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Effect of the preparation method on the catalytic activity and stability of Au/Fe_2O_3 catalysts in the low-temperature water–gas shift reaction

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ABSTRACT

The low temperature water–gas-shift reaction has been studied over a series of nanosized Au/Fe_2O_3 catalysts. The effect of the synthesis method on the catalytic activity has been analysed. A series of catalysts with different Au loadings has been prepared by different methods: deposition–precipitation (DP), liquid phase reductive deposition (LPRD) and double impregnation method (DIM). The Au/Fe_2O_3 catalysts prepared by DP showed the highest CO conversion. The catalysts were characterised by hydrogen temperature programmed reduction (TPR-H_2), high-resolution transmission electron microscopy (HRTEM), X-ray powder diffraction and X-ray photoelectron spectroscopy. TPR-H_2 analysis revealed that gold promotes the reducibility of the Fe_2O_3 support, which is crucial in this redox reaction. HRTEM evidences a very good dispersion of gold over the iron support, with nanoparticles in the range 2.2–3.1 nm for the DP and LPRD series, and a negligible increase in the average particle size of the used samples. For the DIM series, much larger Au particles (~6.6 nm) were obtained.

1. Introduction

The water–gas shift (WGS) reaction (Eq. (1)) is widely used in the chemical industry to convert CO from syngas into CO_2 and produce additional H_2 [1].

$$H_2O + CO \leftrightarrow CO_2 + H_2 \; \Delta H^0{}_{298\,K} = -41\,kJ\,mol^{-1} \quad (1)$$

This is an important process to produce CO-free hydrogen or to adjust the H_2/CO ratio. The latter is especially desirable for downstream processes, such as Fischer–Tropsch and methanol synthesis [2]. On the other hand, high purity hydrogen is very important to use in fuel-cell power systems and ammonia synthesis, since CO is a poison for the iron catalyst used in ammonia production and for the anodic platinum electrode of the fuel cells [3,4].

The WGS has the advantage that is a mildly exothermic equilibrium-limited reaction, thus is thermodynamically favoured at lower temperatures but it has the disadvantage that the reaction kinetics is reduced under such conditions, decreasing so the yield of H_2 and increasing the amount of catalyst required to reach valuable CO conversions. Traditionally, in order to achieve high reaction rate and a high CO conversion, the WGS reaction is carried out in two catalytic reaction steps including high-temperature shift (HT-WGS) and low-temperature shift (LT-WGS) reactors [1,5]. The first step, HT-WGS, operates in the temperature range of 350–450 °C, which has fast reaction rate but low CO equilibrium conversion values. The second stage, LT-WGS, generally performed in the range of 200–250 °C, is thermodynamically favourable to further convert CO, but relatively slow in terms of reaction rate [6–10].

There are two main classes of materials used in industry for the WGS reaction: Fe–Cr oxide mixtures for HT-WGS and Cu–Zn or Co–Mo oxides for LT-WGS [1,11]. It is also known that oxide-supported noble metals (Pt, Au, etc.) are also able to catalyse the LT-WGS reaction [12–18], for which better catalysts are required.

In spite of their high cost, noble metal catalysts have been gaining increased interest in the last decades, due to their promising usage in fuel cell applications [11,19]. Basically, *in situ* fuel cell grade production of hydrogen requires a WGS reactor loaded with catalysts that: (i) are non-pyrophoric, (ii) do not require pre-reduction treatment, and (iii) are robust in cycles of rapid heating and cooling. Cu-based conventional catalysts require strict reduction conditions that, after activation, are highly reactive towards air (pyrophoric),

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being hazardous during start-up and shut-down cyclic operation [20–22]. Au-based catalysts can be successfully used in those applications because they are able to overcome these drawbacks.

Different oxides (i.e. Fe_2O_3, TiO_2, ZnO, Zr_2O, CeO_2) have been described as supports for gold-based catalysts [14–18,23–25]. The increase in activity when gold is added to these oxides in LT-WGS was explained as a synergetic effect between gold and the metal oxide [24–26]. The nature of the support plays an important role in the activity of Au-based catalysts. Particularly, in the case of Fe_2O_3 support, the Fe^{2+}/Fe^{3+} redox couple has a significant role in the WGS because the reaction takes place via a redox mechanism [25,27,28].

Deposition–precipitation (DP) and co-precipitation (CP) are the most common methods used for the synthesis of Au-based catalysts for LT-WGS reaction [20,24,25,29–31]. Recently, liquid-phase reductive deposition (LPRD) and double impregnation (DIM) techniques have been also used to prepare these catalysts [32,33]. These not so common and relatively new methods are environmentally and economically more favourable for the production of highly active Au-based catalysts. Moreover, Au-based catalysts prepared by LPRD and DIM have shown good performances towards the CO oxidation reaction [33–36]. To the best of our knowledge, Au-based catalysts prepared by LPRD or DIM techniques have not been used for WGS reaction yet.

The aims of this work are: (i) to study how the preparation method and the amount of Au affect the activity of Au-based samples for the LT-WGS reaction, and (ii) to gain insight into the physicochemical properties influencing the activity and stability of Au/Fe_2O_3 catalysts for the mentioned reaction.

2. Experimental

2.1. Catalysts preparation

2.1.1. Double impregnation method (DIM)

The DIM method is similar to the traditional wetness impregnation, but it involves a second impregnation step with the addition of an aqueous solution of Na_2CO_3 [33,37,38]. First, the support was impregnated with an aqueous solution (5×10^{-3} M) of $HAuCl_4 \cdot 3H_2O$ (Alfa Aesar) and then with an aqueous solution of Na_2CO_3 (10^{-2} M), under constant ultrasonic stirring. The slurry was then thoroughly washed with distilled water and dried in an oven at 120 °C overnight. α-Fe_2O_3 (Sigma Aldrich) was used as support. Different amounts of Au (1.5, 3 and 5 wt.%) were used, thus providing samples with different metal loads. The experimental content of gold in similar samples prepared by DIM was checked by means of ICP and was reported in several previous works [34,39–41].

2.1.2. Liquid phase reductive deposition (LPRD)

An aqueous solution of $HAuCl_4 \cdot 3H_2O$ (5×10^{-3} M) was mixed with an aqueous solution (2×10^{-2} M) of NaOH (1:4 weight ratio) with stirring at room temperature [32,36,42,43]. The resulting solution was aged in the dark, at room temperature, for 24 h, in order to complete the hydroxylation of Au^{3+} ions. Then, the appropriate amount of support (α-Fe_2O_3) was added to the solution and, after ultrasonic dispersion for 30 min, the suspension was aged in the oven, at 100 °C, overnight. The resulting solid was washed repeatedly with distilled water for chloride removal and again dried in the oven at 100 °C overnight. Different Au-based catalysts with 1.5, 3 and 5 wt.% of Au were prepared. The actual gold loading for samples prepared by LPRD was assessed by ICP as reported in several previous works [41,43].

2.1.3. Deposition–precipitation (DP)

Several samples containing 1.5, 3 and 5 wt.% of Au were prepared by the DP method [44]. A solution of NaOH (1 M) was added to an aqueous solution of $HAuCl_4$ (5×10^{-3} M) in order to rise the pH of the solution to 9. The support (α-Fe_2O_3) was then added with stirring at room temperature (1 g per 50 ml of solution). The resulting suspension was heated to 70 °C and vigorously stirred for 1 h; after cooling the solid obtained was filtered, thoroughly washed with deionized water and then vacuum-dried at room temperature.

In all the methods reported above, a commercial α-Fe_2O_3, with a BET surface area of $6\ m^2\ g^{-1}$ and an average particle size of 63 nm [38], was used as support. The catalysts prepared by DP, LPRD and DIM techniques were labelled as xAu/Fe_2O_3_DP, xAu/Fe_2O_3_LPRDP and xAu/Fe_2O_3_DIM, respectively, where x represents the nominal loading of Au in wt.%. For the DP series, the actual gold loading was 1.6 ± 0.1, 2.5 ± 0.1 and 4.6 ± 0.2 wt.% for samples $1.5Au/Fe_2O_3$_DP, $3Au/Fe_2O_3$_DP and $5Au/Fe_2O_3$_DP, respectively, as determined by absorption atomic spectroscopy (AAS–cf. Section 2.3).

The Au/Fe_2O_3 (5 nominal wt.% of Au) catalyst, supplied by the World Gold Council (WGC), was also used for comparison purposes. This catalyst was labelled as $5Au/Fe_2O_3$_ reference and contains 4.7 ± 0.2 wt.% of Au as determined by AAS.

2.2. Catalytic activity runs

Activity measurements were carried out in a fixed-bed reactor. This reactor consists in a stainless steel tube with a length of 60 mm and 10 mm o.d., loaded with 0.2 g of Au-based catalyst (Ø < 200 μm) diluted with glass beads (Sigma Aldrich 212–300 μm) and framed in both ends by two discs of stainless steel mesh (10–15 μm).

Before WGS tests, the catalyst was heated in situ up to 200 °C (5 °C/min) under $50\ ml_N/min\ N_2$ flow. Then, the catalyst was reduced at this temperature using $50\ ml_N/min$ of a 15% H_2/N_2 feed mixture. After 45 min of reduction, a $50\ ml_N/min$ of N_2 flow was used during 30 min to sweep H_2 from the system. The catalyst was then exposed to a standard water–gas shift composition feed of 4.7 vol.% CO, 10.1 vol.% CO_2, 35.4 vol.% H_2O and 28.5 vol.% H_2, balanced with N_2. The catalytic tests were performed at atmospheric pressure, at different temperatures between 150 and 300 °C, with a total flow rate of $50\ ml_N/min$ (thus the contact time was $W/Q = 6.67 \times 10^{-5}\ g\ h\ ml_N^{-1}$).

Fig. 1 shows the setup used for the catalytic activity measurements in the LT-WGS reaction. The feed gases were controlled by mass flow controllers (Bronkhorst). A Controlled Evaporation and Mixing (CEM, Bronkhorst) unit was used to evaporate the water while mixing the generated steam with the feed gases. The reactor was encased in an electric oven (Memmert, Type UNE200), controlled by a programmable temperature controller. The tubes between the CEM and the reactor were heated at 115 °C in order to prevent steam condensation. Moisture in the product reaction gases was condensed by a peltier cooling placed at the reactor output (Marlow industries, model RC 12-6L).

The dry product gases were analysed with a DANI 1000 gas chromatograph equipped with a chromatographic column (Supelco Carboxen 1010 Plot, from Sigma-Aldrich, 30 m × 0.32 mm i.d.) and a micro-thermal conductivity detector (TCD) and operated with He as carrier gas ($1\ mL_N\ min^{-1}$). The catalytic activity was expressed as percentage of the CO conversion (X_{CO} (%)) calculated as $[(F^{in} - F^{out})/F^{in}] \times 100$, where F^{in} and F^{out} are the CO molar flow at the input and output of the reactor, respectively.

Thermodynamic equilibrium CO conversion (X_{COeq}) was calculated by means of the Gibbs free energy minimization method via ASPEN-HYSYS software, as described elsewhere [45].

2.3. Catalysts characterisation

The gold loading was determined by atomic absorption spectrometry (AAS) by means of a Unicam 939 atomic absorption spectrophotometer equipped with a deuterium lamp background correction. An Au hollow cathode lamp (Heraeus), operating at