



## Nanodispersed Au/Al<sub>2</sub>O<sub>3</sub> catalysts for low-temperature CO oxidation: Results of research activity at the Boreskov Institute of Catalysis

B.L. Moroz<sup>a,b,\*</sup>, P.A. Pyrjaev<sup>a</sup>, V.I. Zaikovskii<sup>a,b</sup>, V.I. Bukhtiyarov<sup>a,b</sup>

<sup>a</sup> G.K. Boreskov Institute of Catalysis, Siberian Branch of Russian Academy of Sciences, 5 Avenue Akademika Lavrentieva, 630090 Novosibirsk, Russia

<sup>b</sup> Novosibirsk State University, 630090 Novosibirsk, Russia

### ARTICLE INFO

#### Article history:

Available online 21 December 2008

#### Keywords:

Low-temperature CO oxidation  
Au/Al<sub>2</sub>O<sub>3</sub> catalysts  
Gold dispersion

### ABSTRACT

This paper presents some important results of the studies on preparation and catalytic properties of nanodispersed Au/Al<sub>2</sub>O<sub>3</sub> catalysts for low-temperature CO oxidation, which are carried out at the Boreskov Institute of Catalysis (BIC) starting from 2001. The catalysts with a gold loading of 1–2 wt.% were prepared *via* deposition of Au complexes onto different aluminas by means of various techniques (“deposition-precipitation” (DP), incipient wetness, “chemical liquid-phase grafting” (CLPG), chemical vapor deposition (CVD)). These catalysts have been characterized comparatively by a number of physical methods (XRD, TEM, diffuse reflectance UV/vis and XPS) and catalytically tested for combustion of CO impurity (1%) in wet air stream at near-ambient temperature. Using the hydroxide or chloride gold complexes capable of chemical interaction with the surface groups of alumina as the catalyst precursors (DP and incipient wetness techniques, respectively) produces the catalysts that contain metallic Au particles mainly of 2–4 nm in diameter, uniformly distributed between the external and internal surfaces of the support granules together with the surface “ionic” Au oxide species. Application of organogold precursors gives the supported Au catalysts of egg shell type which are either close by mean Au particle size to what we obtain by DP and incipient wetness techniques (CVD of (CH<sub>3</sub>)<sub>2</sub>Au(acac) vapor on highly dehydrated Al<sub>2</sub>O<sub>3</sub> in a rotating reactor under static conditions) or contain Au crystallites of no less than 7 nm in size (CLPG method). Regardless of deposition technique, only the Cl-free Au/Al<sub>2</sub>O<sub>3</sub> catalysts containing the small Au particles ( $d_i \leq 5$  nm) reveal the high catalytic activity toward CO oxidation under near-ambient conditions, the catalyst stability being provided by adding the water vapor into the reaction feed. The results of testing of the nanodispersed Au/Al<sub>2</sub>O<sub>3</sub> catalysts under conditions which simulate in part removal of CO from ambient air or diesel exhaust are discussed in comparison with the data obtained for the commercial Pd and Pt catalysts under the same conditions.

© 2008 Elsevier B.V. All rights reserved.

### 1. Introduction

For a long time, metallic gold was considered as a bad catalyst. However, as was discovered in 1987 by Haruta et al. [1], Au particles with a size of <5 nm supported on some metal oxides manifested a very high catalytic activity in oxidation of carbon monoxide at ambient temperature. In succeeding years, the number of communications devoted to catalytic properties of nanosized Au particles has progressively increased, especially very rapidly from 1997 [2]. It was shown that they are also catalytically active in a series of practically important reactions including hydrocarbon selective

oxidation [3] and hydrogenation [4], water–gas shift reaction [5], etc. At the same time, low-temperature CO oxidation is still considered most promising area for application of supported Au catalysts. The possibilities of using gold catalysts for indoor air-quality and industrial pollution control, automobile exhaust gas treatment (in particular, during the period of engine “cold start”), removal of CO from hydrogen fuel for fuel cells, for applications in gas masks, as CO sensors, etc. are extensively studied [6].

It is commonly known that the catalytic activity of gold nanoparticles in CO oxidation is strongly dependent on the support nature [7–9]. Most active catalysts were prepared by depositing gold onto first-row transition metal oxides (TiO<sub>2</sub>, Co<sub>3</sub>O<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub>, NiO) as well as onto Be(OH)<sub>2</sub> and Mg(OH)<sub>2</sub>. These catalysts were studied in sufficient detail but, for different reasons, they are not suitable for large-scale applications.

From the practical point of view alumina would be preferable support for Au catalysts as compared with other metal oxides

\* Corresponding author at: G.K. Boreskov Institute of Catalysis, Siberian Branch of Russian Academy of Sciences, 5 Avenue Akademika Lavrentieva, 630090 Novosibirsk, Russia. Tel.: +7 3833269521; fax: +7 3833308056.

E-mail address: [blmoroz@mail.ru](mailto:blmoroz@mail.ru) (B.L. Moroz).

because of its cheapness, high and thermally stable surface area, well controllable porosity, and relative inertness toward steam. That is why we chose the “gold on alumina” catalysts prepared by different techniques as the principal objects for our own research on catalysis by gold which has started since 2001 in the Laboratory of Surface Studies at the Boreskov Institute of Catalysis (BIC). The main aims of our studies are as follows: (1) characterization of activity and stability of Au/Al<sub>2</sub>O<sub>3</sub> catalysts in low-temperature CO oxidation depending on the catalyst preparation procedure and reaction conditions; (2) elucidation and investigation of reasons (including size effect) determining the catalytic activity of Au nanoparticles in CO oxidation; (3) optimization of methods for preparation of nanosized Au particles supported on various modifications of Al<sub>2</sub>O<sub>3</sub>; (4) estimation of potentialities of Au/Al<sub>2</sub>O<sub>3</sub> catalysts as applied for combustion of CO impurities contained in air and automobile exhaust. Some important results obtained are discussed in the paper.

## 2. Experimental

### 2.1. Catalyst preparation

Microspherical  $\gamma$ -Al<sub>2</sub>O<sub>3ms</sub> (BIC; particle size, 0.5–0.7 mm; BET surface area, 185 m<sup>2</sup>/g) pre-calcined in a dry airflow at 700 °C, an ultrathermostable  $\theta$ -Al<sub>2</sub>O<sub>3</sub> powder (Sasolchemie GmbH, Germany; particle size, 0.2–0.5 mm; BET surface area, 110 m<sup>2</sup>/g) pre-calcined in a dry airflow at 600 °C, and commercial “active alumina” of AOA-2 grade (Dneprodzerzhinsk, Ukraine; particle size, 1–3 mm) were used as supports. A sample of AOA-2 representing initially a mixture of  $\gamma$ - $\chi$ -Al<sub>2</sub>O<sub>3</sub> and pseudoboehmite AlOOH (30–40 wt.% AlOOH) was calcined in air at 475 °C for 6 h to convert it to almost pure  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (lattice constant  $a = 0.798$  nm) with the BET surface area of 250 m<sup>2</sup>/g.

The nanodispersed Au/Al<sub>2</sub>O<sub>3</sub> catalysts were prepared by the following techniques: (1) adsorption of anionic gold hydroxyl complexes from an alkalinized aqueous solution of HAuCl<sub>4</sub> (the so-called “deposition-precipitation” method [10]); (2) incipient wetness impregnation using an aqueous HAuCl<sub>4</sub> solution; (3) adsorption of organogold complex from a non-polar organic solvent (the “chemical liquid-phase grafting” method [11]); (4) chemical vapor deposition of a highly volatile organogold precursor on a support surface at subatmospheric pressure.

#### 2.1.1. “Deposition-precipitation” (DP)

A support was treated with an aqueous HAuCl<sub>4</sub> + NaOH solution at certain pH and temperature for 1 h, washed several times with large portions of warm distilled water (200 mL H<sub>2</sub>O/1 g sample), dried and calcined in air at 400 °C for 4 h.

#### 2.1.2. Incipient wetness impregnation (IMP)

A solution of HAuCl<sub>4</sub> taken at a required concentration was added to a weighed amount of Al<sub>2</sub>O<sub>3</sub>, the volume of the impregnating solution being equal to the total pore volume of the support. The resulting paste was mixed for 1 h and allowed to stay at 20 °C for 20 h. The impregnated ‘HAuCl<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub>’ samples were dried in air at 110 °C overnight and reduced with H<sub>2</sub> at 400 °C for 4 h.

#### 2.1.3. “Chemical liquid-phase grafting” (CLPG)

A weighed amount of  $\gamma$ -Al<sub>2</sub>O<sub>3ms</sub> previously dehydrated at 300 °C under air was immersed in a fresh pentane solution of (CH<sub>3</sub>)<sub>2</sub>AuL (L = acetyl acetate (acac) or dipivaloyl methanoate (dpm)) synthesized by a procedure described elsewhere [12]. The suspension was vigorously stirred at 20 °C for 4 h and allowed to stay at 7–10 °C overnight. The sample was suction filtered,

outgassed at 20 °C and calcined in air at 400 °C for 4 h in a muffle furnace pre-heated to this temperature.

#### 2.1.4. Chemical vapor deposition (CVD)

Among several tested dimethylgold(III) chelates, for further CVD experiments we chose dimethylgold(III) acetylacetonate as the precursor for preparation of supported Au catalysts due to its accessibility, high volatility and thermal stability (saturated vapor pressure is  $5.5 \times 10^{-2}$  Pa at 25 °C; decomposition temperature in vapor state is 54 °C) [13]. To prepare the supported Au catalysts by the CVD technique we employed two different approaches. The first approach was to pass (CH<sub>3</sub>)<sub>2</sub>Au(acac) vapor through a stainless steel column containing a fixed bed of  $\gamma$ -Al<sub>2</sub>O<sub>3ms</sub> which was preliminarily evacuated at 100 °C to  $10^{-5}$  Pa and cooled to room temperature. Then air was admitted into the column, and the sample was calcined at 325 °C for 0.5 h. In the second approach,  $\gamma$ -Al<sub>2</sub>O<sub>3ms</sub> (0.5 g) was loaded in a glass ampoule (reactor) connected to a MI-1201 mass-spectrometer through a vacuum leak valve for on-line monitoring of the composition of the gas phase (sampling rate 0.1 cm<sup>3</sup>/s). The support was evacuated at 300–350 °C and  $10^{-5}$  Pa until the water peak vanished from the mass spectrum of the gas phase. After the reactor was cooled to room temperature, it was filled with (CH<sub>3</sub>)<sub>2</sub>Au(acac) vapor and vertically rotated at a constant rate. As soon as the signals derived from the complex were not detected by mass spectrometry any more, another portion of the complex was introduced in the reactor, and this was repeated until the support surface was saturated with the adsorbed complex or until the whole amount of the complex (6 mg) evaporated. Then air was admitted into the reactor, the sample was heated in air up to 325 °C and calcined at this temperature for 0.5 h. The more detailed information about the experimental procedures and apparatus for preparation of Au/Al<sub>2</sub>O<sub>3</sub> catalysts by CVD is presented in our article [13].

### 2.2. Catalyst characterization

The Au and Cl contents of the catalysts were measured using X-ray fluorescence (XRF) technique on a VRA-30 instrument equipped with a Cr-anode. The diffuse reflectance UV–vis spectra were recorded on a Shimadzu UV-2501 PC spectrometer equipped with an ISR-240 integrating sphere attachment for diffuse reflectance measurements, using BaSO<sub>4</sub> as a reference, in the range of 10,000–50,000 cm<sup>-1</sup> and presented in Kubelka–Munk function  $F(R)$ –wavenumber coordinates. The transmission UV–vis spectra of solutions of colloidal gold and gold complexes were obtained using a quartz cell with a path length of 2 mm, with water as a reference liquid. X-ray diffraction (XRD) was performed using a HZG-4 X-ray diffractometer with Cu K $\alpha$  radiation and a graphite monochromator. The data were collected for 5 s per step with a step size of 0.05° within the range of  $20^\circ \leq 2\theta \leq 90^\circ$ . Transmission electron microscopy (TEM) studies were carried out on a JEOL JEM-2010 electron microscope operated at 200 kV and giving an information limit of 0.14 nm. Prior to TEM study, a sample was ground and suspended in ethanol. A drop of suspension was mounted on a copper grid coated with a holey carbon film, and the solvent was allowed to evaporate. X-ray photoelectron (XP) spectra were measured with a VG ESCALAB HP photoelectron spectrometer using a non-monochromatized Al K $\alpha$  radiation ( $E_{hv} = 1486.6$  eV) operated at 200 W as the excitation source. The binding energy ( $E_b$ ) scale was calibrated against the positions of the Au 4f<sub>7/2</sub> ( $E_b = 84.0$  eV) and Cu 2p<sub>3/2</sub> ( $E_b = 932.6$  eV) core level peaks from polycrystalline foils of gold and copper, respectively. The samples were loaded in the form of granules or powder applied to conductive double-sided scotch. The charging effect was corrected using the Al 2p peak from Al<sub>2</sub>O<sub>3</sub> at 74.5 eV as the

Download English Version:

<https://daneshyari.com/en/article/57307>

Download Persian Version:

<https://daneshyari.com/article/57307>

[Daneshyari.com](https://daneshyari.com)