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Au/ZrO$_2$ catalysts for LT-WGSR: Active role of sulfates during gold deposition

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ABSTRACT

The effect of the addition of various amounts of sulfates to a zirconia support and its possible role during the Au deposition–precipitation step was examined. The high activity showed by the Au/ZrO$_2$ catalysts in the WGS reaction was enhanced by the action of sulfates on the support. SO_4^{2-} addition to zirconia brings a higher gold dispersion due to (i) the larger surface area and (ii) the positive role of SO_4^{2-} groups that determine the deposition of Au in the form of highly dispersed non-metallic gold clusters in close contact with the support.

1. Introduction

Catalysis by gold nanoparticles is a topic of current interest, as proved by the exponential growth of the papers on this subject [1]. In fact gold supported on oxides or carbon, once considered catalytically inert, is now firmly established as an effective catalyst. The catalogue of reactions that it can catalyze is really wide. In particular, supported gold particles are effective catalysts for low-temperature CO oxidation, selective oxidation of propene to propene oxide, water-gas shift reaction, NO reduction, selective hydrogenation of acetylene (or butadiene) [2].

The relationship between activity, microstructure and nature of the catalytically active gold sites is, up to now, not fully understood. There is still a big debate on the role played by the preparation method and by the acidity of the support and its modification with surface species like sulfates on the nature of the resulting gold species. Experimental data on selective oxidation [3] indicate that there is a limiting diameter size (1.5–2 nm) that discriminates between active samples from the inactive ones. This is the same limiting size observed for both "active" and "inactive" supports, as BN, SiO$_2$ and C on which Au is dispersed. It appears related to an intrinsic modification of the electronic structure of non-metallic gold nanoclusters with respect to the metallic nanoparticles. As for the water-gas shift reaction, cationic gold or highly dispersed non-metallic gold clusters in close contact with the support are usually considered active sites [4]. Very recently, an unprecedented reactivity in the HCOOH decomposition into H$_2$ and CO$_2$ of Au-based catalysts for fuel cells designed for portable use has been reported [5]. It has been shown that the reactivity derives from highly dispersed and stable Au species, undetectable by transmission electron microscopy. The primary role of the support is to have a high concentration of nucleation sites for gold and to avoid coalescence and agglomeration. Characteristics such as surface area, presence of surface hydroxyl groups, density of defects, modification of the surface acidity and of the predominant crystalline phase can influence its adsorption ability [1]. We have recently focused our attention on gold based catalysts supported on zirconia [6,7]. The choice of zirconia as support is due to its intrinsic chemical and physical characteristics that can be adjusted by choosing different precursors and synthesis conditions. Moreover, the addition of dopants, in particular sulfates, increases surface acidity, retards crystallization and enhances the surface area [8]. ZrO$_2$ has also been found to be a very suitable support for gold [9–11]. We have optimised a method for dosing low coordination sites exposed at the surface of gold supported on different oxides [12]. This procedure is based on the combined use of pulsed CO chemisorption measurements and FTIR spectroscopy of adsorbed CO, both techniques being applied in well controlled experimental conditions. It has been shown that the amount of low

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coordinated gold sites exposed at the surface of some Au/ZrO_2 systems [7] is up to 10 times higher than the one observed for standard Au/TiO_2 by WGC (World Gold Council). In fact, a very good relationship between catalytic activity and chemisorption data has been evidenced [13], indicating that the chemisorption test is suitable for a preliminary evaluation of the Au/ZrO_2 systems used for the LT-WGSR. We have recently demonstrated [13] that gold supported on sulfated zirconia is more active than the samples on plain zirconia in the LT-WGSR. This higher activity is probably due to a larger surface area of sulfated zirconia that leads to a better dispersion of gold on the surface. It would be very interesting to clarify the role of SO_4^{2-} in the delicate phase of gold deposition on the support and subsequently on dispersion and catalytic activity. The goal of the present work is to examine the effects of the addition of various amounts of sulfates to a zirconia support and to check their role during the Au deposition–precipitation step.

2. Experimental

2.1. Catalyst preparation

Zirconia was prepared by a two-step synthesis technique. $Zr(OH)_4$ was prepared by precipitation from $ZrOCl_2 \cdot 8H_2O$ at constant pH (pH = 8.6) and then aged under reflux conditions for 20 h at 363 K, washed free from chloride ($AgNO_3$ test) and dried at 383 K overnight. The hydroxide was then sulfated with $(NH_4)_2SO_4$ (Merck) by incipient wetness impregnation in order to obtain a 1, 2, 4, 8 wt% amount of sulfates respectively on the final support. Sulfated zirconium hydroxides were then calcined in air (30 mL/min STP) by slowly heating from room temperature to 923 K over 7 h, and keeping this temperature for 6 h. The different SO_4^{2-} amount is defined in the denomination of the supports: ZS1, ZS2, ZS4 and ZS8 respectively. 1 wt% of gold was added by deposition–precipitation (dp) at pH = 8.6: the oxide support was suspended in an aqueous solution of $HAuCl_4 \cdot 3H_2O$ for 3 h and the pH was controlled by the addition of NaOH (0.5 M).

Moreover, a sample was synthesized by dp after the sulfates removal from the zirconia. A complete extraction of sulfates was obtained, as previously reported [14], by suspending the calcined support in an aqueous solution of NaOH (0.5 M) at pH = 8.6. Then gold was deposited by dp as previously reported (inverted sample denoted with the initial letter I). After filtrations all samples were dried at 308 K overnight and part of the catalysts were finally calcined in air for 1 h by slowly heating (60 K/h) from 298 to 453 K.

2.2. Methods

Surface area and pore size distributions were obtained from N_2 adsorption/desorption isotherm at 77 K, using a Micromeritics ASAP 2000 Analyser. Sulfated zirconia supports (400 mg) were pre-treated at 570 K for 2 h under vacuum, while the final catalysts (300 mg) were pre-treated at room temperature for 6 h under vacuum. Surface area was calculated from the N_2 adsorption isotherm by the BET equation [15] and pore size distribution was determined by the BJH method also applied on the adsorption branch [16]. Total pore volume was taken at $p/p_0 = 0.99$.

The sulfate content of all samples was determined by ion chromatography (IC) [14]. Sulfate concentration was calculated as the average of two independent analyses, each including two chromatographic determinations.

The gold amount was determined by atomic adsorption spectroscopy after microwave disgregation of the samples (100 mg).

X-ray powder diffraction (XRD) patterns were measured by a Bruker D8 Advance diffractometer equipped with a Si(Li) solid state detector (SOL-X) and a sealed tube providing Cu K_α radiation. Measuring conditions were 40 kV × 40 mA. Apertures of divergence, receiving and detector slits were 1°, 1°, and 0.3° respectively. Data scans were performed in the 2θ ranges 15–55° and 35–40° with 0.02° step size and counting times of 3 s/step and 10 s/step respectively.

CO pulse chemisorption measurements were performed at 157 K in a lab-made equipment. Before the analysis the following pretreatment was applied: the sample (200 mg) was reduced in a H_2 flow (40 mL/min) at 423 K for 60 min, cooled in H_2 to room temperature, purged in He flow and finally hydrated at room temperature. The hydration treatment was performed by contacting the sample with a He flow (10 mL/min) saturated with a proper amount of water. The sample was then cooled in He flow to the temperature chosen for CO chemisorption (157 K) [7].

Thermal analyses (TG/DTA) were performed on a NETZSCH STA 409 PC/PG instrument in flowing air (20 mL/min) with temperature rate set at 5 K/min in the 300–1300 K temperature range.

TPO measurements were carried out to determine the substances released during the TG/DTA thermal treatment, in a lab-made equipment: samples (100 mg) were heated with a temperature rate of 10 K/min from 300 to 1300 K in air (40 mL/min). The effluent gases were analyzed by a Genesys 422 quadrupole mass analyzer (QMS). The signals for masses 18, 28, 44, 48, 64 were recorded.

FTIR spectra were taken on a Perkin-Elmer 1760 spectrometer (equipped with a MCT detector) with the samples in self-supporting pellets introduced in a cell allowing thermal treatments in controlled atmospheres and spectrum scanning at controlled temperatures (from 120 to 300 K). From each spectrum, the spectrum of the sample before the inlet of CO was subtracted. Band integration and curve fitting have been carried out by Spectra Calc (Galactic Industries Co.). The spectra were normalised with respect to the gold content of each pellet. The pretreatment of the samples was: (i) reduction in H_2 at 423 K; (ii) outgassing H_2 to room temperature (r.t.); (iii) hydration at r.t.; (iv) outgassing water at r.t. to obtain the same residual pressure (2.5×10^{-2} mbar H_2O).

2.3. Catalytic activity measurement

WGSR was performed in a fixed-bed flow reactor at atmospheric pressure and in a temperature range from 423 to 453 K. The following conditions were applied: space velocity = 9400 h^{-1}; catalyst volume = 0.5 cm^3 (35–50 mesh) diluted to 1.5 cm^3 with quartz sand (Carlo Erba; 35–50 mesh); gold supported samples were previously subjected to a slow (60 K/h) thermal activation in air (50 mL/min) from room temperature to 453 K, kept at this temperature for 1 h in the same air flow and then cooled in N_2

Table 1
Surface features and SO_4^{2-} amounts of the supports.

Sample	Nominal SO_4^{2-} (wt%)	Found SO_4^{2-} (wt%)	Surface area (m^2/g)	Pore diameter (nm)	SO_4^{2-} (groups/nm^2)
ZS1	1	1.0	79	10.9	0.79
ZS2	2	2.0	99	8.7	1.27
ZS4	4	3.6	115	7.0	1.96
ZS8	8	4.0	119	6.7	2.11