Cl presence were registered. The gold-containing samples were denoted as Au*x*YCeIM and Au*x*YCeCP, correspondingly.

All the initial salts used were "analytical grade".

2.2. Sample characterization

The BET surface area (S_{BET}) of the samples was determined on a Carlo Erba Sorptomat 1900 instrument. The fully computerized analysis of the nitrogen adsorption isotherm at −196 °C allowed estimating the specific surface areas of the samples in the standard pressure range 0.05–0.3 p/p_o. Prior to the measurements, the samples were outgassed at 200 °C for 30 min under vacuum.

The actual gold loading for each catalyst was 3 (±0.05) wt%, as measured by Atomic Absorption spectroscopy using Varian Vista MPX apparatus.

X-ray powder diffraction (XRD) measurements were performed using aD5000 diffractometer (Bruker AXS), with Cu sealed tube operating at 40 kV and 40 mA. The setup employed Bragg-Brentano focusing geometry with 1 deg. beam divergence and LynxEye strip detector. The data were analyzed using PeakFit program (Jandel Scientific) fitting XRD profiles to $K\alpha$ 1,2 doublets having PEARSON VII analytical form. The crystal size of gold particles was estimated from FWHM (full width at half maximum) of the strongest (1 1 1) reflection. The CeO_2 phase was analyzed on the basis of 14 well measured reflections and Williamson-Hall plot [17,18] and the average crystal size (average column length over all available crystallographic directions) was calculated.

High resolution transmission electron microscopy (HRTEM) and high angle annular dark field (HAADF) observations of the gold

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