Surface Science 618 (2013) 132–139

Contents lists available at ScienceDirect

Surface Science

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

Surface structures of Au–Pt bimetallic nanoclusters on thin film Al_2O_3/NiAl(100) probed with CO

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ARTICLE INFO

Article history:
Received 8 July 2013
Accepted 12 September 2013
Available online 19 September 2013

Keywords:
Au–Pt bimetallic nanoclusters
Alumina
NiAl
Infrared reflection absorption spectra
Temperature-programmed desorption
CO probe

ABSTRACT

With infrared reflection absorption spectra and temperature-programmed desorption of CO as a probe molecule, we investigated the surface structure of Au–Pt bimetallic nanoclusters on thin-film Al_2O_3/NiAl(100) under ultrahigh vacuum conditions. Vapor Au and Pt (0.0–2.0 ML) were sequentially deposited onto Al_2O_3/NiAl(100) at 300 K to form bimetallic clusters; under the kinetic constraint, the order of the metal deposition made a variation in the surface structure of the grown clusters. For the deposition of Au onto Pt clusters (first Pt and then Au), the deposited Au decorated preferentially and then aggregated the edge sites of Pt clusters, instead of decorating the rest of Pt surface. For the metal deposition in the reverse order, the deposited Pt covered uniformly the surface of existing Au clusters and no preferential adsorption site was indicated. The infrared absorption for CO on Au sites was significantly enhanced when alloying occurred; this enhancement is primarily a local field effect depending on the coordination of CO-binding Au, and hence provides additional structural characterization of the grown clusters.

1. Introduction

Platinum (Pt) catalysts for the oxidation of methanol (CH_3OH) have been extensively investigated as the principal reaction is applied in direct methanol fuel cells (DMFC), providing a prospect of direct conversion of methanol to electricity with great efficiency [1–5]. The Pt catalysts are, however, readily poisoned by CO-like reaction intermediates. With the objective to diminish the poisoning effect, the supported Au–Pt bimetallic nanoclusters have been explored. These supported Au nanoclusters were shown to exhibit an unprecedented catalytic reactivity for CO oxidation. The alloying is expected to suppress the poisoning, through either a bifunctional mechanism — methanol oxidation at Pt sites and CO oxidation at Au sites [6,7] or synergistic effects that involve a variation of electronic band structures and lattice parameters [8–10]. These alloying effects rely heavily on the surface structure and composition of the bimetallic clusters. The knowledge and control of the surface structure and composition of the bimetallic system thus become crucial. The present work is in response to this demand.

With probe molecule CO, infrared reflection absorption spectroscopy (IRAS) and temperature-programmed desorption (TPD), we investigated the Au–Pt bimetallic nanoclusters formed on sequential vapor deposition of Au and Pt (0.0–2.0 ML) on thin-film Al_2O_3/NiAl(100) at 300 K under ultrahigh vacuum (UHV) conditions. The bimetallic clusters were previously characterized with scanning tunneling microscopy (STM), reflection high-energy electron diffraction (RHEED) and synchrotron-based photoelectron spectroscopy (PES). The STM images showed that, for the deposition of Au and Pt in either order, when 0.5 ML, most subsequently deposited metal joined the existing clusters and formed bimetallic clusters; the increased cluster size and few newly formed clusters resulted in cluster coalescence, and thus a bimodal distribution of the cluster diameter — the coalescing clusters had a greater diameter and a dumbbell shape [11,12]. These clusters generally had a diameter $\leq$6.0 nm and height $\leq$0.8 nm, and grew in a fcc phase and with their facets either (111) or (001) parallel to the θ-Al_2O_3(100) surface [11,12]. Alloying of Au with Pt was reflected in an evident shift of binding energy (BE) of Au 4f core levels in the PES spectra [11,12]. The IRAS spectra of adsorbed CO were also employed to characterize the evolving surface sites of the bimetallic clusters with elevated temperature [12]. These authors concluded that alloying was active, position interchange was possible, and both Au and Pt coexisted at the cluster surface; on elevating the sample temperature, segregation of Au from Pt occurred but Au preferred to migrate to the surface, leading to a structure with an Au shell and a Pt core [12]. The present work with a CO probe provides, based on techniques in another combination, structural information on the surface of the bimetallic clusters during growth.

Our results show that, under the kinetic constraint at 300 K, the order of metal deposition leads to varied surface structures of the grown bimetallic clusters, and these structures contrast theoretical predictions. For deposition of Au onto Pt clusters (first Pt and then Au), the deposited Au preferred to decorate the edges of Pt clusters (low-coordination sites) and nucleate with the subsequently deposited Au; the Pt surface was thus little covered by the deposited

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0039-6028/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.susc.2013.09.013

Au. Although the deposited Au was theoretically expected to cover the Pt surface, because of a smaller surface energy of Au [13,14], the segregation of Au from Pt, due to their miscibility gap, was dominant at 300 K. The phase-segregation growth might contribute to the formation of the dumbbell-shape clusters observed with STM [11,12]. For metal deposition in the reverse order, the deposited Pt covered the surface of Au clusters in a more uniform manner and no preferential adsorption sites were indicated. Both structures contradict the Au shell–Pt core structure, an energetically preferred one [13,14], and differ from the comparable systems, Fe–Pd, Co–Pd, Au–Pd, Au–Rh and Au–Pt bimetallic clusters on varied oxide surfaces [15–21], of which the structural features were largely governed by the preferential decoration at, or segregation to, the cluster surface of metals with smaller surface energies [15–21].

Moreover, a significantly enhanced intensity of infrared absorption was observed for CO on Au sites of Au–Pt bimetallic clusters. The enhancement is primarily a local field effect [22–24] resulting fundamentally from the decoupling of the CO bond to the low-coordinated metal from other metal atoms embedded in the metal surface [24], so depending on the coordination of the CO-binding Au. This enhancement effect thus provides complementary structural information on the grown bimetallic clusters.

2. Experimental

Our experiments were performed in UHV chambers with a base pressure 4×10^{-10} Torr. A NiAl(100) sample (MaTeck GmbH) was polished to a roughness less than 30 nm and an orientation accuracy better than 0.1°. To obtain a clean surface, the sample was subjected to alternating cycles of sputtering and subsequent annealing before each experiment. The cleanliness of the sample was monitored with Auger electron spectra, low-energy electron diffraction and STM. An ultra-thin θ-Al_2O_3 film was formed on oxidation of a NiAl(100) alloy surface at 1000 K; the formation of Al_2O_3 thin films is described elsewhere [11,12,25–28]. To achieve a homogeneous crystalline Al_2O_3 surface with no NiAl facets [28,29], we refrained from protracted annealing after oxidation of the oxide films. The grown θ-Al_2O_3 thin film had a thickness 0.5–1.0 nm [25,28]. The sample was then quenched to 300 K for vapor deposition of Pt and Au from ultra-pure Pt and Au rods heated by electron bombardment in commercial evaporators (Omicron EFM 3). The rate of deposition of metal was fixed about 0.1 ML/min, calculated according to the coverage prepared at 300 K [30,31]. The coverage was estimated from the volume of the Pt (or Au) clusters observed with STM; 1 ML corresponds to density 1.5×10^{15} (1.4×10^{15}) atoms/cm^2 of fcc Pt(111) (Au(111)) surface atoms. After the deposition, the sample was cooled to the desired adsorption temperature (100 K) for CO. CO gas was dosed with a doser pointing to the sample, with a background pressure about 5×10^{-9} Torr.

TPD spectra were recorded by ramping the sample at 3 K/s and monitoring the various masses on a quadruple mass spectrometer (Hiden), which was shielded and placed near (about 2 mm) the sample. IRAS spectra were recorded with a Fourier-transform infrared spectrometer (FTLA 2000, HgCdTe detector cooled with liquid nitrogen) with external optics aligned for incident angle 75° from the sample normal. The IRAS spectra are presented as a ratio of data of the sample and the oxide surface (or the clusters) measured at the same surface temperature (100 K), and are typically the average of 256 scans at resolution 4 cm^{-1}.

3. Results and discussion

Our Au–Pt bimetallic clusters were formed on vapor deposition of Au (or Pt) onto pre-deposited 1.0 ML Pt (or Au) on Al_2O_3/NiAl(100) at 300 K. Because of the high coverage of the pre-deposited metal, most post-deposited metal was incorporated into the existing clusters, indicated by little increased density of the clusters. This sample preparation warrants that the acquired TPD and IRAS data resulted mostly from bimetallic clusters, rather than separate Au and Pt clusters; the presented spectral data also show significant alloying features.

3.1. Au–Pt nanoclusters formed with Au deposited on Pt clusters/Al_2O_3/NiAl(100)

Fig. 1 shows the TPD spectra of CO adsorbed molecularly on Pt clusters and on Au–Pt bimetallic clusters formed on deposition of Au onto 1.0 ML Pt on thin-film Al_2O_3/NiAl(100). The top panel, for comparison, presents the CO desorption from Pt clusters, ranging from 300 to 550 K [32]. With the incorporation of Au, a broader desorption feature between 180 and 300 K grew (Fig. 1(b)–(d)), ascribed to the CO desorption from Au sites; this CO desorption feature resembles those

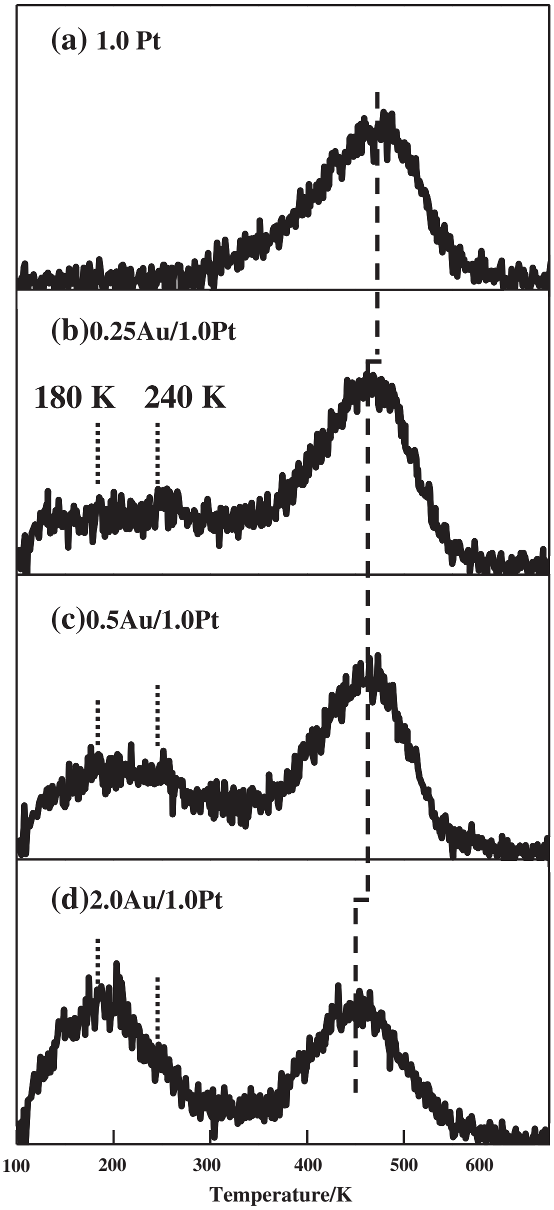

Fig. 1. CO TPD spectra for (a) Pt and (b)–(d) Au–Pt bimetallic clusters on thin-film Al_2O_3/NiAl(100) exposed to CO (3.0 L) at 100 K. The bimetallic clusters were formed on deposition of (b) 0.25, (c) 0.5, and (d) 2.0 ML Au onto pre-deposited 1.0 ML Pt on the oxide at 300 K. 3.0 L CO is sufficient to saturate the surface and no CO adsorbed on the oxide at 100 K.