



# Pd–Au single-crystal surfaces: Segregation properties and catalytic activity in the selective hydrogenation of 1,3-butadiene

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## Abstract

Pd<sub>70</sub>Au<sub>30</sub> (111) and (110) surfaces have been characterized by low energy electron diffraction, Auger electron spectroscopy and low energy ion scattering spectroscopy. The reactivity of Pd–Au(111) towards the gas phase hydrogenation of 1,3-butadiene has been investigated in a static reactor, and compared to those of Pd–Au(110), Pd(111) and Au(111). Both Pd–Au surfaces are unreconstructed and exhibit strong surface segregation of gold. The gold concentrations in the top layer of Pd<sub>70</sub>Au<sub>30</sub> (111) and (110) are found equal to 75 at.% and 85 at.%, respectively. The hydrogenation of butadiene has been performed at room temperature and 5 Torr in a large excess of hydrogen. While Au(111) is inactive, Pd–Au(111) is initially less active than Pd–Au(110) and Pd(111) for the formation of butenes. However, a spectacular increase in the reaction rate is observed upon evacuation of the reacted gases and introduction of a fresh reactant mixture. Unlike Pd(111), Pd–Au(111) is weakly active for the conversion of butenes to butane. Its subsequently higher selectivity towards butenes could originate from an increased desorption of butenes from the Pd–Au surface. Moreover, a substantial absorption of hydrogen in the course of the reaction is evidenced, and its possible impact on the surface properties is discussed.

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## 1. Introduction

Transition metals of the Pt group are commonly used as heterogeneous catalysts for e.g. gas phase hydrogenation reactions. Alloying several metals is often a good way to improve the

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catalytic performances. Thus numerous surface science studies devoted to catalysis have tried to understand the way alloy surfaces work, looking for specific active sites for chemisorption and elementary reactions [1]. Several types of alloying effects have been identified, such as ensemble, ligand and strain effects. However, the strong interplay between these effects [2] hampers a complete understanding of the alloying effect at present. Hence surface science still has to analyze specific systems in order to derive clearer tendencies.

We have started a multi-technique study of Pd<sub>70</sub>Au<sub>30</sub> (111) and (110) single-crystal surfaces. Our idea was to combine palladium, a very active metal widely used in heterogeneous catalysis, with gold, which is poorly reactive in its bulk phase. Moreover, considering the recent observation that gold is highly active when dispersed as nanoparticles [3–5], we wanted to build a thin strained Au-rich layer above the Pd-rich substrate using the surface segregation of gold. Alloy surfaces were chosen over Au/Pd deposits due to their potentially higher stability under reactive mixtures at elevated temperature and pressure. To our knowledge, the only published work on Pd–Au single-crystals concerns structural studies of Au<sub>3</sub>Pd(100) [6] and (113) [7] by Heiland and co-workers. They find that these surfaces are both 100% Au-terminated. Gold segregation was also reported from experimental studies of Pd–Au polycrystals [8–10] and from calculations [11].

The interest for Pd–Au catalysts has increased in recent years, as they were found to be superior to pure Pd and Au supported catalysts in various reactions [12–15]. The Pd-catalyzed partial hydrogenation of 1,3-butadiene (C<sub>4</sub>H<sub>6</sub>) produces three isomers of butene (C<sub>4</sub>H<sub>8</sub>): 1-butene, *cis*-2-butene and *trans*-2-butene. The complete hydrogenation leads to the formation of butane (C<sub>4</sub>H<sub>10</sub>). From an applied point of view, it is interesting to fully convert butadiene to 1-butene without forming butane, since the reaction is part of the purification process of 1-butene, which is used as a feed in the polymer industry [16]. Among the metals and metal oxides suggested to promote Pd in the selective hydrogenation of butadiene (see e.g. Refs. [16,17]), gold turned out to be a very interesting additive. Joice et al. reported that the yield of

butane decreased as the gold content increased in pumice-supported Pd–Au catalysts [18]. More recently, Miura and co-workers observed that the selective deposition of Au on Pd/Al<sub>2</sub>O<sub>3</sub> by wet chemical methods suppressed the formation of butane at high conversion [19,20]. Krauth et al. showed that the addition of Au to Pd/SiO<sub>2</sub> micro-fabricated catalysts increased the activity at low temperature and modified the selectivity [21]. The few groups who studied the butadiene hydrogenation over well-defined surfaces [22–26] have emphasized the crucial importance of parameters such as metal identity, crystalline orientation and alloy surface morphology on the reaction activity and selectivity.

The first part of this paper concerns the preparation and characterization of the Pd<sub>70</sub>Au<sub>30</sub> (111) and (110) surfaces under ultra-high vacuum (UHV). The second part presents a kinetic study of the butadiene hydrogenation reaction over Pd<sub>70</sub>Au<sub>30</sub> (111), Pd<sub>70</sub>Au<sub>30</sub> (110) and Pd(111). The measurements were performed at an initial pressure of 5.5 Torr (C<sub>4</sub>H<sub>6</sub>:H<sub>2</sub> = 1:10) at room temperature (RT) in a new reaction apparatus, presented in the experimental section. In the third part of this paper, we discuss the most striking results, i.e. the effect of gold and surface orientation on selectivity, and the impact of hydrogen absorption.

## 2. Experimental

### 2.1. Sample preparation and AES/LEED

Standard preparation and characterization of the surfaces was performed in a UHV system (base pressure  $3 \times 10^{-10}$  Torr) composed of two chambers separated by a gate valve. The preparation chamber is equipped with an airlock for rapid sample introduction, an argon ion gun for surface sputtering, an infrared lamp for sample annealing up to 1000 °C and a retractable K-type thermocouple for direct temperature measurement at the sample surface. Samples are supported by stainless steel VG<sup>TM</sup>-type “stubs”, which allow easy manipulation inside the system, toward the reactor (see Section 2.3) and toward external techniques without exposure to air. The analysis chamber contains

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