



## Gold catalysts for the abatement of environmentally harmful materials: Modeling the structure dependency

Krisztina Frey<sup>a,\*</sup>, Gábor Pető<sup>a</sup>, Katalin V. Josepovits<sup>b</sup>, László Guzzi<sup>a,c</sup>

<sup>a</sup> Department of Surface Chemistry and Catalysis, Institute of Isotopes, Konkoly Thege Miklós út 29-33, H-1121 Budapest, Hungary

<sup>b</sup> Department of Atomic Physics, Budapest University of Technology and Economics, Budafoki út 8, H-1111 Budapest, Hungary

<sup>c</sup> Institute of Nanochemistry and Catalysis, P.O. Box 17, H-1525 Budapest, Hungary

### A B S T R A C T

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FeO<sub>x</sub>, TiO<sub>2</sub> and CeO<sub>x</sub> layers were deposited by pulsed laser deposition (PLD) technique onto Au films or Au nanoparticles supported on SiO<sub>2</sub>/Si(100). The samples were characterized by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), secondary ion mass spectrometry (SIMS) and their reactivity was studied in catalytic CO oxidation. Comparison was made with reference samples of FeO<sub>x</sub>/SiO<sub>2</sub>/Si(100), TiO<sub>2</sub>/SiO<sub>2</sub>/Si(100), CeO<sub>x</sub>/SiO<sub>2</sub>/Si(100) and Au/SiO<sub>2</sub>/Si(100) layers. The catalytic activity of the metal-oxide/Au/SiO<sub>2</sub>/Si(100) samples must be attributed to active sites located on the metal-oxides overlayer modified by gold underneath, since no Au was exposed to the surface according to the XPS and SIMS. We found a promoting effect of gold on the catalytic activity of the FeO<sub>x</sub> overlayer and an inhibiting effect of gold on the TiO<sub>2</sub> and CeO<sub>x</sub> overlayers. These findings are discussed in terms of electronic interactions at the Au/metal oxide interface.

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### 1. Introduction

Automotive exhaust gas contains high concentrations of NO<sub>x</sub>, CO, and hydrocarbons, which are harmful to human health. Although these components can be drastically reduced by the use of a three-way catalyst, nitrous oxide (N<sub>2</sub>O), which has a strong greenhouse effect, is produced during the catalytic reaction.

In the year 2000 over 500 million cars were produced and used worldwide. Of an annual worldwide production of new cars approaching 60 million, the majority of these vehicles (automobiles and trucks) use gasoline or diesel engines. Gasoline and diesel emissions contribute significantly to the increasing air pollution, meaning that larger efforts are necessary for their control and reduction. Catalytic converters have been proved to be effective in controlling harmful gaseous emissions (CO, un-burnt HC and NO<sub>x</sub>) under normal working conditions, for a stoichiometric air/fuel ratio. Indeed, it is commonly accepted that three-way catalysts for gasoline engines, along with lambda sensors, have been one of the most remarkable innovative technologies in the automotive field during recent years. However, for exhausts which have an oxygen content exceeding the stoichiometric value, the CO and HC conversion is high but at the expense of NO<sub>x</sub> reduction [1]. All commercial three-way catalysts (TWCs) in use at present are

based on platinum, palladium and rhodium (PGM) on a support comprised of zirconia-stabilized ceria, zirconia and  $\alpha$ -alumina. Additives include barium oxide and zinc oxide. These PGM-based catalysts perform the task of emission control very well and many aspects of this technology are very well established, but there are areas, such as low light off and lean-burn diesel combustion, where significant problems remain. Gold-based catalysts may play a role in the future in finding a remedy.

A gold-based material has been formulated for use as a Three Way Catalysts in gasoline and diesel applications [2]. This catalyst, developed at Anglo American Research Laboratories in South Africa, consisted of 1% Au supported on zirconia-stabilized-CeO<sub>2</sub>, ZrO<sub>2</sub>, and TiO<sub>2</sub>, and contained 1% CoO<sub>x</sub>, 0.1% Rh, 2% ZnO, and 2% BaO as promoters. The catalytically active gold-cobalt oxide clusters were 40–140 nm in size. This catalyst was tested under conditions that simulated the exhaust gases of gasoline and diesel automobiles and survived temperatures as high as 773 K for 157 h, with some deactivation occurring.

Research on gold-based catalysts has significantly increased in the last decade and is today considered as one of the systems for future applications in catalysis. Haruta et al. discovered exceptionally high activity of gold nanoparticles supported on oxides such as Co<sub>3</sub>O<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> in CO and H<sub>2</sub> oxidation, NO reduction, water-gas shift reaction, CO<sub>2</sub> hydrogenation and catalytic combustion of methanol, provided the dispersion of the gold particles was very high. Haruta et al. explained that the unique

\* Corresponding author.

E-mail address: [frey@mail.kfki.hu](mailto:frey@mail.kfki.hu) (K. Frey).

catalytic activity is attributed to the gold/metal oxide perimeter interface activating at least oxygen in the oxidation reaction [3–5].

The present study is aimed at developing a novel family of catalysts, based on gold, to replace the more expensive platinum and rhodium metals. Such precious metals are the most promising alternative candidates as active catalysts for the abatement of automotive exhaust gas pollutants.

In the present work, our studies on the reactivity of different oxide overlayers ( $\text{FeO}_x$ ,  $\text{TiO}_2$ ,  $\text{CeO}_x$ ) affected by the underlying Au film or nanoparticles deposited by electron beam evaporation of gold are summarized. We report on the structural and chemical characterization of these samples and provide initial rate studies for CO oxidation over the “inverse model systems”. Comparison will be made with reference systems free of either Au or metal oxide ( $\text{FeO}_x$ ,  $\text{TiO}_2$ ,  $\text{CeO}_x$ ).

## 2. Experimental

Thin gold films were deposited by electron gun evaporation in a VT 460 evaporator at UHV onto Si(100) wafer covered with native  $\text{SiO}_2$  of nanometer thickness range. The gold layer thicknesses were around 8, 10, 60 and 80 nm, respectively. The film thickness was monitored by measuring the vibrating frequency shift. In order to prepare the nanosized gold elements (nanoparticles, islands, etc.), the 10 nm-thick gold film was ion-implanted with  $\text{Ar}^+$  ions at 40 keV and a  $10^{15}$  atom/cm<sup>2</sup> dose. The native oxide layer on the Si

substrate served as a barrier against the Si/Au interaction, but it was thin enough to avoid electrical charging.

Transition metal oxide layers ( $\text{FeO}_x$ ,  $\text{TiO}_2$ ,  $\text{CeO}_2$ ) were deposited with different thicknesses onto supported nanosized Au particles or Au films. To provide a reference, a pure  $\text{SiO}_2/\text{Si}(100)$  substrate was likewise covered by oxides. PLD with 100–750 pulses of Nd laser source was applied with about 2 J and 30 ns pulse length while keeping the pressure at  $10^{-6}$  mbar for details, see Ref. [6]. The PLD method is commonly accepted in the literature to produce homogeneous and defectless film [7]. Simultaneously, an oxide layer ( $\text{FeO}_x$ ,  $\text{TiO}_2$ ,  $\text{CeO}_2$ ) was also deposited on blank  $\text{SiO}_2/\text{Si}(100)$  wafer using the same geometry by positioning both wafers side by side.

Surface characterization of the samples was performed in an ES-300 photoelectron spectrometer. The core level and valence band spectra were measured by X-ray photoelectron spectroscopy (XPS) using a non-monochromatic Mg K $\alpha$  radiation of the source at 150 W and a hemispherical analyzer operating in the constant pass energy mode at  $E_p = 50$  eV.

The samples were characterized in a TOF SIMS (time-of-flight secondary ion mass spectrometry) instrument at a base pressure of  $1.2 \times 10^{-9}$  mbar. The analysis was carried out in the static mode (SSIMS) using a pulsed (7.7 kHz) beam of 5 keV  $\text{Ar}^+$  ions and a reflectron analyzer. Positive secondary ions extracted at 1400 V

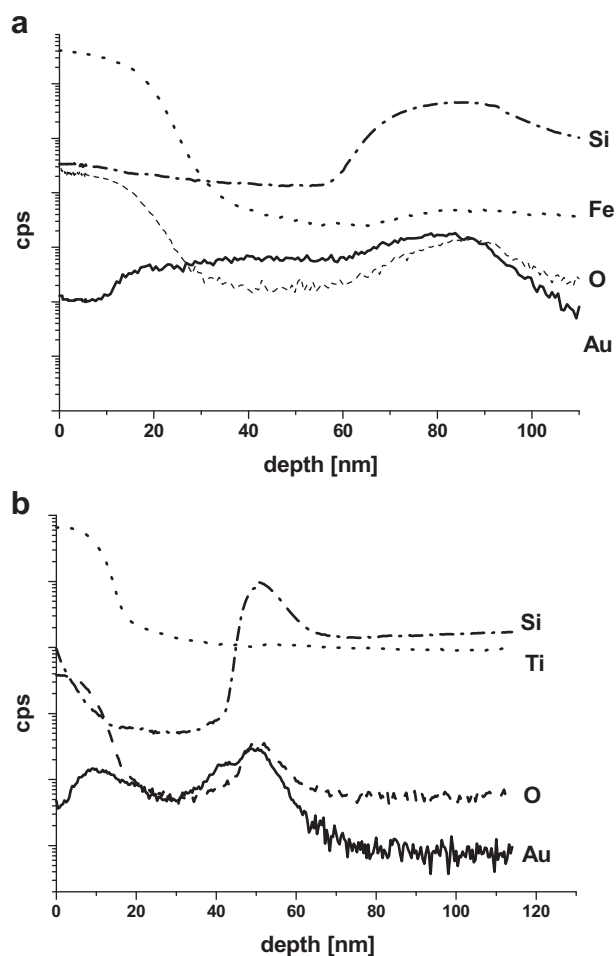


Fig. 1. SIMS spectra of (a)  $\text{FeO}_x/\text{Au}$  film/ $\text{SiO}_2/\text{Si}(100)$  sample and (b)  $\text{TiO}_2/\text{Au}$  film/ $\text{SiO}_2/\text{Si}(100)$ .

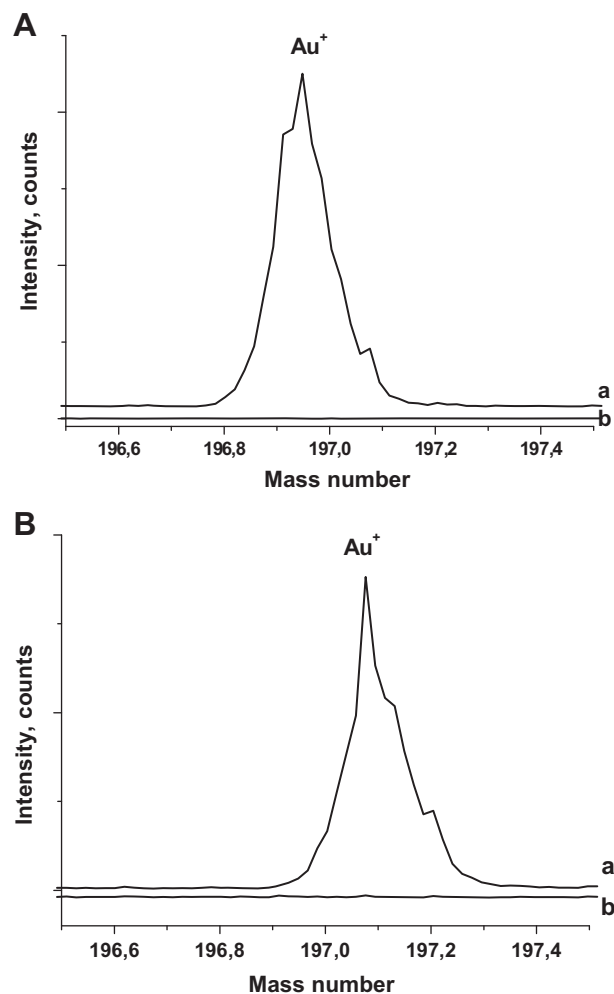


Fig. 2. Selected mass region of TOF-SIMS spectra (A) for the  $\text{FeO}_x/\text{Au}/\text{SiO}_2/\text{Si}(100)$  sample and (B) for the  $\text{TiO}_2/\text{Au}/\text{SiO}_2/\text{Si}(100)$  sample before (a) and after (b) metal-oxide deposition by PLD onto the  $\text{SiO}_2/\text{Si}(100)$  wafer.

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