



The role of Au, Cu & CeO₂ and their interactions for an enhanced WGS performance



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ARTICLE INFO

Article history:

Received 12 October 2015

Received in revised form 7 January 2016

Accepted 12 January 2016

Available online 14 January 2016

Keywords:

WGS

Gold catalysts

Cerium oxide

Copper oxide

ABSTRACT

The WGS reaction over multicomponent Au/Ce_{1-x}Cu_xO₂/Al₂O₃ catalysts is studied in this work. The systems are carefully designed aiming to take advantage of every active phase included in the formulation: gold, ceria and copper. Special emphasis is given to the CeO₂-CuO synergy and its influence on the displayed catalytic performance with and without gold. To this aim a meaningful correlation between the physicochemical properties of the mixed materials and their activity/stability is proposed. In general terms the developed catalysts present high activity under realistic WGS reaction conditions, with fairly good long term stability. In addition, the systems successfully withstand start-up/shut-downs situations, indispensable requisite for real applications in the field of pure hydrogen production for fuel cell goals.

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1. Introduction

Bulk metallic gold is commonly known due to its high inertness and non-changing character being ideal for jewelry proposes. Its low chemical and catalytic activity converts gold in the least reactive transition metal, so that it is often referred to as the “coinage metal” [1–3]. However, gold becomes extremely active when subdivided into nanoscale (usually less than 5 nm) and dispersed over an adequate metal oxide and/or activated carbon supports [4–8]. Nanogold based catalysts have demonstrated outstanding efficiency in a broad range of catalytic reactions including hydrogenation, complete and selective oxidation and nucleophilic addition among other processes [7].

In particular, a stretch relationship between gold and the WGS reaction started twenty years ago with the seminal work of Andreev's group in which they report a very good performance of Au/Fe₂O₃ catalysts [9]. From then on, WGS and gold based catalysts have evolved together with a marked influence of the emerging hydrogen technologies and the use of the shift reaction as a fundamental stage gate for the pure hydrogen production [10]. In this context, the nature of the support and the effects

of metal ↔ support interactions (i.e. charge transfer between the oxide and gold) are of paramount importance to produce well performing gold based catalysts for the WGS reaction [3]. Despite the broad range of supports traditionally employed for gold nanoparticles, there is a general agreement that redox active supports are the most suitable ones. In particular, ceria has attracted big attention due to its excellent behavior in oxidation reactions and it is one of the most appropriate supports for the WGS [11–14].

The combination of ceria with Cu/CuO species has been also proposed as promising catalyst for the WGS and the preferential CO oxidation (PrOx) in both direct (Cu/CeO₂) and inverse configuration (CeO₂/Cu) [15,16]. The excellent activity of both type of configuration underlines the importance of the metal/oxide interface as a “hot spot” where most of the relevant reaction steps take place. As indicated by Flytzani-Stephanopoulos et al. [17] a redox reaction mechanism can be imagined for these Cu/CeO₂ systems. This process involves the oxidation of CO adsorbed on the Cu cluster by oxygen supplied to the metal interface by ceria, followed by H₂O filling of the oxygen vacancies on ceria. It is therefore desirable a fast oxygen migration from ceria to Cu sites at the metal-support interface. Furthermore, Cu itself is rather active for the shift reaction and indeed it is regarded as the active phase in the state of the art WGS catalyst in the low temperature regime (Cu/ZnO/Al₂O₃) [10].

On the other hand, the nano size of the ceria and copper particles is a key factor governing the catalytic activity [15]. In this regard, highly dispersed ceria particles with small particle size can

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be achieved by supporting ceria on a high surface carrier as carbon or alumina [18,19]. This approach also leads to enhanced oxygen mobility and reduces ceria expense while increasing the metal-surface extension due to the smaller size of the oxide crystal. The same behaviour is expected for CeO₂-CuO mixed systems, converting CeO₂-CuO/Al₂O₃ combinations into ideal supports and/or co-catalysts for gold nanoparticles.

In this scenario, a new family of carefully designed Au/Ce_{1-x}Cu_xO₂/Al₂O₃ catalysts for the WGS reaction is proposed in this work. The systems are studied under realistic conditions and submitted to demanding stability tests targeting a hypothetical application in the field of fuel cells. The effect of the Au-support interaction and the physicochemical phenomena behind the Ce-Cu synergy are also a subject of this study due to their strong impact on the catalytic performance.

2. Experimental

2.1. Catalyst preparation

2.1.1. Support preparation

The supports were synthesized by co-impregnation method. The necessary amounts of metal nitrate precursor (cerium and copper nitrates, Sigma-Aldrich) were co-impregnated on γ -alumina powder (Sasol). The impregnation was carried out in 50 mL of ethanol, evaporated at reduced pressure in rotary evaporator (Heidolph) at 50 °C till obtaining a dry solid. The support was then filtered, dried and calcined at 500 °C during 4 h. The intended composition of the samples was 15 wt.% of Ce-Cu mixed oxide dispersed on alumina with a diverse Ce_xCu_{1-x}O₂ stoichiometry. For sake of simplicity subscripts and decimals have been replaced by entire numbers and oxygen is omitted in the selected nomenclature. For example, the support labelled as Ce8Cu2/Al contains 15% of Ce-Cu mixed oxide with the stoichiometry Ce_{0.8}Cu_{0.2}O₂ dispersed on Al₂O₃.

2.1.2. Gold deposition

Gold was deposited by the direct anionic exchange method (DAE), assisted by NH₃ as described in literature [20]. A 10⁻⁴ mol L⁻¹ aqueous solution of the gold precursor HAuCl₄ (Alfa Aesar) was used in order to obtain a final Au loading of 2 wt.%. The support was sieved and the 100–200 μ m fractions retained was used to prepare the gold based catalysts. After Au deposition, the solid was dried at 100 °C overnight and calcined in air at 350 °C for 4 h.

2.2. Catalyst characterization

X-ray microfluorescence spectrometry (XRMF) was used to determine the chemical compositions and the analysis was performed in EDAX Eagle III spectrophotometer with Rh source of radiation.

The specific surface area was determined by N₂ adsorption-desorption measurements at liquid nitrogen temperature. The experiments were carried out on a Micrometrics Tristar II instrument. Before the analysis, the samples were degassed for 2 h at 250 °C in vacuum. BET equation was applied to obtain the specific surface area of the studied samples.

X-ray diffraction (XRD) analysis was carried out on X'Pert Pro PANalytical instrument. Diffraction patterns were recorded using Cu K α radiation (40 mA, 45 kV) over a 2 θ -range of 10–80° and using a step size of 0.05° and a step time of 240 s.

The Raman spectra were recorded in a dispersive Horiba Jobin Yvon LabRam HR800 spectrometer, with a 20 mW He-Ne green laser (532.14 nm) operating at 5 mW. The microscope used a 50 \times objective and a confocal pinhole of 1000 μ m.

The UV-vis spectra were recorded on an Avantes spectrometer model AvaLight-DH-S-BAL and using BaSO₄ 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 $F(\alpha)$. From UV-data, ceria band gap was estimated by plotting $[(F(R) h\nu)]^{1/2}$ against energy and the linear part of the curve further extrapolated to $[(F(R) h\nu)]^{1/2} = 0$.

For the oxygen storage capacity (OSC) measurements 100 mg of catalyst were loaded and activated into a U-shaped quartz reactor at 350 °C during 1 h in 5% O₂/He flow (50 mL/min). Then, the system is cooled and set to the desired temperature (200, 250 and 300 °C). For each temperature, ten O₂ pulses of 1 mL were injected every 2 min. The sample is then subjected after 10 min He degasification to four alternating series of pulses (CO-O₂-CO-O₂-CO-O₂-CO-O₂). The OSC is determined by the average amount of CO₂ per pulse formed after the first CO pulse of the alternated ones. This methodology is adapted from previous works published by Duprez et al. [21,22]. The gas composition at the exit of the reactor was analyzed by a mass spectrometer PFEIFFER Vacuum PrismaPlus controlled by Quadera[®] software.

Several assumptions were contemplated for the OSC calculations. Concretely, it was considered that i only oxygen atoms bonded to the cerium participate in the oxygen storage process; ii the surface is assumed homogeneous iii only one of the four oxygen atoms of ceria is involved in the storage (CeO₂ \rightarrow Ce₂O₃ + "O"); same for copper oxide (CuO \rightarrow Cu + "O") and iv null gold metal contribution to the reduction, e.g. the gold metal could not be reoxidized. Similar assumptions to estimate the overall OSC were reported elsewhere [19]. Furthermore, a possible underestimation of OSC due to carbonates formation would be rather equal for all samples allowing a meaningful comparison.

Temperature-programmed desorption (TPD) experiments were performed in a homemade apparatus coupled to a mass spectrometer Thermostar-QMS 200, Pfeiffer Vacuum. The m/e ratios in the 2–60 range were registered but only m/e = 44 (CO₂) signal is represented. 80 mg of the samples were heated in 25 mL/min flowing argon up to 800 °C at 10C/min.

2.3. Catalytic activity

Water-gas shift reaction was performed in a stainless steel tubular flow reactor (0.75 cm ID) at atmospheric pressure in the 140–350 °C temperature range. The catalysts were pelletized and sieved with the 600–800 μ m fraction employed for the test. The following conditions were applied: catalyst bed volume 1.5 cm³, space velocity 4000 h⁻¹ and gas composition: 30% vol. H₂O + 4.5% vol. CO balance in N₂. Water was injected into flowing gas stream by HPLC pump, vaporized and homogenized with the gas feed before entering the reactor. The CO and CO₂ content was determined by on line ABB gas analyzer and the activity expressed in terms of CO conversion. Diffusion limitation tests were investigated over a gold-based catalyst similar to the ones presented in this study and using different particle sizes (100–200 μ m, 420–500 μ m, and 600–800 μ m). The catalytic activity was rather similar in the whole temperature range for all the tested particle sizes pointing the absence of internal mass transport resistances in our set-up.

The most active samples were studied using gas composition imitating the outlet of an ethanol reformer: 30% H₂O, 9% CO, 11% CO₂ and 50% H₂. The start-up/shutdown tests were carried out by cooling the system until room temperature without interrupting the WGS flow. Once the system reaches room temperature the reaction feed was passed through the catalytic bed during 30 min. Afterwards, the reactor was heated to the chosen temperature (280 °C)

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