



## Pt vs. Au in water–gas shift reaction



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### ARTICLE INFO

#### Article history:

Received 12 February 2014

Revised 18 March 2014

Accepted 26 March 2014

Available online 18 April 2014

#### Keywords:

Gold catalyst

Platinum catalyst

Mixed oxides

Water–gas shift (WGS)

### ABSTRACT

This work presents a comparison of the gold- and platinum-based catalysts behavior in the water–gas shift (WGS) reaction. The influence of the support, e.g., its composition and electronic properties, studied in detail by means of UV–Vis spectroscopy, of the metal nature and dispersion and of the stream composition has been evaluated. The catalytic performance of the samples is directly correlated with the electronic properties modification as a function of metal and/or support. Both metals present high activity in the selected reaction although in a different operation temperature window.

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### 1. Introduction

Nowadays, steam reforming is the main hydrogen source, especially when the final objective is the generation of pure hydrogen. The hydrogen yields generally increase via water–gas shift (WGS) reaction, with the additional value of CO abatement. The WGS reaction ( $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$ ) is a classic industrial process commonly carried out in a series of adiabatic converters where the effluent from the reformer system is treated in two WGS reactors, a high-temperature shift (HTS) and low-temperature shift (LTS) ones. The industrial HTS catalysts are based on iron–chromium mixed oxides while the LTS catalysts on copper–zinc mixed oxides [1–3]. Since the WGS reaction is an exothermic and equilibrium-limited reaction, in which the  $\text{H}_2$  production decreases with the increase in the temperature, a LTS reactor is preferred for hydrogen yield rising. In spite of the wide use of the copper–zinc LTS catalysts, this catalytic system still requires specific reduction procedures and safety cautions on air exposure due to its pyrophoricity. These drawbacks are well controlled in the hydrogen production plants, but when mobile applications are envisaged, the requirements for the WGS catalysts are quite different from those of the traditional catalysts [4]. Thereby, (i) a non-pyrophoric low-temperature catalyst, (ii) an essential reduction in the volume and weight of the reactor, and (iii) a sufficient withstanding to start-up/shut-down cycles are critical conditions for a successful techno-economic implementation. In response to these needs, noble metal (NM)-based catalysts such as Pt [1,5] or Au [3,6] are under intense development.

Despite the extended number of studies concerning platinum- or gold-based catalysts for the WGS reaction, still at present in the scientific community, no clear preference for the use of one or another system exists. Burch [6] summarizes the advantages and drawbacks of gold catalysts in comparison with their platinum analogs for the WGS reaction. According to this review, gold catalysts can offer some advantages in the low-temperature range (180–250 °C) where the platinum catalysts are insufficiently active. However, at higher temperatures, the reported inherent activity of the gold catalysts is lower than that of properly activated platinum ones [7].

The pretreatment employed for the Pt-based catalysts appears to be essential for their performance which is not the case of gold catalysts, which could be used as prepared. It is very difficult to draw a general conclusion about the importance of one or another NM from the data available in the literature based only on the discussion of the catalytic behavior of the catalysts. No matter the metal, a strong influence of the preparation method is generally reported [8,9]. The gold-based catalysts are only active when present in a highly dispersed state, which imposes, for a proper comparison with the platinum-based catalysts, the use of a suitable preparation method. Moreover, the choice of the support is also of primordial importance for both metals [10–12]. In general, the most active formulations are commonly based on NMs supported on reducible oxides as  $\text{CeO}_2$  [13–15]. The enhanced activity of the  $\text{CeO}_2$  supported NM catalysts is frequently attributed to the ceria ability to undergo fast storage/release of oxygen cycles via a reversible conversion between  $\text{Ce}^{4+}$  and  $\text{Ce}^{3+}$  oxidation species [16,17]. These redox cycles imply a mechanism of oxygen vacancies formation that is indirectly correlated with the catalyst ability to activate oxygen species through electronic transfer and hence,

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to the catalytic activity in oxidation reactions. CeO<sub>2</sub> lattice modifications, such as the incorporation of trivalent metals ions, allow the improvement of the oxygen exchange ability and thus the catalytic performances of the catalytic systems. The incorporation of metallic promoters, as for example Fe or Zr, was recently reported to successfully modify the CeO<sub>2</sub> electronic band structure, thus increasing its reducibility and WGS activity [18,19].

A meaningful comparison for the reported catalytic activity in the WGS reaction of Au and Pt catalysts is difficult since the authors proposed different catalyst formulations that are tested in a variety of feedstock compositions and reaction conditions. For example, Trovarelli et al. [20] have compared Au and Pt supported on zirconia-promoted ceria concluding that the synergism between the precious metal and the oxide can be affected by the chosen synthesis parameters and structural and morphological properties of the support.

On these bases, the aim of this paper is to compare the catalytic behavior of gold and platinum catalysts supported on ceria modified materials in the WGS reaction, correlating its activity to the nature of the support and of the NM. In order to avoid more variables, the same support and metal loading has been kept for all the catalysts. The preparation methods were chosen in order to obtain comparable metal particle size and dispersion during the reaction. The catalytic activity and stability have been measured in both model and simulated realistic post-reforming WGS streams.

## 2. Experimental

### 2.1. Catalyst synthesis

$\gamma$ -Alumina powder (Sasol) has been employed as a main component of the evaluated materials. The supports (CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and Ce<sub>0.8</sub>Fe<sub>0.2</sub>/Al<sub>2</sub>O<sub>3</sub>) used in this study have been prepared by incipient wetness impregnation using Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (Aldrich) and Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (Aldrich) as oxides precursors. Supports were designed to present 15 wt.% of CeO<sub>2</sub>, 2 wt.% of FeO<sub>x</sub>, and 80–85 wt.% of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The impregnation was carried out in 50 ml ethanolic solution and evaporated at 50 °C at reduced pressure in a rotatory evaporator till a dry solid was obtained. The solid was then treated with NH<sub>3</sub> solution (10 mol L<sup>-1</sup>) for 30 min in order to assure the full conversion of the nitrates to hydroxides. The supports were then filtered, dried, and finally calcined at 450 °C for 4 h.

Platinum-based catalysts were obtained via aqueous impregnation using tetrammonium nitrate platinate (Johnson Matthey) as Pt precursor at reduced pressure in a rotatory evaporator at 80 °C. The as-obtained solids were then dried and calcined at 350 °C for 8 h at a heating rate of 5 °C/min.

The gold-based catalysts were prepared by the direct anionic exchange method, assisted by NH<sub>3</sub> using HAuCl<sub>4</sub> (Alfa Aesar) as gold precursor [21]. The calcination was carried out in the same conditions than for the platinum-based ones but for 4 h. The NM total loading was set to 2 wt%. As mentioned above, the preparation methods have been intentionally selected in order to achieve comparable precious metal particle sizes and dispersions.

In the adopted nomenclature, the oxygen and the stoichiometric coefficients into the mixed oxide were omitted for simplicity. For example, Pt (2%)/Ce<sub>0.8</sub>Fe<sub>0.2</sub>/Al<sub>2</sub>O<sub>3</sub> is named as Pt/CeFeAl.

### 2.2. Catalyst characterization

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

The textural properties were studied by N<sub>2</sub> adsorption-desorption measurements at liquid nitrogen temperature. The experiments were carried out on a Micromeritics Tristar II instrument. Before the analysis, the samples were degassed for 2 h at 250 °C in vacuum.

X-ray diffraction (XRD) analysis was carried out on a X'Pert Pro PANalytical instrument. Diffraction patterns were recorded using Cu K $\alpha$  radiation (40 mA, 45 kV) over a 2 $\theta$ -range of 10–95° and a position-sensitive detector using a step size of 0.05° and a step time of 240 s.

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

The UV–Vis spectra were recorded on a Varian spectroscopy model Cary 100, equipped with an integrating sphere using BaSO<sub>4</sub>. All spectra were collected in diffuse reflectance mode and transformed to a magnitude proportional to the extinction through the Kubelka–Munk function  $F(\alpha)$ .

CO chemisorption measurements were performed on fresh and post-reacted platinum samples by using a Micromeritics Autochem II apparatus. Prior to chemisorption, the samples were heated with a ramping rate of 10 °C/min from ambient temperature to 350 °C and treated with flowing hydrogen (10% H<sub>2</sub> in helium) for 2 h at this temperature. The samples were then cooled to room temperature under vacuum. It was assumed that each surface platinum atom was one CO chemisorption site.

Gold dispersion was estimated through high-angle annular dark field-scanning transmission electron microscopy (HAADF-STEM). The images were recorded on a JEOL2010F instrument. The HAADF-STEM studies were performed using an electron probe of 0.5 nm diameter and a diffraction camera length of 10 cm. It should be pointed that the chemical composition of the sample was studied in STEM mode using an energy-dispersive X-ray spectrometer (Oxford Instrument, Inca Energy-200). Loose powder samples were supported on a holey carbon-coated copper grid without using any liquid. The excess of sample was removed from the grids using a flow of N<sub>2</sub>. This approach allows us to obtain electron transparent thin regions.

### 2.3. Catalytic activity

The water–gas shift reaction was carried out placing 1 g of catalyst in a tubular flow reactor at atmospheric pressure in the 180–350 °C temperature range using two reaction schemes named model and realistic conditions. Pt-based catalysts were activated during 2 h at 350 °C in a H<sub>2</sub> stream (10 vol.%), while a pretreatment was not necessary for gold-based samples. For the model WGS reaction, just water and CO diluted in nitrogen were used, while for the realistic WGS reaction, a reformat gas surrogate containing hydrogen and carbon dioxide was selected. The experimental mixtures and conditions are summarized in Table 1. The model reaction mixture is the one usually employed for testing catalysts for the clean H<sub>2</sub> production via WGS. The conditions used to test the

**Table 1**  
Experimental conditions of the catalytic tests.

	Model	Realistic
CO (vol.%)	4.5	9
H <sub>2</sub> O (kPa)	31.1	31.1
CO <sub>2</sub> (vol.%)		11
H <sub>2</sub> (vol.%)		50
N <sub>2</sub> (vol.%)	Balance	
Bed volume (cm <sup>3</sup> )	1.5	1.5
GHSV (h <sup>-1</sup> )	4000	4000

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