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H_2 oxidation as criterion for PrOx catalyst selection: Examples based on Au–CoO_x-supported systems

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ABSTRACT

A new approach for understanding PrOx reaction over gold catalysts is proposed in this work. The competition between H_2 and CO oxidation has been studied over a series of Au/MO_x/Al_2O_3 (M = Ce and Co) catalysts in simulated post-reforming gas stream, containing H_2O and CO_2 for H_2 cleanup goals. The catalysts' behavior is correlated to their oxygen storage capacity, redox behavior, and oxidation ability. The estimation of the reaction rates reveals that in these solids the H_2 combustion, the selectivity limiting factor in the PrOx process, is mainly controlled by the support and not by the gold presence. The possible use of the hydrogen oxidation reaction as a catalyst selection criterion is discussed.

1. Introduction

One of the most important issues related to the hydrogen technology is the serious difficulty encountered for onboard H_2 storage as well as for distribution from a centralized production facility [1]. As a result, many efforts have been focused on the conversion of more readily available fuels to hydrogen, either for on-board or for stationary applications. Hydrogen is mainly produced by hydrocarbons- or alcohols-reforming reactions [2] in which the hydrogen stream is often accompanied by relatively high levels of carbon oxides and steam [1,3].

An essential requisite for fueling the polyelectrolyte membrane fuel cells (PEMFC) with hydrogen is the absence of CO or at least its presence within the ultra-low trace levels, preferably less than 10 ppm. Therefore, CO abatement processes must be applied to reduce its level within the H_2 stream. The CO purification processes are commonly composed by a combination of high- and low-temperature water–gas shift reactions, allowing CO decrease to 1–2 vol.% level [4–6] and the preferential oxidation with air of the pre-cleaned reformate (PrOx) to reduce the CO to ultra-low level. The PrOx reaction is often preferred as a cheap and effective solution for the final purification step, since the range of working temperatures matches that of the PEM fuel cells operation [7].

For PrOx reaction, the gold-based catalysts are potentially advantageous [8,9]. Earlier studies on Au/ceria catalysts found high activity and good selectivity of those systems in the 70–120 °C temperature range, caused by the active participation of ceria in the oxidation process governed by gold [10–12]. It is often reported that the presence of structural defects in the ceria lattice, for example, oxygen vacancies, potentiates the activity of the gold-based catalyst in the CO oxidation reaction [9,13]. As a common strategy, the inclusion of aliovalent cations in the ceria lattice is employed to increase the number of those defects [13–16]. The CO oxidation activity is then directly related to the concentration of those defects in such a way that higher the number of defects, greater the oxygen mobility and higher the oxidation activity.

However, those systems, together with the high efficiency in the CO oxidation, in terms of activity show limited selectivity due to their ability to burn H_2 with the same facility. As a result, all future applications of those systems are questioned more by the selectivity than by its activity. Then it is essential to study the selectivity of the PrOx gold-based catalysts with the consideration of the H_2 oxidation, as a separate process. Several authors have studied H_2 oxidation and also the effect of H_2 presence on the selective CO oxidation on gold catalysts with contradictory results [17–20]. An enhancement of the CO oxidation activity in the presence of hydrogen was found in some studies [17,19], and negative effect was reported by others [18,20]. In addition, numerous reports comparing the PROX activity and selectivity of a variety

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of supported gold catalysts in dry and post-reformate conditions could be found in the literature [21–24]. Notwithstanding the valuable information that can be extracted from these works, the influence of the realistic reforming streams, for example, the presence of H_2O and CO_2 and its effect on the hydrogen combustion, was obviated. This major topic and some other questions, such as, *which is the role of the support in the H oxidation? Is there a support-dependent hydrogen effect on the CO oxidation? Are the gold nanoparticles the only responsible for the hydrogen oxidation?* remain unclear.

In order to address these issues, the main goal of this work was to study the hydrogen combustion and PrOx activity in presence of CO_2 and H_2O over a series of gold–cobalt-based catalysts. The H_2 oxidation has been discussed as a criterion for providing clues focused toward proper catalyst design and selection.

2. Experimental

2.1. Catalyst preparation

2.1.1. Support preparation

The supports were synthesized by a conventional impregnation method. The necessary amounts of metal precursor (cobalt and/or cerium nitrate, Aldrich) were impregnated on γ-alumina powder (Sasol). The impregnation was carried out in 50 mL of ethanol in rotary evaporator at reduced pressure and temperature of 50 °C. The obtained dry solid was treated with NH_3 solution (10 mol L^{-1}) during 30 min in order to assure the full conversion of the nitrate precursors to hydroxides. The supports were then filtered, dried, and calcined at 500 °C for 4 h. The fraction of 100–200 μm was retained for the gold deposition process.

Cerium or cobalt spinel oxide amount was fixed to 15 wt.% in the case of binary supports. For the ternary Al_2O_3-supported cerium–cobalt mixed oxides, 1 and 2 wt.% of Co_3O_4 loadings were chosen and correspond to 0.067 and 0.134 Co/Ce molar ratio, respectively. In the adopted nomenclature, the oxygen is omitted for simplification and the dopant contents are expressed as the corresponding theoretical loadings. For example, the CeCo2/Al solid should contain 15 wt.% cerium oxide and 2 wt.%. of Co_3O_4 both deposited on Al_2O_3.

2.1.2. Gold deposition

The gold (2 wt.% nominal value) was deposited by direct anionic exchange method, assisted by NH_3 as described elsewhere [25] using $HAuCl_4$ (Alfa Aesar) as gold precursor. After Au deposition, the solid was dried at 100 °C overnight and calcined in air at 350 °C for 4 h.

2.2. Characterization

The chemical composition of the samples was determined by X-ray microfluorescence spectrometry (XRMF) in an EDAX Eagle III spectrophotometer with a rhodium source of radiation working at 40 kV.

X-ray diffraction (XRD) analysis was performed on X'Pert Pro PANalytical equipment. Diffraction patterns were recorded with Cu Kα radiation (40 mA, 45 kV) over a 2θ-range of 10–80° and a position-sensitive detector using a step size of 0.05° and a step time of 240 s.

High-resolution transmission electron microscopy (HRTEM) and high-angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) images were recorded on a JEOL2010F instrument. The spatial resolution at Scherzer defocus conditions in HRTEM mode is 0.19 nm, while the HAADF-STEM studies were performed using an electron probe of 0.5 nm of diameter and a diffraction camera length of 10 cm.

The UV–Vis spectra were recorded on Varian spectrometer model Cary 100, equipped with integrating sphere and $BaSO_4$ as reference. All the spectra were collected in a diffuse reflectance mode and transformed to a magnitude proportional to the extinction coefficient through the Kubelka–Munk function $F(\alpha)$.

H_2-TPR was carried out on 50 mg of sample charged in a conventional U-shaped reactor as a function of temperature with constant heating rate of 10 °C min^{-1} till 900 °C. 50 mL min^{-1} certified 5% H_2 in Ar gas mixture was used, and the H_2 consumption was followed by TCD detector and quantified by using CuO standard (99,999%).

For the oxygen storage complete capacity (OSCC) measurements, 100 mg of sample were loaded into a U-shaped quartz reactor, and the temperature raised in 5% O_2/He flow (50 mL min^{-1}) till 350 °C with 10 °C min^{-1} heating rate. The system was then cooled down, and the temperature stabilized at the desired value in Ar flow (50 mL min^{-1}). Then, 10 O_2 pulses of 1 mL each were injected every 2 min. After 10 min of inert gas flow, 10 H_2 pulses (1 mL each) were sent to saturate the surface with H_2. In the next step, after 10 min of inert gas flow, the samples were submitted to 10 CO pulses (1 mL each). Again the sample is degassed during 10 min in Ar flow and subjected to new series of oxidizing pulses (10 O_2 pulses, 1 mL) followed by five alternating pair of CO–O_2 pulses, allowing the determination of the oxygen storage capacity (OSC). This methodology was employed at three different temperatures with the gas composition analyzed at the exit of the reactor by PFEIFFER Vacuum Prisma Plus mass spectrometer controlled by Quadera® software. The CO_2 pulses were calibrated after each measurement. Following the same procedure, several CO–H_2 pulses were alternatively flowed through the reactor, in order to study CO/H_2 oxidation competition.

It should be mentioned that these experiments do not correspond to purely defined oxygen storage capacity (OSCC and OSC) measurements as proposed by Duprez et al. [26], but only intend to simulate the oxygen availability of the solid under the PrOx conditions, oxygen behavior under H_2-saturated atmosphere, and solid surface.

2.3. Catalytic activity

The preferential CO oxidation reaction was carried out at atmospheric pressure in a stainless steel fixed-bed reactor of 9 mm inner diameter, with a 100 mL min^{-1} reaction feed composed by 1% CO, 1.5% O_2, 10% H_2O, 10% CO_2, 50% H_2, and N_2 as balance. For the hydrogen combustion, CO was removed from the stream (1.5% O_2, 10% H_2O, 10% CO_2, 50% H_2 balanced in N_2), and for the direct CO oxidation, H_2 was not included (1% CO, 1.5% O_2, 10% H_2O, 10% CO_2 balanced in N_2). The catalyst (100 mg, $100 < \phi < 200$ μm) was diluted with crushed glass particles with the same particle size forming a bed of about 5 mm in length. Products and reactants were separated and quantified by online gas chromatography (Agilent® 6890) equipped with HP PLOT Q and HP-5 columns and TCD detector. Prior to the catalytic measurements, the samples were treated under a 100 mL min^{-1} flow of air, at 300 °C during 1 h.

The CO conversion was calculated according to Eq. (1) where CO_{in} is the inlet CO concentration and CO_{out} is the outlet one.

$$\text{CO conversion } (\%) = \frac{CO_{in} - CO_{out}}{CO_{in}} \times 100 \quad (1)$$

The selectivity toward CO_2 formation was calculated using Eq. (2) where O_{2in} corresponds to oxygen in the inlet and O_{2out} to outlet concentration.