Studying the evolution of catalytic surfaces under realistic conditions : $Pd_{70}Au_{30}(110)$ surface properties under CO, O_2 and CO+O_2 elevated pressures

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Introduction

Elevated pressure *in situ* STM studies were crucial to show that CO adsorption on gold surfaces strongly modifies their surface structures [1-3]. However oxygen dissociation does not occur spontaneously on such surfaces preventing efficient CO oxidation. The addition of an oxygen-dissociative metal (such as Pd) to gold may overcome this difficulty. In this work we present results concerning the behaviour of $Pd_{70}Au_{30}(110)$ under elevated pressures of CO and O_2 and compare them to the results obtained on Au(110) under similar conditions.

Materials and Methods

The STM and PM-IRRAS in situ experiments were developed at IRCELYON based on a modified MicroLH STM (Omicron) and on a NEXUS spectrometer (Thermo Nicolet), respectively. The XPS experiment was performed at ALS beamlines 9.3.2 & 11.0.2 (Berkeley, USA)) and the SXRD was performed at ESRF beamline BM32 (Grenoble, France) on a reactor developed at the Institut Néel. Under UHV, the outmost surface layer of the $Pd_{70}Au_{30}(110)$ (from Surface Prep Lab) is strongly enriched (above 85% of Au as shown by LEISS).

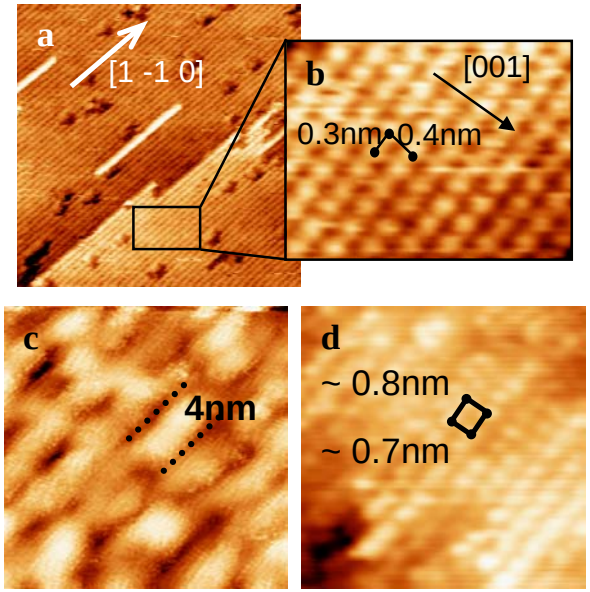
Results and Discussion

Brief $Pd_{70}Au_{30}(110)$ under UHV conditions exhibits a (1x1) un-reconstructed surface (Fig. 1a,b). Under CO pressure the surface roughens and a "rice grain" morphology is observed with typical domain sizes around 4 nm and 0.05 nm corrugation (Fig. 1c) that prevails up to 500Torr. PM-IRRAS of CO adsorption on $Pd_{70}Au_{30}(110)$ (at different CO pressures: 0.02Torr to 100Torr) shows three vibration bands : 2115cm^{-1} (CO top on Au), 2090cm^{-1} (CO top on Pd) and 1980-1990cm^{-1} (bridged CO). Complementary studies by XPS show the building up of high energy shoulders on the Pd-$3d_{3/2}$ peak with increasing CO pressure. These shoulders can be related to chemical and/or structural effects induced by CO chemisorption. Under O_2 pressure (<1 Torr) XPS reveals a strong oxidation of Pd. At higher pressures (500 Torr) a structure close to a p(2x2) building on a roughened surface is observed by STM (Fig. 1d). SXRD showed that the surface (1x1) structure disappears under CO pressure. Addition of O_2 (pressure 500Torr) induces the formation of a bulk-like Pd oxide at the surface as shown by the increase of the oxide peak (k=1.47) at T=473K.

SXRD and XPS in situ studies at different pressure ranges revealed the catalytic efficiency of the surface under reaction conditions (CO in high excess of O_2).

The use of complementary in situ techniques enabled us to study the evolution of $Pd_{70}Au_{30}(110)$ surface characteristics upon adsorption of CO and O_2 at elevated pressures, unavailable otherwise. STM shows a strong modification of the surface structure whereas XPS reveals a strong influence of CO and O_2 on the electronic properties of Pd, with oxidation at high pressure/temperature in the latter case. SXRD yields consistent results with both.

Figure 1. STM images of the $Pd_{70}Au_{30}(110)$ surface under : (a,b) UHV conditions (20x20 nm^2 and 4.7x3 nm^2 respectively); (c) 1Torr of CO (20x20 nm^2); (d) 500 Torr of O^2 (10x10 nm2)..



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