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## Surface properties of PdAu and PdAgAu alloys under dynamic conditions: NAP-XPS study

## Content

Pd binary and ternary alloys have attracted extensive attention in a wide range of applications such as catalysis, hydrogen detection and separation, being their performance often influenced by surface composition and/or structure. Particularly, for hydrogen separation materials, the permeation mechanism is complex, since it involves different stages related to hydrogen adsorption, absorption, and diffusion processes, which are dependent on surface composition, structure, and morphology. Long-term hydrogen dissociation on Pd-based alloys has been related to surface segregation effects, induced by the interaction with strongly adsorbing species. To elucidate the inhibition mechanism under exposure to CO or CO2-containing streams, PdAgAu and PdAu alloys were studied using ambient pressure X-ray photoelectron spectroscopy (NAP-XPS). The samples were synthesized by sequential electroless deposition of pure metals on top of non-porous 316 L stainless-steel substrates (10 mm diameter and thickness of 1 mm). Once the metals were deposited, the samples were heated up to 773 in a H2 atmosphere to form a homogeneous binary or ternary alloy by thermal diffusion. Dynamic changes, in the near surface region, were monitored upon exposure to several streams (H2/Ar, H2/CO and H2/CO2) at 573, 623 and 673 K. The gas evolution was followed by an online mass spectrometer. Pd 3d corelevel showed the contribution of several species at higher binding energies than Pd0 for both, the PdAu and PdAgAu alloys. The proportion of those species increased when the temperature during the operando measurements. Silver enrichment in the near surface region was observed for the PdAgAu under all the analyzed conditions, with a higher increment in the presence of CO2. These observations will be discussed taking into account the hydrogen permeation measurements in mixtures containing CO and CO2.

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