Catalysis Communications 26 (2012) 225–230

Contents lists available at SciVerse ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short Communication

Deposition–precipitation versus anionic-exchange Au/Al_2O_3 catalysts: A comparative investigation towards the selective reduction of NO_x

D.L. Nguyen [a], S. Umbarkar [a,b], M.K. Dongare [a,b], C. Lancelot [a], J.-S. Girardon [a], C. Dujardin [a], P. Granger [a,*]

[a] Université Lille Nord de France, CNRS UMR 8181, Unité de Catalyse et de Chimie du Solide, UCCS, USTL, bâtiment C3, 59650, Villeneuve d'Ascq, France
[b] National Chemical Laboratory, Dr. Homi Bhabha Road, Pune - 411008, India

ARTICLE INFO

Article history:
Received 6 February 2012
Received in revised form 19 May 2012
Accepted 4 June 2012
Available online 12 June 2012

Keywords:
Au catalyst
Anionic-exchange
Deposition–precipitation
NO_x abatement
Selective catalytic reduction

ABSTRACT

Catalytic properties of supported gold catalysts on γ-Al_2O_3 prepared by a conventional deposition–precipitation method were compared with those obtained by anionic-exchange for the reduction of NO_x by hydrocarbon under lean conditions that simulate Diesel engine exhaust gas. Interestingly, a catalytic activity enhancement is observed after thermal ageing under reactive conditions at 500 °C on anionic-exchanged samples which make them suitable for practical developments. On the other hand, the reverse trend is observed on the solids prepared by deposition–precipitation which deactivate at low temperature. Such changes in catalytic properties have been tentatively explained on the basis of textural and structural modifications taking place during thermal ageing under wet atmosphere.

1. Introduction

Gold catalysts have received a considerable interest in the past two decades for the oxidation of CO at low temperature [1–3]. More recently, the potentialities of such catalysts were pointed out for the catalytic oxidation of unburned hydrocarbons at low temperature from stationary and mobile sources [4,5]. Interestingly, high catalytic activity and selectivity have been related to the deposition of hemispherical ultrafine gold particles on selected support materials [6].

Up to now, only few investigations concern the development of gold in $DeNO_x$ catalysis whereas silver, having similar chemical properties in the same column of the Mendeleiev's periodic classification, was found as the most active and selective element for the conversion of NO_x from Diesel engine exhaust gas [7,8]. First attempts revealed promising performances of supported Au catalysts in the CO/NO reaction but partly inhibited in the presence of oxygen [9,10]. In spite of those investigations report catalytic features far from the real exhaust gas conditions, a prominent observation was associated with the beneficial effect of water as earlier reported [10–12]. In fact, this promotional has been related to the occurrence of the Water-Gas-Shift reaction with an extra H_2 production that makes gold as very promising catalysts especially for low temperature NO_x abatement processes. However, the high sensitivity of gold particles to thermal sintering after running in three-way conditions at 500 °C has been demonstrated which can be a serious obstacle for further practical development in post-combustion catalysis [13]. Ueda et al. [11] also demonstrated that gold catalysts synthesized via deposition–precipitation and co-precipitation methods can efficiently convert NO_x to N_2 by reaction with C_3H_6 under lean conditions up to 5 vol.% O_2. Interestingly, they observed a rate enhancement in NO_x conversion to N_2 when Mn_2O_3 is added to Au/Al_2O_3 explained by a sharp enhancement in NO_2 production which would react more readily with propene adsorbs on the surface of gold particles via a complex chemistry previously described on silver based catalysts [14] and more recently on Au/Al_2O_3 from *operando* spectroscopic measurements [15]. Accordingly, the nature of the support plays also a crucial role since the highest activity of gold in $DeNO_x$ reactions was observed on alumina but at the highest temperature compared to ZnO or Fe_2O_3. As a general trend, gold catalysts usually suffer from deactivation generally ascribed to strong accumulation of carbonates on the support [16]. Reversible deactivation leads to the development of strategies to restore their intrinsic activity for moderate temperature applications. On the other hand, the aggregation of nano-sized gold particles at high temperature leads to irreversible deactivation [17]. The nature of the thermal pre-treatment was found to determine the extent of interaction between gold particles and the support and the related activity and stability [18] for the water-gas-shift reaction on Au/CeO_2. Indeed, El-Moemen et al. [18] found that a pre-treatment of Au/CeO_2 in 10 vol.% O_2/N_2 at 400 °C has a beneficial effect on the catalytic activity in the WGS reaction compared to reductive thermal treatment in 10 vol.% H_2/N_2 at the same temperature. On the other hand, the reverse trend was found for the stability.

This study reports significant changes of the catalytic properties due to the thermal stability of Au/Al_2O_3 after ageing overnight at 500 °C in reaction conditions. The nature of the pre-treatment prior

---

* Corresponding author. Tel.: +33 320 434 938; fax: +33 320 436 561.
E-mail address: pascal.granger@univ-lille1.fr (P. Granger).

1566-7367/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.catcom.2012.06.004

to reaction, as well as, the protocol implemented for the gold deposition via anionic-exchange or deposition–precipitation also influence the extent of surface reconstructions which governs the catalytic performances.

2. Experimental

2.1. Catalyst synthesis and characterization

γ-alumina support was synthesized by a sol–gel method using alkoxide precursors [19]. The solid obtained after successive drying at 100 °C and calcination in air at 500 °C exhibited a specific surface area of 450 $m^2.g^{-1}$. Gold was deposited by a conventional deposition–precipitation (DP) method [20] or by anionic-exchange (AE) as earlier described [21] using $HAuCl_4.3H_2O$ (99.999%, Alfa Aesa). According to the DP protocol, the pH of the $HAuCl_4$ solution was adjusted to 7 by adding appropriate amount of 0.1 mol/L NaOH. Then, Al_2O_3 powder, with average grain size of 150 μm, was dispersed and maintained under agitation for 0.5 h to promote the precipitation of $Au(OH)_3$ on the alumina surface. Regarding anionic-exchange, alumina was added to a solution of $HAuCl_4$ with concentration of 1.0×10^{-4} mol/L heated to 70 °C for 1 h. The pH was maintained constant at ~4 to stabilize the complex $[Al(Cl)_2(OH)_2]^-$ [21]. According to those conditions, further reactions with alumina surface were expected to form preferentially bidentate species more resistant to thermal sintering during calcination in air [21]. After gold incorporation the solids were dried at 100 °C overnight. The precursors thus obtained were calcined in air for 4 h at 300 °C or 500 °C.

Nitrogen adsorption–desorption isotherms were obtained at −196 °C on a Micromeritics ASAP 2010 apparatus, and the pore size distribution of calcined samples was calculated from the nitrogen adsorption isotherm by using the BJH (Barrett–Joyner–Halenda) method. X-ray diffraction (XRD) patterns were recorded on a HUBER G-670 diffractometer equipped with a Cu Kα (λ = 0.154 nm) radiation. XPS spectra were obtained with a Kratos AXIS Ultra DLT spectrometer using Al source. Raw data were treated by using Casa XPS software. Gold and chlorine were analyzed by inductively coupled plasma emission spectroscopy at the center chemical analysis of the CNRS.

2.2. Catalytic measurements

Temperature-programmed reaction experiments (TPR) were performed from 75 to 500 °C in a fixed bed flow reactor on 360 mg of catalyst exposed to 300 ppm NO, 300 ppm CO, 300 ppm propene, 100 ppm decane, 0.2 vol.% H_2, 5 vol.% H_2O, 10 vol.% CO_2, 10 vol.% O_2 diluted in He that simulated the composition of Diesel engine exhaust gas. The total flow rate was adjusted to 18 $L.h^{-1}$ in order to get a Gas Hourly Space Velocity of 50,000 h^{-1}. The temperature was gradually increased with dT/dt = 2 °C min^{-1}. Reactants and products were analyzed by a CP4900 Varian microGC fitted with Thermal Conductivity Detectors. Prior to detection, they were separated on molecular sieve (MS5A) and Porapak Q columns. CO, NO and NO_2 concentrations were measured from specific multigas MIR9000 analyzers supplied by SA Environment. Prior to Temperature-Programmed Reaction experiments, the catalyst samples were systematically reduced in pure H_2 at 250 °C or 500 °C. A first TPR-1 experiment was achieved according to the above-mentioned conditions up to 500 °C and the catalyst was aged overnight at that final temperature in the reaction conditions. Then, after cooling down at room temperature, a second TPR-2 was performed to evaluate the impact of the thermal ageing on the catalyst performances. NO_x conversion and selectivity to nitrogen production were calculated based on Eqs. (1) and (2) respectively:

$$X_{NO} = \frac{2\left(F_{N_2} + F_{N_2O}\right)}{F^0_{NO}} \qquad (1)$$

$$S_{N_2} = \frac{F_{N_2}}{F_{N_2O} + F_{N_2}} \qquad (2)$$

where F_{N_2O} and F_{N_2} are respectively the outlet flow rates of N_2O and N_2 and F^0_{NO} the inlet flow rate of NO.

3. Results and discussion

3.1. Induced effect of thermal ageing on the textural and surface properties

N_2 physisorption isotherms measured at −196 °C during the adsorption and desorption processes underline a classical hysteresis loop that predominantly characterizes ink-bottle-type pores on calcined Au/Al_2O_3 at 300 °C with a plateau for high P/P_0 values [22] (see Fig. 1). Thermal ageing under reactive conditions at 500 °C leads to drastic changes in the hystereris profile characterizing the predominance of larger cylindrical-type pores. Similar trends are observable when the precursor is calcined in air at 500 °C. Data collected in Table 1 do not evidence changes in the pore volume but essentially in the specific surface area and the average pore size values. XRD patterns reported in Fig. 2 indicate the presence of a poorly crystallized phase consistent with the presence of a bohemite phase after calcination at 300 °C characterized by the presence of broad X ray lines at 2θ = 28.2, 48.9, 55.3 and 72.1°. On the other hand, the γ-Al_2O_3 phase prevails on aged samples. Calcination of the precursors in air at 500 °C emphasizes the fact that the bohemite phase completely transforms to γ-Al_2O_3 at that temperature as earlier observed [22]. As a general trend, it seems obvious that thermal ageing in reaction conditions with 10 vol.% H_2O leads to a more open porous structure reflected by a significant increase of the pore size diameter. The examination of the characteristic X-ray lines ascribed to bulky metallic gold species at 2θ = 38.19, 44.4, 64.5, 77.58°, also reveals significant changes of the gold crystallite size essentially on Au/Al_2O_3(AE) depending on the calcination temperature. As exemplified in Fig. 2A(d), a significant broadening of the X-ray lines is observable on aged Au/Al_2O_3(AE) initially calcined at 300 °C. X-ray diffraction was not sufficiently sensitive to detect the presence of bulk Au species on solids prepared via the DP method.

Surface composition was essentially investigated by X-ray photoelectron spectroscopy. Spectral features extracted from the examination of the characteristic Al 2p used as internal reference (74.6 eV in Al_2O_3) and the Au $4f_{7/2}$ core levels are summarized in Table 1. The characteristic Au $4f_{7/2}$ B.E. values for metallic Au are currently reported at 84 eV [3,23]. Contributions earlier reported at higher B.E. values, of respectively 84.9 and 86.5 eV, have been assigned to $Au^{\delta+}$ and Au^{3+} species. It is worthwhile to note that the B.E. values on calcined samples reported in Table 1 essentially characterize the presence of metallic gold particles. This underlines the usual effect of X-ray irradiation during

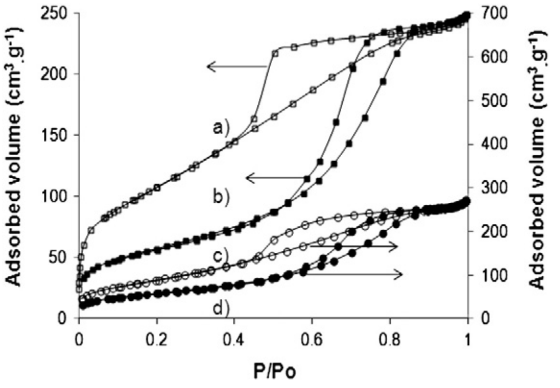

Fig. 1. N_2 physisorption isotherms on anionic-exchange Au/Al_2O_3(AE) catalysts calcined in air at 300 °C (a); calcined at 300 °C and aged at 500 °C in reaction conditions (b); calcined at 500 °C (c); calcined at 500 °C and aged at 500 °C in reaction conditions (d).