

# A comparative study of the adsorption and hydrogenation of acrolein on Pt(111), Ni(111) film and Pt–Ni–Pt(111) bimetallic surfaces

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## Abstract

In this study we have investigated the reaction pathways for the decomposition and hydrogenation of acrolein ( $\text{CH}_2=\text{CH}-\text{CH}=\text{O}$ ) on Ni/Pt(111) surfaces under ultra-high vacuum (UHV) conditions using temperature programmed desorption (TPD) and high-resolution electron energy loss spectroscopy (HREELS). While gas-phase hydrogenation products are not observed from clean Pt(111), the subsurface Pt–Ni–Pt(111), with Ni residing below the first layer of Pt, is active for the self-hydrogenation of the C=O bond to produce unsaturated alcohol (2-propenol) and the C=C bond to produce saturated aldehyde (propanal), with the latter being the main hydrogenation product without the consecutive hydrogenation to saturated alcohol. For a thick Ni(111) film prepared on Pt(111), the self-hydrogenation yields for both products are lower than that from the Pt–Ni–Pt(111) surface. The presence of pre-adsorbed hydrogen further enhances the selectivity toward C=O bond hydrogenation on the Pt–Ni–Pt(111) surface. In addition, HREELS studies of the adsorption of the two hydrogenation products, 2-propenol and propanal, are performed on the Pt–Ni–Pt(111) surface to identify the possible surface intermediates during the reaction of acrolein. The results presented here indicate that the hydrogenation activity and selectivity of acrolein on Pt(111) can be significantly modified by the formation of the bimetallic surfaces.

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## 1. Introduction

Bimetallic surfaces often show novel properties that are not present on either of the parent metal surface [1–4]. Our group has recently investigated the electronic and chemical properties of model bimetallic surfaces, using a combination of experimental studies and density functional theory (DFT) calculations to gain insights into the effects of bimetallic formation [5–8]. For example, we have utilized the hydrogenation of cyclohexene [5,9–11], 1-hexene [12] and 1-butene [12] to demonstrate the novel low-temperature hydrogenation activities on Pt-based bimetallic surfaces. In this study we use the hydrogenation of acrolein ( $\text{CH}_2=\text{CH}-\text{CH}=\text{O}$ ) as a probe reaction on Pt(111),

Ni(111) film, and Pt–Ni–Pt(111) to determine how the formation of the bimetallic surface affects the hydrogenation activity and selectivity of organic molecules containing multiple unsaturated functional groups.

Studies of the selective hydrogenation of unsaturated aldehydes, such as  $\alpha,\beta$ -unsaturated aldehydes, have been of growing interest for the production of fine chemicals and pharmaceutical precursors. Most of these studies have been carried out on supported group VIII transition metal catalysts by exploring the influence of different factors that promote the formation of the desirable unsaturated alcohols [13]. Some of those factors are: the nature of the support that influences the metal-support interaction [14,15], the electronic and steric effects of the support [16], the particle size distribution [17,18], and the impact of adding a second metal to make bimetallic alloys [19–24], among others.

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Comparing to monometallic surfaces, bimetallic surfaces have shown promise due to their better selectivity toward the hydrogenation of the C=O bond of some  $\alpha,\beta$ -unsaturated aldehydes. Koel et al. have studied the hydrogenation of crotonaldehyde (methyl substituted acrolein at the  $\beta$  carbon) on Sn/Pt(111). They found that the hydrogenation activity was enhanced on the bimetallic Sn/Pt(111) surfaces in comparison with Pt(111) by using a batch reactor at relative low pressures [25]. Beccat et al. observed an enhancement on the selectivity of crotonaldehyde and methylcrotonaldehyde toward the corresponding unsaturated alcohols on Pt<sub>80</sub>Fe<sub>20</sub>(111) surfaces [26]. The enhancement in the selectivity to C=O hydrogenation was attributed to alloy formation in the case of crotonaldehyde. However, the effect on the selectivity toward the corresponding unsaturated alcohol was found to be higher by the addition of a methyl group in methylcrotonaldehyde than that induced by alloy formation. Thermal activation of crotonaldehyde using temperature programmed desorption (TPD) was performed by Zaera and de Jesus [27] on Pt(111). The main reaction pathway was decarbonylation leading to the production of CO and propene.

The hydrogenation of acrolein, which is the smallest  $\alpha,\beta$ -unsaturated aldehyde, is an important probe reaction for the understanding of factors that govern the selectivity toward the corresponding unsaturated alcohol. As illustrated in Scheme 1, the hydrogenation of the C=O bond of acrolein leads to the formation of the desirable unsaturated alcohol (2-propenol), while the hydrogenation of the C=C bonds results in the formation of the undesirable saturated aldehyde (propanal). Both products can undergo further hydrogenation to produce the saturated alcohol (1-propanol). Single crystal studies of acrolein reaction pathways have provided insights into the adsorption mechanisms for the activation of either C=C or C=O bond. Studies of thermal activation of acrolein on Pt(111) [27], Rh(111) [28], and Pd(110) [29] have shown that decomposition pathways toward the formation of CO and H<sub>2</sub> occur simultaneously with the formation of small hydrocarbon molecules, such as ethane and ethylene. The formation of both ketene and propene was also reported by Zaera and de Jesus on the Pt(111) surface [27,30]. However, on Pd(111) the formation of propanal from acrolein was reported [31]. High-resolution electron energy loss spectroscopy (HREELS) showed that at low temperature

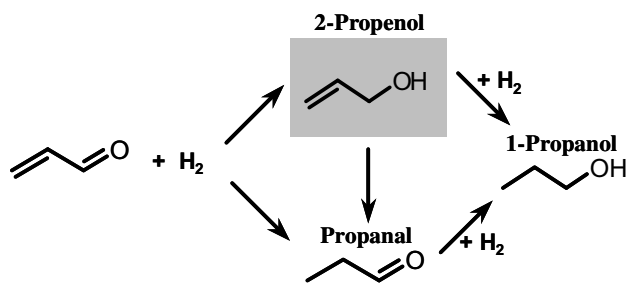
(<170 K) acrolein was bound to both Rh(111) and Pd(111) in an  $\eta^2(\text{C},\text{O})$  configuration, which was strongly rehybridized to an  $\eta^4(\text{C},\text{C},\text{C},\text{O})$ -bound species upon heating the substrate to  $\sim 200$  K [28,31]. The self-hydrogenation of acrolein to propanal on Pd(111) was explained in terms of a C=C interaction with the substrate [31].

Recent studies have attempted to explain the absorption configurations of acrolein on different single crystals and surface alloys by using theoretical approaches and/or in combination with HREELS experiments [32–37]. Specifically, Loffreda et al. reported coverage dependence in the adsorption modes of acrolein on Pt(111) using DFT and HREELS [37]. Two configurations were found to be dominant at low coverages (up to 0.15 ML) on Pt(111), a flat  $\eta^4$ -trans and a  $\eta^3$ -cis configuration. On the other hand, at higher coverages (0.20 and 0.25 ML),  $\eta^2$ -cis and -trans configurations through the C=C bond were found to be more stable. These authors also confirmed HREEL spectra simulations of the different vibrational modes in the most stable configurations with experimental HREEL spectra at different coverages. In the current work we have focused on the high coverage region, where the  $\eta^2$ -bonding via the C=C bond of acrolein was considered to be the stable configuration. Loffreda et al. also reported that the hydrogenation of C=O bond of acrolein occurs on Pt(111). However, the desorption step of the saturated aldehyde was favored over that of the unsaturated alcohol, making the net selectivity higher for the gas phase desorption of mainly the saturated aldehyde under catalytic conditions [38,39].

In a recent publication we reported the selective hydrogenation of acrolein on two types of bimetallic surfaces, Ni–Pt–Pt(111) with Ni atoms occupying the top-most surface and Pt–Ni–Pt(111) with Ni atoms occupying the subsurface region [40]. Experimental results and DFT calculations from that study indicated that the hydrogenation of acrolein by the co-adsorbed H atoms occurred on the subsurface Pt–Ni–Pt(111) structure but not on surface Ni–Pt–Pt(111) [40]. In the current study we focused on the comparison of the adsorption and hydrogenation of acrolein on Pt(111) and Ni(111) film to further demonstrate the unique hydrogenation pathways on the Pt–Ni–Pt(111) bimetallic surface. Finally, we also investigated the adsorption of the two main hydrogenation products, 2-propenol and propanal, on the Pt–Ni–Pt(111) surface to further understand the hydrogenation pathways of acrolein on the bimetallic surface.

## 2. Experimental

Two UHV chambers were used in the current study. The TPD experiments were performed in a two-level stainless steel UHV chamber with a base pressure less than  $1 \times 10^{-10}$  Torr. This chamber is equipped with an Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), and a quadrupole mass spectrometer (QMS) for the TPD measurements. The Pt(111) single crystal (Metal Crystals and Oxides, Ltd., Cambridge),



Scheme 1. Hydrogenation pathways of acrolein.

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