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Application of Au/TiO_2 catalysts in the low-temperature water–gas shift reaction

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ABSTRACT

Au/TiO_2 catalysts were synthesized by three different methods, with different gold loadings, and tested for the low temperature water–gas shift (WGS) reaction. Gold was loaded by a Double Impregnation Method (DIM), Deposition–Precipitation (DP) and Liquid Phase Reductive Deposition (LPRD). For each procedure, catalysts were synthesized with three different loadings of gold, up to ca. 2.5 wt.%, identified as 1, 2 or 3 for low, intermediate or high amounts of nanosized gold, respectively. The prepared materials were characterized by High-Resolution Transmission Electron Microscopy (HR-TEM), X-Ray Diffraction (XRD), X-Ray Photoelectron Spectroscopy (XPS), Temperature Programmed Reduction (TPR) and Absorption Atomic Spectroscopy (AAS).

The performance of the catalysts was compared based on the CO conversions (X_{CO}) and turnover frequencies (TOFs) obtained in the WGS reaction. The two best catalysts obtained were Au/TiO_2-DP-3 and Au/TiO_2-LPRD-3. Both showed X_{CO} and TOF values higher than that of the commercial Au/TiO_2-WGC (supplied by the World Gold Council). Although TOF was higher for Au/TiO_2-LPRD-3 (at 250–300 °C), this sample suffers deactivation. The Au/TiO_2 DP-3 material was thus selected as the best synthesized catalyst, with a $X_{CO} \approx 85\%$ at 300 °C (X_{CO} of the WGC sample was ≈52% at 300 °C). The Au/TiO_2 DP-3 material has small gold nanoparticles before and after use, which can account for the improved catalytic activity, well known to be related with gold nanoparticle size. However, stability was found to be better for the WGC sample.

Introduction

The promotion and use of alternative sources of energy are important topics of concern nowadays. The use of hydrogen as an energy carrier is attractive, since the combustion of this gas is completely clean, without pollutants release [1,2]. The water–gas shift reaction (WGS, Eq. (1)), specifically the low temperature (LT) stage (200–400 °C), allows the production of highly pure hydrogen for fuel cells [3] and other purposes [3–9]:

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$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H^{\circ}_{298K} = -41.1 \text{ kJ/mol} \tag{1}$$

In this stage, the level of CO is reduced to very low levels, which requires operation at low temperatures, due to the exothermal nature of this thermodynamically limited reaction (Eq. (1)).

Gold-based catalysts are good candidates for low temperature CO oxidation [10–16] and also have high activity for the WGS reaction [6,8,11,17–29]. Several supports have been tested for gold nanoparticles on this reaction [30], like Fe_2O_3 [19,27,31–33], CeO_2 [17,34,35], Al_2O_3 [24], ZrO_2 [19,36,37], among others. In particular, Au/TiO_2 catalysts have been used with great success already since the pioneer work of Haruta and co-workers [38] and later on by other authors [24–26,29,39–43]. Indeed TiO_2 is a good choice support since it has low cost, very good chemical stability, and is non-toxic. Other supports, like CeO_2, are beneficial only for higher oxidation states of gold [44].

The WGS reaction was studied on model Au/TiO_2 (110) catalysts [45]. A reaction mechanism was proposed, involving a cooperative interaction between Au and TiO_2, where each catalyses different steps of the WGS reaction [24,45].

It was also shown that gold nanoparticles of smaller size (1–5 nm) have better activity for WGS [41,45–47]. Williams et al. [24,41] showed that the rate of CO converted per mole of Au per second in WGS on Au/TiO_2 depends strongly on the Au particle size. The same authors also showed that corner atoms with less than 7 neighbouring gold atoms are the dominant active sites and that the number of corner sites does not vary as particle size increases above 1 nm, showing that the rate per gold cluster/active site is independent of size [24,26,41]. As the particle size increases, the metal particles can expose more stable faces of the bulk metals in which the atoms have a large number of neighbours, and the WGS is a structure sensitive reaction that proceeds faster on surfaces having metal centres with a relatively low coordination [45,48]. It has also been showed that atomically dispersed gold species with surrounding extra surface –OH groups are the active sites for the WGS reaction on titania, as well as on other oxide supports [26].

In this work, TiO_2 supported gold catalysts were prepared by three different techniques: Double Impregnation Method (DIM), Deposition–Precipitation (DP) and Liquid Phase Reductive Deposition (LPRD), and their activities were compared for the LT-WGS reaction. The effect of the gold content was also analysed, by preparing materials with different Au-loadings.

Experimental

Gold was deposited on TiO_2 P25 Degussa [49] by different methods (described below), in order to achieve different gold loadings. The obtained catalysts were compared with the 1.5% wt. Au/TiO_2 Type A reference material from the World Gold Council (WGC).

Catalysts preparation methods

Double Impregnation Method (DIM)

The Double Impregnation Method (DIM) is similar to traditional impregnation (the support is impregnated with a solution of $HAuCl_4$, with pH ≈ 6, using sonication), but a second impregnation step is used with addition of an aqueous solution of Na_2CO_3 (1 M), under constant ultrasonic stirring [50]. The solution was aged for 12 h and then filtered, washed and dried in the oven at 110 °C overnight. Catalysts obtained with this method were named DIM-1 (for the lowest Au wt.%), DIM-2 (for intermediate Au wt.%) and DIM-3 (for the highest Au wt.%).

Deposition–precipitation (DP)

Deposition–precipitation (DP) consists in raising the pH of a $HAuCl_4$ solution until 9 with a NaOH solution (0.1 M), followed by addition of the support [51]. After aging for 12 h, the precipitate was filtered, washed and dried in the oven at 110 °C overnight. The catalysts obtained were named DP-1 (for the lowest Au wt.%), DP-2 (for intermediate Au wt.%) and DP-3 (for the highest Au wt.%).

Liquid phase reductive deposition (LPRD)

The liquid phase reductive deposition (LPRD) method consists in raising the pH of the gold precursor ($HAuCl_4$) until approximately 6 with a solution of NaOH (with a ratio of 1:4 by weight) and stirring at room temperature. The resulting solution was aged for 24 h in the dark at room temperature to complete the hydroxylation of Au^{3+} ions. Then the appropriate amount of support was added to the liquid and, after ultrasonic dispersion for 30 min, the suspension was aged in the oven at 100 °C overnight [52]. The solid was washed and dried in the oven at 110 °C overnight. The catalysts obtained were named LPRD-1 (for the lowest Au wt.%), LPRD-2 (for intermediate Au wt.%) and LPRD-3 (for the highest Au wt.%).

Catalysts characterization

Characterization of the supported catalysts was carried out by the following methods: Atomic Absorption Spectroscopy (AAS), X-Ray Diffraction (XRD), Temperature Programmed Reduction (TPR), X-Ray Photoelectron Spectroscopy (XPS) and High-Resolution Transmission Electron Microscopy (HR-TEM). The conditions employed in these techniques are briefly described below.

Atomic Absorption Spectroscopy (AAS)

The actual loading of gold in % wt. was determined by AAS using a Unicam 939/959 apparatus with a deuterium lamp background correction. A gold hollow cathode lamp (Heraeus), operating at 242.8 nm, was used as a radiation source. A sample of 20 mg was digested with *aqua regia* (prepared with a 1:3 vol. proportion of HNO_3 70% solution and HCl 37% ACS reagent from Sigma–Aldrich, respectively), with stirring at room temperature, followed by dilution with distilled water to obtain 50 ml. The error of the analyses was within ±5%.

X-ray diffraction (XRD)

The XRD patterns were recorded with a Phillips PW1710 diffractometer using the CuK_α radiation. Data from JCPDS