Catalysis on nanoporous gold–silver systems: Synergistic effects toward oxidation reactions and influence of the surface composition

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ABSTRACT

Au–Ag nanoporous systems were prepared by a recently developed method. Contrary to the electrochemical dealloying, the methodology applied in this work proved that it allowed to prepare bimetallic AuAg NP systems with controlled chemical compositions. Compared with monometallic Au or Ag catalysts, the alloy catalysts exhibited high activity toward CO and/or H$_2$ oxidation and exceptionally high selectivity at low temperature for CO oxidation in the presence of H$_2$ showing a synergistic effect between Au and Ag. Among the different characterizations, Low-Energy Ion-Scattering Experiments provided composition data about the *topmost* atomic layer, i.e., where catalytic reactions occur and allowed us to establish a clear correlation between top layer surface concentration and reactivity. A pronounced dependence of the reaction rate on the silver concentration has been observed only for H$_2$ oxidation. This strong dependence has been correlated with the number of surface sites constituted of adjacent Ag atoms required for dissociative oxygen adsorption. The high selectivity of the Au–Ag alloys with respect to pure gold has been ascribed to a large segregation of silver, especially on low coordination sites, inhibiting the H$_2$ adsorption.

1. Introduction

Gold has been generally considered catalytically inactive but since the pioneering work of Haruta [1] numerous studies have shown that finely dispersed gold nanoparticles on suitable oxide supports can achieve remarkable catalytic activity for several oxidation reactions. Among these, the water–gas shift reaction [2], the epoxidation of propylene [3], the direct synthesis of H$_2$O$_2$ from H$_2$ and O$_2$ [4], CO oxidation and preferential oxidation (PrOx) of CO in the presence of hydrogen [5–11] are all known to be catalyzed by gold. These last two reactions being important ones for pollution control and energy production. In addition, low-temperature CO oxidation and PrOx have been used as test-reactions to investigate the mechanisms of oxygen activation and/or H$_2$ adsorption and dissociation that proceed in a more complex way on gold than over platinum group metals.

Indeed for oxide-supported gold nanoparticles, the classical Langmuir Hinchelwood mechanism does not hold anymore. In fact, all the surface science experiments and DFT calculations show that dissociative adsorption of oxygen and hydrogen is a very unlikely process on gold surfaces [12]. This is consistent with the idea that Au is a difficult metal to oxidize, with DFT suggesting that O$_2$

dissociation is unfavorable compared to molecular desorption even on high index surfaces of the bulk metal [13,14]. Concerning small gold nanoparticles, while CO is known to adsorb on gold atoms [15], several classes of active sites have been suggested for oxygen activation: interfacial metal–oxide sites [13,16–18], cationic gold sites [19,20] or low-coordination gold atoms [21].

Despite these studies, the mechanisms responsible for the catalytic activity are still under debate especially on the size, charge state and support effects, the nature of the active site, and especially in what way and on which site O$_2$ is activated. The general opinion is that neutral gold clusters alone cannot chemisorb and/or activate the O–O bond without some influence from the substrate such as charge-transfer processes or specific interfacial sites. Hence, in the case of nonreducible (inert) supports, such as Al$_2$O$_3$ and SiO$_2$, the adsorption of both CO and O$_2$ has to be carried out on the gold surface. In that case, very poor CO conversion is observed due to the lack of O$_2$ activation [5,22].

An alternative way to modify the gold-based catalysts is to search for a second metal that can form an alloy with gold and possesses stronger affinity with O$_2$ than gold [23]. That is, where two surface partner metal atoms are neighbors to each other, the activated O$_2$ can easily react with the activated CO at gold atom. In that way, alloy gold compounds such as AuSr [24], AuCu [25], or AuAg [23] deposited on inert supports such as silica or MgO

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have shown superior catalytic properties toward CO oxidation when compared to their constituent elements.

Other molecules and their interactions with gold surfaces have been investigated although to a lesser extent than CO or O_2. Among them, hydrogen adsorption and activation, which is a key step in many reactions like hydrogenations, the reverse water–gas shift reaction and other processes as CO preferential oxidation (PrOx) [12,26–31].

In contrast to supported gold catalyst systems, unsupported systems, such as gold powder, have not yet drawn much attention even though several groups have shown that some nanoporous (NP) gold exhibit very high activity for CO oxidation at low temperature [8,32–40]. Some of these groups [33–39] have related this high activity to the presence of residual impurities which should play a role in the activation of O_2. This agrees with our recent study of the intrinsic catalytic properties of very pure NP gold which revealed a very poor activity toward CO oxidation [41].

Following this previous work, the present paper aims to synthesize NP AuAg alloys with controlled silver amounts and study the variations of catalytic activities with respect to changing temperature and composition. The obtained materials were tested in three catalytic reactions, the oxidation of CO, the selective oxidation of CO in the presence of H_2, and the oxidation of H_2.

2. Experimental

2.1. Sample preparation

As described in a previous paper [42], the synthesis of an intimate mixture of a skeletal gold structure with ZrO_2 nanoparticles is possible by mild oxidation of an $Au_{0.5}Zr_{0.5}$ intermetallic alloy. If zirconia is then selectively dissolved in fluorhydric acid, we obtained pure nanoporous gold system under the shape of a micrometric powder [41].

Here, this two-step method has been also applied to ternary (Au,Ag)–Zr intermetallics.

The objective is to prepare an alloy constituted by a single silver-doped phase to be transformed into a mixture of (Au,Ag) and zirconia. Indeed, it is essential to start with a ternary precursor because some binary compounds cannot be nano-structured at low temperature using this method. So, we tried to benefit from the specific nano-structuration property of the AuZr phase by using a silver-doped ternary alloy, e.g. $(Ag_xAu_{1-x})Zr$. This route implies the existence of a solid solution of Ag in the AuZr phase, Ag atoms being placed at the atomic positions of Au. Taking into account that (Ag, Au) is a random solid solution in the entire composition range, we may infer the existence of the $Ag_xAu_{1-x}Zr$ solid solution, which will be used as a silver-doped precursor. Park and Lee [43] reassessed the Ag–Au system including the size effect and calculated several phase diagrams of Ag–Au alloy system for nanoparticle size of 5 nm, 10 nm, 20 nm, 50 nm and 100 nm using the FactSage Module [44]. It is noteworthy that they found that the solid solution (Ag, Au) exists in the entire composition domain of the Ag–Au system for bulk alloy as well as for nanoparticles.

Nevertheless, the arc-melting of the starting elements, Ag, Au and Zr, needs some handling precautions. It is well known that silver exhibits a very high value of saturated vapor pressure (one hundred times higher than those of gold or zirconium,) e.g. at the melting temperature of zirconium (2128 K) the value of the vapor pressure of silver is 0.120 bar [45]. The final alloy composition will thus depend on the silver weight losses. In order to assert the composition of the ternary precursor, it is necessary to take into account this phenomenon by introducing an excess of silver in the starting preparation before melting. The composition is then adjusted by performing successive melting until the weight losses drive approximately to the expected one.

Considering that the $Ag_xAu_{1-x}Zr$ solid solution exists, it is then necessary to determine the limit of the solubility of Ag in the AuZr phase in order to prepare a single-phase alloy. A metallographic study of the phase diagram of the ternary Ag–Au–Zr system has been undertaken by means of scanning electron microscopy (SEM). After arc-melting, the ingots were annealed in order to homogenize the composition of the alloy. The annealing was performed in a sealed quartz tube under inert atmosphere with a piece of zirconium used as oxygen getter. Pure zirconium and ternary sample were wrapped in a tantalum foil in order to avoid any reaction between samples and silica. Equilibrium annealing needed 60 days at 850 °C. This temperature was chosen with regard to the phase diagrams of the Ag–Zr and Au–Zr binary systems, in order to perform the heat treatment at the solid state getting the maximum of atom mobility without any presence of liquid. After annealing, the samples were quenched in water. The primary phase is clearly identified: the morphology of the large and elongated grains of the $Ag_xAu_{1-x}Zr$ phase is in keeping with its congruent type of formation. Their composition was measured by EDX allowing us to propose a value of the limit of the solubility of Ag in the AuZr phase: 12.5 at.% Ag. For the single-phase samples, the compositions measured by EDX were found to be coherent with those calculated by weighting.

The metallic samples are then oxidized at 80 °C under wet atmosphere and the zirconia is selectively dissolved into fluoridric acid.

2.2. Physico-chemical characterization

The actual metal loadings of the NP systems were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES, Activa-Horiba Jobin Yvon).

BET measurements were recorded on Micromeretics ASAP 2002 equipment. The specific surface area of the samples was measured by determining nitrogen adsorption isotherms at 77 K (the data were processed using the Brunauer, Emmet, and Teller (BET) method).

The X-ray Photoemission Spectroscopy (XPS) experiments were carried out in a KRATOS AXIS Ultra DLD spectrometer equipped with a hemispherical analyzer and a delay line detector. The base pressure in the analysis chamber was $5 \cdot 10^{-9}$ mbar. All the data were acquired (using monochromated Al Kα X-rays 1486.6 eV, 150 W), at a normal angle with respect to the plane of the surface. The survey scans were obtained at a pass energy of 160 eV, while high-resolution core-level spectra of the Au 4f, Ag 3d, Zr 3d, F 1s, C 1s and O 1s were measured at 20 eV pass energy.

Low-Energy Ion-Scattering Experiments were conducted in the same apparatus than that used for XPS experiments. The analysis was performed with 1-keV ^{4}He$^+$ ions at room temperature at a scattering angle of 135°. The primary ^{4}He$^+$ beam intensity was 10 nA, focused on an impact spot of about 0.5 mm diameter.

X-ray diffraction (XRD) patterns of the NP materials were obtained using a Bruker D8 X-ray diffractometer equipped with a 9-sample holder. The X-ray source was Cu Kα radiation. 2θ diffraction angle was varied from 5° to 80° during the measurement.

A ESEM FEG New XL30 environmental microscope was used to the direct observation of the different NP systems.

2.3. Catalytic testing

The oxidation of H_2 and the oxidation of CO with (PrOx) or without the presence of hydrogen in the inlet gas mixture was measured in a continuous flow fixed bed reactor at atmospheric pressure and variable temperature. 200 mg or 50 mg of the NP gold