The Adsorption of Ethylene on Au/Pd(100) Alloy Surfaces

Zhenjun Li, Theodore Thuening and Wilfred T. Tysoe*

Department of Chemistry and Laboratory for Surface Studies, University of Wisconsin-Milwaukee, Milwaukee, WI 53211, USA

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Abstract

The surface chemistry of ethylene is explored on model Au/Pd(100) alloy surfaces using a combination of temperature-programmed desorption and reflection-absorption infrared spectroscopy. The heat of adsorption of ethylene on the model alloy surface is found to increase monotonically with increasing palladium coverage in the alloy, from ~33 kJ/mol for a completely gold-covered surface to ~80 kJ/mol as the gold coverage decreases to zero. A large change in heat of adsorption is found for palladium coverages between 0 and ~0.35 monolayers, where previous studies have shown that the surface comprises exclusively isolated palladium sites. The heat of adsorption changes more slowly for higher palladium coverages, when palladium-palladium bridge sites appear. Vinyl species are identified for palladium coverages above ~0.8 ML from a vibrational mode at $\sim 1120\text{ cm}^{-1}$, which disappears when the sample is heated to ~250 K, due to vinyl decomposition.

Keywords: Infrared absorption spectroscopy, temperature-programmed desorption, chemisorption, palladium gold alloy, ethylene

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* Author to whom correspondence should be addressed

Phone: (414) 229-5222
FAX: (414) 229-5036
E-mail: wtt@uwm.edu

Introduction

The Lambert group carried out much of the early work on small hydrocarbons on Pd(111) surfaces focusing on ethylene [1, 2] adsorption and the cyclotrimerization of acetylene to benzene [3-6]. This work, along with Lambert's early studies showing the formation of acetate species from acetic acid on Pd(111) [7] formed the basis for exploring the mechanism of palladium-catalyzed coupling between ethylene and acetic acid to form vinyl acetate monomer (VAM) on a Pd(111) model catalyst surface. It was demonstrated that the reaction proceeds *via* a pathway first proposed by Samanos [8] in which ethylene reacts with adsorbed acetate species to form an acetoxyethyl-palladium intermediate, which yields VAM *via* a β -hydride elimination reaction [9, 10].

This reaction is catalyzed both by supported palladium and palladium-gold alloys, where alloying with gold leads to a substantial increase in selectivity from ~85% for pure palladium to approximately 92% for the alloy. Catalytic studies on model gold-palladium alloys showed that Au-Pd(100) alloys were the most active and proposed that the active ensemble consists of two gold atoms located at diagonally opposite corners of the square unit cell located on a (100) surface [11-14].

The reaction was found to also proceed *via* the Samanos pathway on Au/Pd(111) alloys, where a combination of electronic, ensemble and coverage effects were found to change the rate-limiting step in the surface reaction pathway [15, 16]. Ethylidyne forms on Pd(111) as the reaction proceeds [17] to maintain a crowded surface that inhibits product decomposition, thereby increasing reaction selectivity. Ethylidyne forms on Pd(111) *via* an intermediate vinyl species [18] and is stabilized by the availability of three-fold sites on the surface [19]. These become less prevalent on Au/Pd(111) alloys as the gold coverage increases; here product

decomposition is inhibited by the alloy. Ethylene adsorption has been studied on clean Pd(100) [20, 21]. In this case, both π - and di- σ -bonded ethylene were found at low temperatures, and the π -bonded form desorbs between 100 and 300 K and the di- σ form has a σ - π parameter of 0.78 [22], where a σ - π parameter of zero indicates an ethylenic species with sp^2 -hybridized carbons, and a σ - π parameter of unity indicates the presence of an ethane-like species with sp^3 -hybridized carbon atoms. This work also suggested that a vinyl intermediate was stabilized, its conversion to ethylidyne being prevented by the absence of three-fold hollow sites on Pd(111). This observation is of particular relevance to VAM synthesis since an alternative pathway suggested by Moiseev [23, 24] proposes that VAM is formed by a direct coupling between vinyl and acetate species.

Accordingly, the surface chemistry of ethylene is studied here on Au/Pd(100) alloys. In addition, it has been shown that alloying palladium with coinage metals, for example gold, results in an enhanced hydrogenation activity and selectivity [25] and has been investigated theoretically using density functional theory (DFT) calculations [26, 27].

The surface chemistry of ethylene has been investigated previously on Au-Pd(111) alloys [28] where it was found that, for gold coverages greater than ~ 0.7 monolayer (ML), ethylene adsorbs with a heat of adsorption less than 55 kJ/mol. At gold coverages between ~ 0.5 and ~ 0.7 ML, ethylene adsorbs on palladium sites in a π -bonded configuration desorbing with an activation energy between ~ 57 and 62 kJ/mol. Varying the gold coverage in the alloy results in an almost linear increase in the ethylene desorption activation energy with increasing palladium coverage, eventually reaching a value of ~ 76 kJ/mol, close to that found on ethylene on clean Pd(111).

The distribution of gold and palladium on the surface of Au/Pd(100) alloys is quite

different from the (111) alloy surfaces. In the latter case, it was found that only nearest-neighbor interactions between the gold and palladium on the surface were important, leading to an almost random distribution on the surface but with a somewhat higher concentration of isolated palladium atoms than expected for a completely random distribution [29]. In contrast, much longer-range interactions (up to third-nearest neighbors) were found on Au/Pd(100) model alloys, resulting in the formation of ordered LEED patterns [30]. It was found for low gold coverages that the surface contained mostly Pd-Pd bridge sites as expected. As the gold coverage increased, the coverage of bridge sites became vanishingly small for gold coverages lower than ~ 0.5 ML, where the surface comprised predominantly isolated palladium atoms with only gold nearest neighbors.

Experimental Methods

The apparatus used to collect reflection absorption infrared spectra (RAIRS) and temperature-programmed desorption (TPD) data has been described in detail elsewhere [31]. Infrared spectra were collected with a Bruker Equinox spectrometer, typically for 1000 scans at a resolution of 4 cm^{-1} . TPD data were collected using a Dichor quadrupole mass spectrometer interfaced to a computer that allowed up to five masses to be monitored in a single experiment. The sample could be cooled to 80 K by thermal contact to a liquid-nitrogen-filled reservoir and resistively heated to ~ 1200 K.

The Pd(100) single crystal was cleaned using a standard protocol and its cleanliness monitored using Auger spectroscopy and TPD collected following oxygen adsorption [32]. Gold was evaporated from a small alumina tube [33], which enabled controlled and reproducible evaporation rates to be achieved. In order to precisely control the temperature of the gold, and

therefore its evaporation rate, a C-type thermocouple was placed into the gold pellet. The amount of gold deposited onto the surface was monitored using Auger spectroscopy from the peak-to-peak intensities of the Au NVV and Pd MNN Auger features and the monolayer coverage was gauged from breaks in the gold uptake signal. The gold palladium alloy was formed according to a recipe developed by Lambert *et al.* [6] on Pd(111) surfaces by initially adsorbing four monolayers of gold, then annealing to various temperatures for a period of five minutes in ultrahigh vacuum to produce the desired Au/Pd atomic ratio on the surface. The ethylene (Matheson, Research Grade) was transferred to glass bottles which were attached to the gas-handling line for introduction into the vacuum chamber.

Results

TPD data were collected at a heating rate of 3.7 K/s as a function of ethylene exposure to various Au/Pd(100) alloy surfaces and the ethylene was dosed from a capillary source to minimize the rise in background pressure. Exposures are quoted in Langmuirs ($1 \text{ L} = 1 \times 10^{-6} \text{ Torr s}$) where the dosing source pressure-enhancement factor was calibrated by comparing coverages obtained from the source and by back-filling the chamber with ethylene. Exposures are not corrected for ionization gauge sensitivity.

Figure 1 displays a series of 27 amu (ethylene) desorption profiles as a function of ethylene exposure for some selected alloys with gold coverages of 0.68 (Fig. 1(a)), 0.57 (Fig. 1(b)), 0.24 (Fig. 1(c)) and 0.05 (Fig. 1(d)) ML. When the palladium coverage is relatively low ($\Theta_{\text{Pd}} = 0.32 \text{ ML}$, Fig. 1(a)), the desorption profile consists of a small feature centered at $\sim 258 \text{ K}$ and a larger feature that grows with increasing ethylene exposure and shifts from a peak desorption temperature of $\sim 150 \text{ K}$ at low coverages to lower temperature as the coverage

increases. The shape of the profile at the largest ethylene exposures suggests that it is due to the trailing edge of a peak below the adsorption temperature (~ 80 K). This indicates that the small, high-temperature (~ 258 K) peak is due to ethylene adsorbed on palladium sites, while the low-temperature feature is due to adsorption on gold sites. Reducing the gold coverage to 0.57 ML results in an increase in the ethylene yield in the high-temperature state (Fig. 1(b)) and a decrease in the population of the low-temperature state, consistent with the high-temperature desorption state being due to adsorption on palladium sites. The peak temperature of the high-temperature desorption states decreases from ~ 290 K at low coverages to ~ 260 K at saturation, indicative of repulsive lateral interactions between adsorbed ethylene molecules. A lower-temperature state grows at ~ 130 K after an ethylene exposure of ~ 4 L, decreasing to lower temperatures as the exposure increases further.

This trend continues when the gold coverage is reduced to ~ 0.24 ML (Fig. 1(c)) where the high-temperature feature increases in intensity and shifts to ~ 287 K at saturation. The desorption spectrum found with only 0.05 ML of gold (Fig. 1(d)) has a high-temperature desorption feature at ~ 280 K at saturation and a broad, lower-temperature feature.

In order to explore the most stable ethylene adsorption sites on Au/Pd(100) alloys in greater detail, various alloy surface were dosed with low exposure (0.25 L) of ethylene and the resulting 27 amu desorption profiles are displayed in Fig. 2. This shows that, for very low palladium coverages, ethylene adsorbs weakly at gold sites and desorbs at ~ 133 K. As the gold coverage decreases, there is a significant increase in desorption temperature up to a gold coverage of ~ 0.24 ML, after which the peak temperature remains constant at ~ 311 K for lower gold coverages. The heat of adsorption is estimated from the desorption activation energy using the Redhead equation [34] using the experimental heating rate (3.7 K/s) and assuming a standard

pre-exponential factor of $1 \times 10^{13} \text{ s}^{-1}$. The results are displayed in Fig. 3 as a function of palladium coverage in the alloy ($\blacktriangle$), which shows a rather smooth increase in heat of adsorption from $\sim 33 \text{ kJ/mol}$ for the completely gold-covered surface ($\Theta_{\text{Pd}} = 0$) to a value of $\sim 80 \text{ kJ/mol}$ when the gold coverage decreases to $\sim 0.4 \text{ ML}$ ($\Theta_{\text{Pd}} = 0.6$), and then remains rather constant at higher palladium coverages. This curve also plots the coverages of Pd-Pd bridge ($\bullet$) and isolated Pd ($\blacksquare$) sites on the Au/Pd(100) alloy surface obtained using Monte Carlo simulations [30]. This indicates that the desorption activation energy remains constant at $\sim 80 \text{ kJ/mol}$ when palladium bridge sites are present on the surface and decreases as isolated palladium sites appear.

The infrared spectra for saturated ethylene overlayer on various Au/Pd(100) alloys (obtained using ethylene doses of 10 or 12 L) are displayed in Figs. 4 and 5 as a function of annealing temperature. The spectra were measured immediately after dosing at 80 K and then after heating to the indicating temperature for a period of 10 s. The spectra were collected at a sample temperature of 80 K.

Fig. 4(a) shows the infrared spectrum of ethylene adsorbed on a gold-saturated surface, which displays features at 957 and 3075 cm^{-1} immediately following ethylene adsorption at 80 K. The 957 cm^{-1} peak is assigned to a CH_2 wagging mode while that at 3075 cm^{-1} is due to a CH stretch. The latter mode should not be infrared allowed if the molecular plane of ethylene lies parallel to the surface [35] and suggests the formation of some second-layer ethylene at 80 K. Heating to $\sim 115 \text{ K}$ yields a single peak at $\sim 957 \text{ cm}^{-1}$ and a similar feature is found on a gold-saturated Au/Pd(111) alloy [28]. This feature is substantially attenuated by heating to $\sim 180 \text{ K}$ and disappears on annealing above $\sim 180 \text{ K}$ in accord with the TPD data (Fig.2).

Similar results are obtained at slightly lower gold coverages ($\Theta_{\text{Au}} = 0.8 \text{ ML}$, Fig. 4(b)) where second-layer ethylene desorbs on heating to $\sim 116 \text{ K}$ and a sharp peak remains at $\sim 953 \text{ cm}^{-1}$.

¹ but which persists to slightly higher temperature (>230 K). This trend continues for a gold coverage of 0.68 ML (Fig. 4(c)) where a $\sim 953\text{ cm}^{-1}$ mode persists on heating to $\sim 253\text{ K}$ and only completely disappears on heating to higher temperatures. This is in accord with the TPD data that shows that ethylene desorbs at $\sim 191\text{ K}$ for a gold coverage of 0.81 ML and increases to 257 K when the gold coverage decreases to 0.67 ML (Fig. 2). The desorption profiles for an alloy with 0.68 ML of gold as a function of ethylene coverage (Fig. 1(a)) exhibit the most-intense desorption state at $\sim 150\text{ K}$, with a broad tail extending to higher temperatures. This is consistent with the change in infrared intensity with temperature seen in Fig. 4(c). The number of isolated palladium atoms (completely surrounded by gold) on the Au/Pd(100) alloy reaches its maximum at this gold coverage, but has no Pd–Pd bridge sites (Fig. 3) [36].

Bridge sites appear on an alloy with a gold coverage of 0.57 ML, which causes significant changes to the infrared spectrum (Fig. 4(d)) and TPD (Fig. 1(b)). Weakly adsorbed ethylene (at $\sim 953\text{ cm}^{-1}$) desorbs by $\sim 180\text{ K}$, corresponding to the low-temperature peak in TPD (Fig. 1(b)), resulting in the appearance of a feature at $\sim 922\text{ cm}^{-1}$, which persists at 253 K and is associated with an intense, high-temperature ($\sim 260\text{ K}$) desorption state (Fig. 1(b)).

Similar infrared spectra appear when the alloy gold coverage is 0.4 ML (Fig. 5(a)) where the isolated palladium site coverage has decreased considerably (Fig. 3) yielding vibrational modes at 942 and 906 cm^{-1} . The 942 cm^{-1} peak disappears on heating to $\sim 200\text{ K}$, while the $\sim 906\text{ cm}^{-1}$ feature persist at 257 K .

As the gold coverage is reduced to 0.24 ML, and only Pd–Pd bridge sites are present on the surface (Fig. 3), the infrared spectrum (Fig. 5(b)) consists of a relatively broad feature at $\sim 904\text{ cm}^{-1}$ that is still present on heating to $\sim 264\text{ K}$ and the corresponding desorption profile (Fig. 1(c)) displays a broad, low-temperature feature and a desorption peak centered at $\sim 287\text{ K}$

consistent with the continued presence of the $\sim 904\text{ cm}^{-1}$ infrared feature when heating to $\sim 264\text{ K}$.

The desorption profiles change little as the gold coverage decreases further (Fig. 1(d)), while the infrared spectra change considerably. At a gold coverage of 0.13 ML (Fig. 5(c)), a new feature appears at $\sim 1119\text{ cm}^{-1}$ along with an intense peak at $\sim 896\text{ cm}^{-1}$. The $\sim 1119\text{ cm}^{-1}$ peak disappears on heating to 264 K, yielding a spectrum with a single feature at $\sim 904\text{ cm}^{-1}$. A similar spectral evolution is seen for a gold coverage of 0.05 ML (Fig. 5(d)), where the spectrum has peaks at 1120 and 896 cm^{-1} . The 1120 cm^{-1} feature disappears on heating to 264 K. The $\sim 896\text{ cm}^{-1}$ feature becomes narrower on heating and shifts to $\sim 906\text{ cm}^{-1}$. Similar frequencies are found for ethylene on clean Pd(100) using high-resolution electron energy loss spectroscopy (HREELS) at 1135 and 920 cm^{-1} [8].

Discussion

The general trends observed for ethylene adsorbed on Au/Pd(100) alloys are similar to those found on Au/Pd(111) alloys [28] where decreasing the gold coverage in the alloy substantially increases the heat of ethylene adsorption and is accompanied by a continuous increase in σ - π parameter as the palladium coverage varies from close to zero (with a σ - π parameter ~ 0.08) to close to unity (with a σ - π parameter ~ 0.8) (Figs. 2 and 3). The infrared spectra of ethylene on Au/Pd(100) alloys at the highest gold coverages exhibit a single vibrational mode at $\sim 955\text{ cm}^{-1}$ (Fig. 4 (a) ($\Theta_{\text{Au}} = 1.0\text{ ML}$), (b) ($\Theta_{\text{Au}} = 0.8\text{ ML}$), (c) $\Theta_{\text{Au}} = 0.68\text{ ML}$), close to the CH_2 wagging mode frequency found for ethylene on Au(111) [11]. A mode at this frequency has been similarly assigned to ethylene adsorbed on gold sites on Au/Pd(111) alloys [28]. Ethylene desorbs from Au(110) in a broad feature centered at $\sim 150\text{ K}$ when collected using a relatively high heating rate (11 K/s). Data collected at a lower heating rate

(2.35 K/s, closer to the value used in this work) reveal a desorption feature centered at ~120 K, with a broad, higher-temperature tail extending to ~200 K [37] in reasonable agreement with the peak desorption temperatures at the highest gold coverages (Figs. 1 (a)-(c)).

For alloys with larger gold coverages, when only isolated palladium sites are present, for Θ_{Pd} from 0 to ~0.35 ML (Θ_{Au} from 1 to ~0.65 ML), ethylene exhibits a vibrational frequency of ~953 cm^{-1} and the desorption activation energy increases from ~33 to 65 kJ/mol (Fig. 3). The vibrational frequency indicates that the ethylene is π -bonded with a low σ - π parameter, which is similar for ethylene adsorbed on gold and isolated palladium sites.

Previous DFT calculations by Ge and Neurock found that the bridge site was the most stable for ethylene on Pd(100) with a heat of adsorption of ~90 kJ/mol [38]. The species is considerably rehybridized and the CH_2 plane is found to be tilted almost 30° away from the surface plane. Slightly less stable adsorption was found on an atop site (~79 kJ/mol) with the C=C axis oriented along {100} with the CH_2 group tilted at 17° from the surface, in reasonable agreement with the energies measured here (Fig. 3). Work by Bernardo and Gomez found a bridge-site adsorption energy of 81 kJ/mol with a CH_2 group tilted about 35° from the surface [39], close to the results found by Ge [38], but found a much lower atop-site adsorption energy of ~32 kJ/mol with a CH_2 group tilted ~ 19° from the surface plane. More recent work, that also examined ethylene adsorption on Au/Pd(100) alloys, gave a heat of adsorption for bridge sites of 90 kJ/mol and 78 kJ/mol on atop sites [40]. Calculations for π -bonded ethylene on Au/Pd(100) alloy clusters yield a binding energy of ~54 kJ/mol with a tilt angle of ~ 8.4° . Thus, while there is a variation in calculated binding energies for π -bonded ethylene on atop palladium sites, the calculated values are in general agreement with the experimental results (Fig. 3).

In the intermediate coverage regime of Θ_{Pd} from 0.35 to ~0.65 ML (Θ_{Au} from 0.65 to

~ 0.35 ML), the number of isolated palladium sites decreases and the number of Pd–Pd bridge sites increases. This results in an increase in the binding energy of the most strongly bound ethylene from ~ 66 to 80 kJ/mol (Fig. 3). This is accompanied by the appearance of infrared peaks at ~ 953 (Fig. 4(d)) and ~ 942 cm^{-1} (Figure 5(a)), which disappear on heating to ~ 200 K, indicating that they are due to remaining π -bonded ethylene. With a gold coverage of 0.57 ML (Fig. 4(d), an additional feature is also evident at ~ 922 cm^{-1} , which persist on heating to 253 K, and at a gold coverage of 0.4 ML (Fig. 5(a)), the peak initially appears at ~ 908 cm^{-1} and shifts to ~ 918 cm^{-1} , consistent with a decrease in σ - π parameter, suggesting more strongly bound species on Pd–Pd bridge sites.

For gold coverages lower than ~ 0.13 ML ($\Theta_{\text{Pd}} > 0.27$ ML), a new mode appears at ~ 1120 cm^{-1} , along with a peak at ~ 900 cm^{-1} (Figs. 5 (c) and (d)). The low-coverage TDP profile is similar to that found for ethylene on Pd(100) [20], which desorbs in two states at 235 and 295 K (at a heating rate of 15 K/s), similar to the TPD data for an Au/Pd(100) alloy with low gold coverage (Fig. 1(d)). An ethylene vibrational frequency ~ 1120 cm^{-1} is suggestive of the presence of di- σ -bonded ethylene [37] with a σ - π parameter of ~ 0.85 [22], and modes assigned to di- σ -bonded ethylene have been detected at similar frequencies on Ni(111) (1088 cm^{-1} [41]), Ru(100) (1130 cm^{-1} [41]) and Pt(111) (1047 cm^{-1} [42]). These peaks were accompanied by a weaker feature above 1400 cm^{-1} , not observed here. Weak CH_2 stretching modes are also found between 2900 and 2950 cm^{-1} , and a very weak mode is detected at ~ 2912 cm^{-1} when the ~ 1120 cm^{-1} peak is present (Figs. 5 (c) and (d)). The peaks at ~ 1120 and ~ 906 cm^{-1} are clearly associated with different surface species since they disappear at different annealing temperatures; heating causes the ~ 1120 cm^{-1} feature to disappear between ~ 228 and 264 K, while the ~ 906 cm^{-1} peak persists. Further insights into the nature of the surface species giving rise to the ~ 1120 cm^{-1}

¹ mode come from DFT calculations of ethylene and vinyl species on Au/Pd(100) alloys [26]. They yield a binding energy for π -bonded ethylene of ~ 54 kJ/mol, in good agreement with the desorption data (Fig. 3) and the frequencies of the most intense CH₂ wagging modes are at ~ 900 and 922 cm^{-1} (Figs. 4 (d) and 5 (a)). The calculations also find a strongly bound vinyl species (with a binding energy of ~ 184 kJ/mol) on an alloy with non-contiguous palladium atoms surrounded by gold. The calculated vibrational frequencies show that the strongest model has an in-plane rocking frequency of $\sim 1154\text{ cm}^{-1}$, suggesting that the 1120 cm^{-1} mode should be assigned to a vinyl species. A similar frequency ($\sim 1160\text{ cm}^{-1}$) has been reported for vinyl on Ni(100) [43].

It has been suggested that the reactive ensemble on model gold-palladium (100) model vinyl acetate synthesis catalysts comprise neighboring Pd–Pd sites [3]. DFT calculations suggest that vinyl species are stable on a surface containing this ensemble while vibrational frequencies consistent with the presence of vinyl species are detected on alloys with relatively low gold coverages. This raises the possibility that VAM formation could occur on these alloy surface *via* the Moiseev pathway from the direct coupling between vinyl and acetate species. However, the vinyl species decompose below the temperatures at which VAM synthesis is carried out, while adsorbed ethylene is stable, implying the VAM formation on Au/Pd(100) alloys is most likely to occur *via* the Samanos pathway as found on Au/Pd(111) alloys.

Conclusions

The heat of ethylene adsorbed on Au/Pd(100) model alloys increases with the palladium content in the alloy from ~ 33 kJ/mol for a completely gold-covered surface, to ~ 80 kJ/mol as the gold coverage decreases to zero. The most rapid change in adsorption energy, from ~ 33 to ~ 65

kJ/mol, is found for palladium coverages between 0 and ~0.35 monolayers when the surface is covered by isolated palladium sites, with the heat of adsorption varying much more slowly at higher coverages. This is accompanied by an increase in the ethylene σ - π parameter.

A vibrational mode is found at $\sim 1120\text{ cm}^{-1}$ for gold coverages below ~ 0.2 monolayers which is assigned to the formation of vinyl species on the surface. The feature disappears on heating to $\sim 250\text{ K}$ indicating that it has decomposed at this temperature. While the presence of vinyl species suggests that vinyl acetate monomer formation could occur through a Moiseev pathway involving a direct coupling between adsorbed vinyl and acetate species, its decomposition at such low temperatures indicates that it is not sufficiently stable to react, implying the VAM formation on Au/Pd(100) alloys is most likely to proceed *via* a Samanos pathway.

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Figure Captions

Figure 1:

Temperature-programmed desorption spectra for various exposures of ethylene adsorbed at 80 K on Au/Pd(100) alloys with gold coverages of (a) 0.68, (b) 0.57 and (c) 0.24 and (d) 0.05 ML, collected using a heating rate of 3.7 K/s. The ethylene exposures are marked adjacent to the corresponding spectrum.

Figure 2:

Temperature-programmed desorption spectra for 0.25 L of ethylene dosed at 80 K on various Au/Pd(100) alloys where the gold coverage is indicated adjacent to the corresponding desorption trace, collected using a heating rate of 3.7 K/s.

Figure 3:

Plot of the low-coverage desorption activation energy of ethylene on various Au/Pd(100) alloys as a function of the gold coverage, where the desorption activation energies are calculated using the Redhead equation from the data of Fig. 2.

Figure 4:

Reflection-absorption infrared spectra of a 12 L of ethylene on Au/Pd(100) alloys with gold coverages of (a) 1.0, (b) 0.8, (c) 0.68 and (d) 0.57 ML as a function of annealing temperature where the annealing temperatures are marked adjacent to the corresponding spectrum.

Figure 5:

Reflection-absorption infrared spectra of a 10 L of ethylene on Au/Pd(100) alloys with gold coverages of (a) 0.4, (b) 0.24, (c) 0.13 and (d) 0.05 ML as a function of annealing temperature where the annealing temperatures are marked adjacent to the corresponding spectrum.

Li *et al*, Fig. 1

Li *et al*, Fig. 2

Li *et al*, Fig. 3

Li *et al*, Fig. 4

Li *et al*, Fig. 5

Graphical Abstract