

# Spectators Control Selectivity in Surface Chemistry: Acrolein Partial Hydrogenation Over Pd

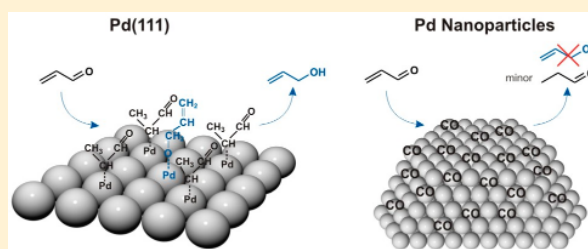
Karl-Heinz Dostert,<sup>†</sup> Casey P. O'Brien,<sup>†</sup> Francisco Ivars-Barcelo,<sup>†</sup> Svetlana Schauermaun,<sup>\*,†,‡</sup> and Hans-Joachim Freund<sup>†</sup>

<sup>†</sup>Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

<sup>‡</sup>Institut für Physikalische Chemie, Christian-Albrechts-Universität zu Kiel, Max-Eyth-Str. 2, 24118 Kiel, Germany

\* Supporting Information

**ABSTRACT:** We present a mechanistic study on selective hydrogenation of acrolein over model Pd surfaces—both single crystal Pd(111) and Pd nanoparticles supported on a model oxide support. We show for the first time that selective hydrogenation of the C=O bond in acrolein to form an unsaturated alcohol is possible over Pd(111) with nearly 100% selectivity. However, this process requires a very distinct modification of the Pd(111) surface with an overlayer of oxopropyl spectator species that are formed from acrolein during the initial stages of reaction and turn the metal surface selective toward propenol formation. By applying pulsed multimolecular beam experiments and *in situ* infrared reflection-absorption spectroscopy, we identified the chemical nature of the spectator and the reactive surface intermediate (propenoxy species) and experimentally followed the simultaneous evolution of the reactive intermediate on the surface and formation of the product in the gas phase.



## INTRODUCTION

Selective partial hydrogenation of multi-unsaturated hydrocarbons, particularly  $\alpha,\beta$ -unsaturated ketones and aldehydes, is of a pivotal importance for numerous applications of heterogeneous catalysis related to fine chemical and pharmaceutical industries. Among the most useful target products in transformations of multi-unsaturated oxygenates are unsaturated alcohols produced by heterogeneous chemoselective hydrogenation of the C=O bond in unsaturated ketones and aldehydes.<sup>1,2</sup> Generally, thermodynamics favors hydrogenation of the C=C bond in these compounds to form the unwanted product, i.e., saturated aldehydes or ketones. Therefore, chemoselective hydrogenation of the C=O bond requires manipulation of kinetic effects by means of a suitable catalyst. This task represents a challenging problem and asks for fundamental studies.

A variety of powdered supported metal catalysts have been already investigated to understand the activity and selectivity of this reaction.<sup>1,2</sup> As key structural parameters controlling the chemoselectivity, a series of ideas conceiving the amount of steric hindrance to adsorption via the C=C bond,<sup>3,4</sup> presence of surface modifiers,<sup>5,6</sup> or alloying with other metals<sup>7</sup> have been put forward. Complementarily, some theoretical work and model studies have been presented in order to understand the chemoselectivity of the underlying elementary processes.<sup>8–14</sup> Despite these efforts, a deep fundamental understanding of this reaction and the parameters governing its activity and selectivity is still missing. Particularly, it remains unclear how the C=O bond is activated on a transition metal surface and

what are the structures of the surface intermediates formed under the reaction conditions. To extract this information on the reaction intermediates would be particularly important for approaching a rational design of new catalytic materials for this class of reactions.

In this article, we present a mechanistic study on selective hydrogenation of the smallest  $\alpha,\beta$ -unsaturated aldehyde acrolein over model Pd surfaces—both single crystal Pd(111) and Pd nanoparticles supported on a planar oxide support—under well-defined ultrahigh-vacuum (UHV) conditions. Previously, acrolein was reported to be hydrogenated almost exclusively on the C=C bond over powdered Pd catalysts forming propanal.<sup>2</sup> In this article, we show for the first time that selective hydrogenation of the C=O bond in acrolein with nearly 100% selectivity is possible over Pd(111). However, this process requires a very distinct modification of the surface with a spectator species that turns the surface selective toward unsaturated alcohol formation. This densely packed overlayer of spectator species is formed from acrolein during the initial stages of surface reaction. By applying a combination of multimolecular beam techniques and *in situ* infrared reflection-absorption spectroscopy (IRAS), we were able to identify the chemical nature of the spectator and the reactive surface intermediate and for the first time experimentally follow the simultaneous evolution of the reactive intermediate on the surface and formation of the product in the gas phase. With this

Received: May 13, 2015

Published: October 20, 2015

study it has been possible to directly identify the reaction intermediate that leads to the formation of the unsaturated alcohol as a final product and obtain atomistic-level insights into the chemoselective hydrogenation chemistry of acrolein. Spectator species were found to play an important role in governing chemoselectivity<sup>15</sup> the observation that might be of great interest for development of new chemo- and enantioselective powdered catalysts such as e.g. ligand-modified nanoparticles.<sup>15,16</sup>

## EXPERIMENTAL SECTION

All experiments were performed at the Fritz-Haber-Institut, Berlin, in a UHV apparatus that has been described in detail previously.<sup>17</sup> Two effusive doubly differentially pumped multichannel array source operated at room temperature were used to supply acrolein and H<sub>2</sub>. Beam intensities of  $4.8 \times 10^{15}$  molecules cm<sup>-2</sup> s<sup>-1</sup> for H<sub>2</sub> and  $0.6 \times 10^{13}$ ,  $1.5 \times 10^{13}$ , or  $4.5 \times 10^{13}$  molecules cm<sup>-2</sup> s<sup>-1</sup> for acrolein (Fluka, 98% purity) were used in these experiments.

The Pd(111) single crystal was cleaned prior to use by repeated cycles of Ar<sup>+</sup> ion bombardment at room temperature, annealing at 1000 K and oxidation in  $1 \times 10^{-6}$  mbar of O<sub>2</sub> at 750 K to remove residual carbon.

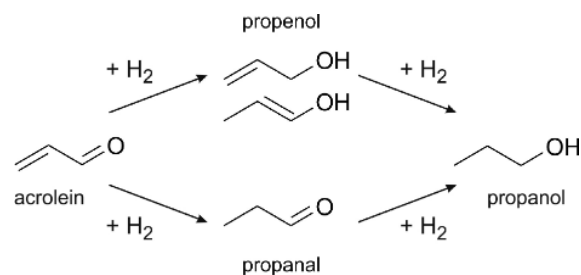
The supported Pd/Fe<sub>3</sub>O<sub>4</sub> model catalyst was prepared as follows: the thin (~100 Å) Fe<sub>3</sub>O<sub>4</sub> film was grown on a Pt(111) single crystal surface by repeated cycles of Fe (>99.99%, Goodfellow) physical vapor deposition and subsequent oxidation.<sup>18,19</sup> Pd particles (>99.9%, Goodfellow) were grown by physical vapor deposition using a commercial evaporator (Focus, EFM3, flux calibrated by a quartz microbalance) while keeping the sample temperature fixed at 115 K. During Pd evaporation the sample was biased to 850 V in order to avoid the creation of defects by metal ions. The final Pd coverage used in these experiments was 7 Å. The resulting surfaces were then annealed to 600 K and stabilized via cycles of oxygen ( $8 \times 10^{-7}$  mbar for 1000 s) and CO ( $8 \times 10^{-7}$  mbar for 3000 s) exposures at 500 K until the Pd particles reached a stable geometry with an average size of 12 nm.<sup>20,21</sup> Residual oxygen was removed by heating in CO ( $1 \times 10^{-6}$  mbar for 300 s) followed by flash-annealing in UHV to 485 K. The STM image of the resulting Pd/Fe<sub>3</sub>O<sub>4</sub>/Pt(111) model catalyst is shown in Figure SI-1 of the Supporting Information. That surface displays Pd particles with an average diameter of 12 nm containing approximately 8100 atoms each and covering the support uniformly with an island density of about  $6 \times 10^{11}$  islands cm<sup>-2</sup>. The majority of the particles are well-shaped crystallites grown in the (111) orientation and are predominantly terminated by (111) facets (~80%), but a small fraction of (100) facets (~20%) are also exposed.

IRAS data were acquired using a vacuum Fourier-transform infrared (FT-IR) spectrometer (Bruker IFS 66v/S) with a spectral resolution of 2 cm<sup>-1</sup> and using a mid-infrared (MIR) polarizer and p-polarized IR light. An automated quadrupole mass spectrometer (QMS) system (ABB Extrel) was employed for the continuous monitoring of the partial pressures of the reactants (acrolein: parent ion at 56 amu; H<sub>2</sub>: at 2 amu) and products (propanal: parent ion and main fragment at 58 amu; propenol: parent ion at 58 amu, main fragment at 57 amu, and further prominent fragment at 31 amu; propanol: parent ion at 60 amu and main fragment at 31 amu).

## RESULTS AND DISCUSSION

Selective partial hydrogenation of acrolein was investigated on two well-defined surfaces prepared *in situ* under UHV conditions: (i) a single crystal Pd(111) and (ii) 12 nm sized Pd nanoparticles supported on a planar model Fe<sub>3</sub>O<sub>4</sub>/Pt(111) oxide support.<sup>20</sup> The catalytic activity of these surfaces was probed under isothermal conditions by using molecular beams<sup>17</sup> with the simultaneous monitoring of the species evolving on the catalytic surface turning over by IRAS. Scheme 1 shows the possible reaction pathways of acrolein hydrogenation.

Scheme 1. Possible Reaction Pathways of Acrolein Hydrogenation



The two investigated catalyst systems were found to show very different selectivity in partial acrolein hydrogenation. Figure 1 shows the formation rates of competing reaction pathways resulting in selective hydrogenation of either the C=C bond to form propanal (Figure 1a,b) or the C=O bond to form the unsaturated alcohol (Figure 1c,d) on both model Pd nanoparticles (left side) and Pd(111) (right side) at different temperatures. For each reported curve, the surface was pre-exposed to a high flux continuous H<sub>2</sub> beam. At time zero the second molecular beam was opened to give a series of acrolein pulses, and the formation rates of reaction products were recorded in the gas phase by quadrupole mass spectrometry. For all investigated catalysts, a short induction period preceded the onset of product formation. On the Pd nanoparticles we observed the only product—propanal—in the first few pulses, after which the reaction rate dropped to zero; no hydrogenation of C=O bond was detected. This behavior is in a good agreement with the results of the earlier studies on powdered Pd catalysts under ambient conditions, showing that essentially only the C=C bond can be hydrogenated.<sup>2,22</sup> In separate experiments carried out on the pristine Fe<sub>3</sub>O<sub>4</sub> support, no hydrogenation of acrolein was detected under identical experimental conditions. Very surprisingly, Pd(111) showed very high catalytic activity toward the desired reaction product—propanol (Figure 1d). The propenol formation rate exhibits clear temperature dependence with a maximum of conversion at 270 K. At this temperature, about 40% of incoming acrolein molecules were converted to propenol. Note that the most likely product of C=O bond hydrogenation is allyl alcohol (H<sub>2</sub>C=CH-CH<sub>2</sub>-OH) and not methyl vinyl alcohol (CH<sub>3</sub>-CH=CH-OH) as the latter one could be transformed to propanal in the gas phase via keto-enol isomerization. Since we do not observe any propanol evolution pattern coinciding with unsaturated alcohol formation, the production of less stable methyl vinyl alcohol is rather unlikely.

To obtain further atomistic-level insight into this catalytic process, we carried out this experiment on the Pd(111) surface using a continuous exposure of both H<sub>2</sub> and acrolein via molecular beams and simultaneously recorded the evolution of the species on the surface turning over by IRAS.

Figure 2a shows the evolution of the gas phase products—propanal and propenol—over Pd(111) with a continuous reactants exposure at 270 K. Specifically, the surface was pre-exposed with H<sub>2</sub>, and then the acrolein beam was switched on at time indicated as zero while the H<sub>2</sub> beam was kept continuously running. Simultaneously, the acquisition of IR spectra started with the time resolution of one spectrum per 45 s. Selected IR spectra are shown in Figure 2b (labeled 1 to 4), which correspond to the time regions 1–4 indicated in Figure 2a. In accordance with the reactivity behavior in a pulsed

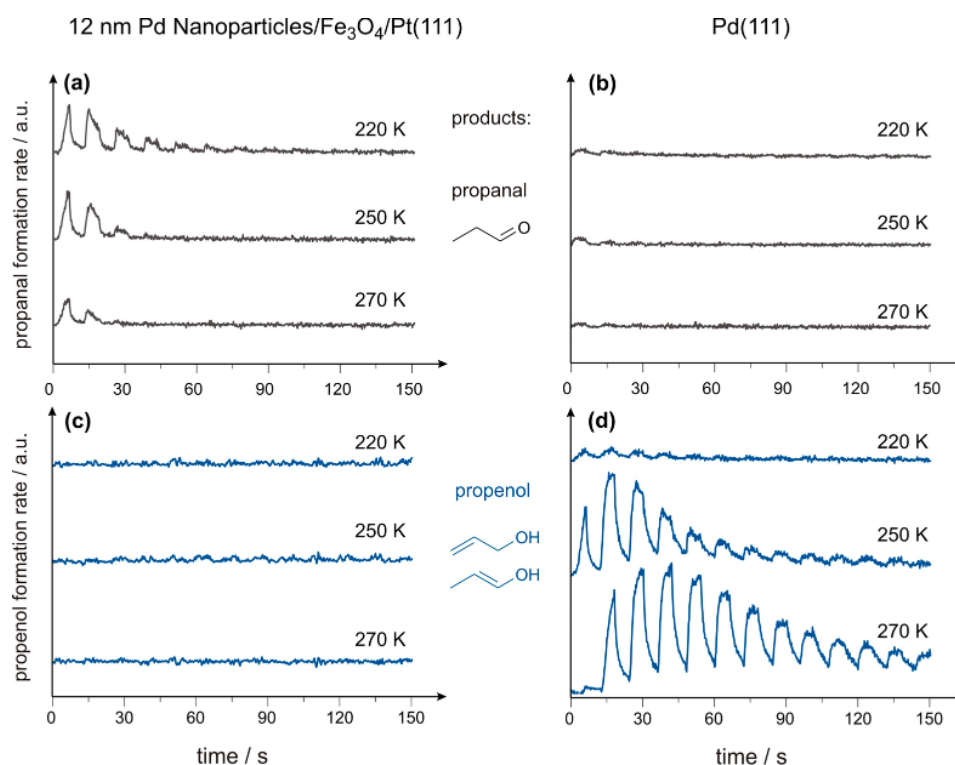


Figure 1. Formation rates of the reaction products□ propanal (upper row) and propenol (lower row)□ on 12 nm sized supported Pd nanoparticle (a, c) and Pd(111) (b, d) during continuous dosing of H<sub>2</sub> and pulsed dosing of acrolein at different temperatures.

experiment (Figure 1d), an onset of the propenol formation rate is observed after an induction period of ~24 s, in which about one acrolein molecule per four Pd atoms on average is irreversibly adsorbed onto the surface. At the end of the induction period the propenol formation rate quickly rises followed by a reactivity decrease after ~95 s. The first three IR spectra (1–3) shown in Figure 2b are obtained during the initial induction period and the period of the maximal activity, while spectrum 4 was collected during the period of decreasing reactivity. The lowest IR spectrum in Figure 2b shows the composition of the surface after its complete deactivation. As a reference for an intact molecule, the IR spectrum of acrolein adsorbed on Pd(111) at 100 K is shown as the uppermost green trace.

Analysis of the IR spectra obtained on the Pd(111) surface under reaction conditions allows us to determine the composition of the active surface turning over and the nature of the reactive intermediate, resulting in formation of propenol. Three major groups of bands corresponding to different surface species can be identified. First, the bands at 1660 and 1755 cm<sup>-1</sup> correspond to the stretching vibration of the C=O bond.<sup>11,12,23</sup> The vibrational band of C=C bond in acrolein (1625 cm<sup>-1</sup>) lies very close to the C=O vibration and appears just as a weak shoulder.<sup>24</sup> While the band at 1660 cm<sup>-1</sup> originates from the adsorbed intact acrolein molecule, in which the C=O bond is still conjugated to the C=C double bond<sup>11,12,23–25</sup> (also see comparison with the uppermost spectrum of intact acrolein), the higher frequency band at 1755 cm<sup>-1</sup> is indicative of the surface species containing the C=O bond not conjugated to the C=C bond anymore.<sup>26,27</sup> The appearance of this vibration under reaction conditions points to the formation of the oxopropyl surface species,

resulting from the partial hydrogenation of acrolein molecule with only one H atom attached to the C=C bond. One of the possible structures of this species is shown in Figure 2b next to the vibrational band at 1755 cm<sup>-1</sup>. The present data do not allow us to make a more precise conclusion on whether the original acrolein molecule was partly hydrogenated on the second or third carbon atom to form this species. Remarkably, this band already appears at very early stages of the reaction, grows in intensity, and remains intense even after the reaction rate recorded in the gas phase vanishes. This observation strongly suggests that this species is not the reaction intermediate leading to the final gas phase product propenol but is merely a spectator (referred in the following as spectator I).

The second prominent band is the very intense vibration at 1120 cm<sup>-1</sup>. Note that this frequency is present neither in adsorbed intact acrolein on Pd (Figure 2b) nor in acrolein ice<sup>11</sup> and therefore cannot be related to any prominent vibration of the molecularly adsorbed acrolein. Further, this band appears only under the reaction conditions: in the presence of H<sub>2</sub> in the temperature range 220–290 K. The most striking observation of this study is that the evolution of this vibrational band shows strong correlation with the evolution of propenol in the gas phase. Indeed, this band starts to appear in the region 1, which comprises the induction period and the region of growing reaction rate (Figure 2a), and then grows in intensity in regions of the highest reactivity 2 and 3. Consecutively, the intensity of this band strongly decreases in region 4 accompanied by the decrease of the propenol formation rate in the gas phase and completely disappears in the lowest spectrum of Figure 2b showing the region of zero reactivity. A few other IR bands in

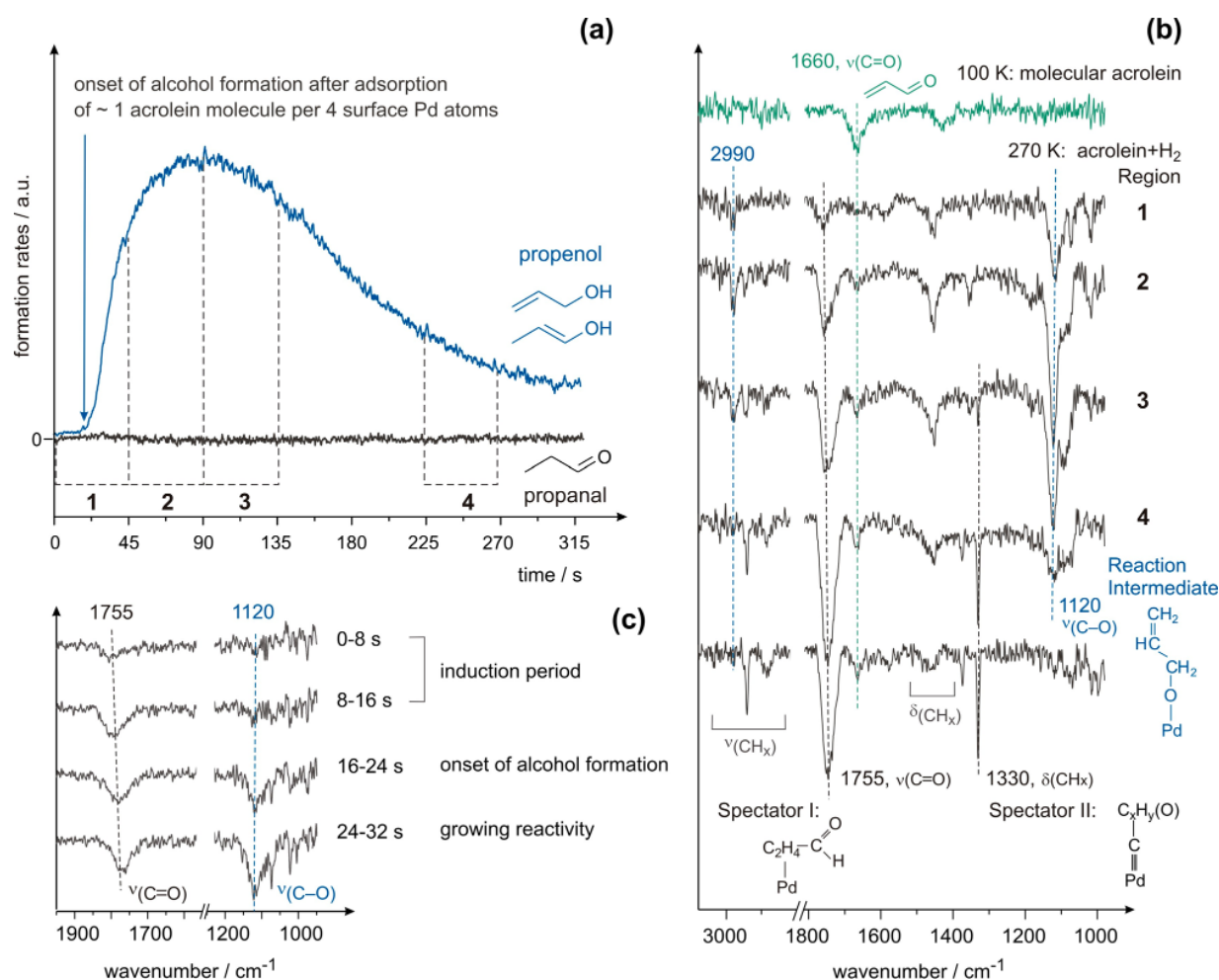


Figure 2. (a) Formation rate of propenol (blue line) and propanal (black line) on Pd(111) at 270 K under continuous exposure of H<sub>2</sub> and acrolein. (b) IR spectra obtained for a monolayer of molecularly adsorbed acrolein at 100 K on pristine Pd(111) (green line) and on Pd surface turning over at 270 K during a continuous exposure to acrolein and H<sub>2</sub>. Spectra 1–4 correspond to the regions 1–4 indicated in (a). The lowest spectrum is obtained after 450 s of acrolein exposure after the propenol formation rate has dropped to zero. (c) IR spectra obtained on Pd(111) surface turning over with higher time resolution during the induction period and period of growing reactivity.

the region of CH<sub>x</sub> stretching and bending vibrations can also be correlated to the gas phase formation rate of propenol.

The observed strong correlation between the gas phase formation rate of propenol and the evolution of the vibrational band at 1120 cm<sup>-1</sup> unambiguously shows that the corresponding surface species is the surface intermediate that is directly involved in the selective hydrogenation of the C=O bond. To the best of our knowledge, this is the first direct experimental observation of such a direct correlation between the evolution of the product in the gas phase and the formation of the corresponding reaction intermediate on the surface obtained under the well-defined and isothermal conditions.

The vibrational range 1050–1200 cm<sup>-1</sup> is typical for the stretching vibration of a single C–O bond in an alkoxy group. Previously, a large class of oxygen coordinated surface adsorbates has been observed in this vibrational region.<sup>28,29</sup> In our case, the most likely species related to the band at 1120 cm<sup>-1</sup> is a propenoxy group CH<sub>2</sub>–CH–O–Pd, in which the C–O entity is attached to Pd through the O atom to form a single C–O–Pd bond. The high intensity of this band, exceeding even the most intense C=O vibration in acrolein

(1660 cm<sup>-1</sup>) and oxopropyl species (1755 cm<sup>-1</sup>; regions 2 and 3, Figure 2b), additionally supports formation of a single C–O bond, which has a large dipole moment that can explain very high IR intensity. The vibrational band at 2990 cm<sup>-1</sup>, which also can be directly correlated to the evolution of propenol in the gas phase, might be indicative of the stretching vibration of the C–H entity, in which C is involved in the C=C double bond,<sup>8</sup> suggesting that the reaction intermediate contains a C=C bond. Please note that the high intensity of the C–O–Pd bond indicates that C–O entity is not lying flat on the surface since otherwise this vibration would be not seeing due to the metal surface selection rule.<sup>30</sup> This consideration also implies that the C=C bond cannot be in the very close proximity to Pd and is most likely is not directly involved into the interaction with the surface.

The most likely reaction intermediate consistent with all observed vibrational signatures is shown in Figure 2b next to the band at 1120 cm<sup>-1</sup>. It contains the C=C bond and is attached to Pd via O forming the C–O–Pd bond. This intermediate can be formed through adsorption of acrolein via the C=O bond and the addition of one H atom at the C next

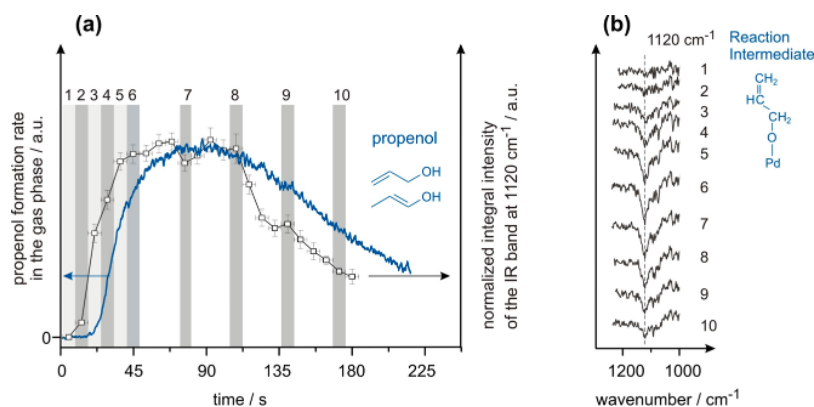


Figure 3. (a) Correlation between the formation rate of propenol in the gas phase (blue line) and the evolution of the integral intensity of the band at  $1120\text{ cm}^{-1}$  related to the surface reaction intermediate (black symbols) measured over Pd(111) at 270 K. (b) The corresponding IR spectra obtained on the Pd(111) surface turning over.

to O. Only one additional step—the insertion of the second H atom into the Pd–O bond—is required to form propenol.

The third prominent band appears at  $1330\text{ cm}^{-1}$  during the period of highest reactivity and steadily grows in intensity, remaining intense even after the complete stop of the reaction. This band was previously related to formation of ethylidyne and ethylidyne-like species.<sup>31</sup> This species can be considered only as the second type of spectator (spectator II) or a surface poison.

IR spectra obtained with  $\sim 6$  times higher time resolution clearly show that the spectator I is formed on the surface prior the onset of formation of the reaction intermediate (Figure 2c). The first two spectra, corresponding to the induction period (0–16 s), directly show that first spectator I (band at  $1755\text{--}1790\text{ cm}^{-1}$ ) is formed followed by formation of the propenoxy reaction intermediate ( $1120\text{ cm}^{-1}$ ) close to the onset of propenol evolution in the gas phase. Figure 3a shows the gas phase formation rate of propenol (blue line) together with the integral intensity of the vibrational band  $1120\text{ cm}^{-1}$  (black squares) of all IR spectra obtained with a high time resolution. The corresponding IR spectra are displayed in Figure 3b. As clearly seen, the integral intensity of the vibrational band  $1120\text{ cm}^{-1}$ , related to the proposed reaction intermediate, directly follows the evolution of the product in the gas phase. This strong correlation between the evolution of the reaction rate in the gas phase and the band at  $1120\text{ cm}^{-1}$  is a clear indication for the interrelation of the gas phase product and the proposed reaction intermediate.

It is important to underline that the surface reaction intermediate is formed not on the clean Pd(111) surface but on the surface strongly modified with spectator I (oxopropyl species). Indeed, about one acrolein molecule per four surface Pd atoms was accumulated on the Pd(111) surface to form a dense overlayer of spectator I species prior to the onset of propenol formation. Most likely, such strong geometrical confinement of an adsorption site for acrolein on the spectator I-covered surface prevents the competing hydrogenation of the C–C bond and allows acrolein to adsorb only via O and to activate the C–O bond. Obviously, the clean Pd surface is not capable of activating the C–O bond toward selective hydrogenation, and the strong modification of the surface by spectator I is required to trigger the desired selective chemistry. Recently, modification of Pd(111) with self-assembled hydrocarbon-based monolayers was reported to result in similar

effects leading to strong enhancement of chemoselectivity of epoxybutene partial hydrogenation.<sup>16</sup>

Potentially, two effects might account for deactivation of the surface after the period of high reactivity. We found that formation of the spectator II—strongly bound ethylidyne-like species (band at  $1330\text{ cm}^{-1}$ )—is correlated with deactivation of the catalytic surface. It might be speculated that it blocks the surface sites that are relevant for the formation of oxopropyl reaction intermediate. Second, dissociative hydrogen adsorption can potentially be inhibited on the surfaces strongly covered with various hydrocarbon species,<sup>32</sup> which might result in decreasing overall hydrogenation activity. However, the latter effect should play rather minor role under the ambient pressure conditions.

It is important to emphasize that a clear-cut conclusion on whether a surface species is a reaction intermediate or not is possible only in case when a direct correlation between the product formation rate in the gas phase and the evolution of this surface species followed by an appropriate surface sensitive technique is observed. It should be also pointed out that spectroscopic differentiation between the reaction intermediate and the spectator species is possible only if (i) the surface process is carried out in such a way that the reaction intermediate follows a different time dependence than the spectator and (ii) a direct correlation between the product formation rate in the gas phase and the evolution of this surface species can be established. Such situation can be achieved e.g. in the transient regime applied in this study, in which the spectators were accumulated on the surface, while the concentration of the reaction intermediate was increasing and then decreasing. This fact allowed us to establish the direct correlation between the time evolution of the gas phase product propenol and the surface reaction intermediate propenoxy group (Figure 3). The more traditional way of carrying out the reaction under the steady state conditions would result in constant concentrations of all surface species and with this prevent their clear assignment to either spectators or a reaction intermediate. To the best of our knowledge, this is the first example in model catalytic studies when such direct correlation between the product formation rate in the gas phase and the evolution of this surface species was observed and with this both requirements discussed above were met.

To understand the absence of selective acrolein hydrogenation to unsaturated alcohol over Pd nanoparticles, we

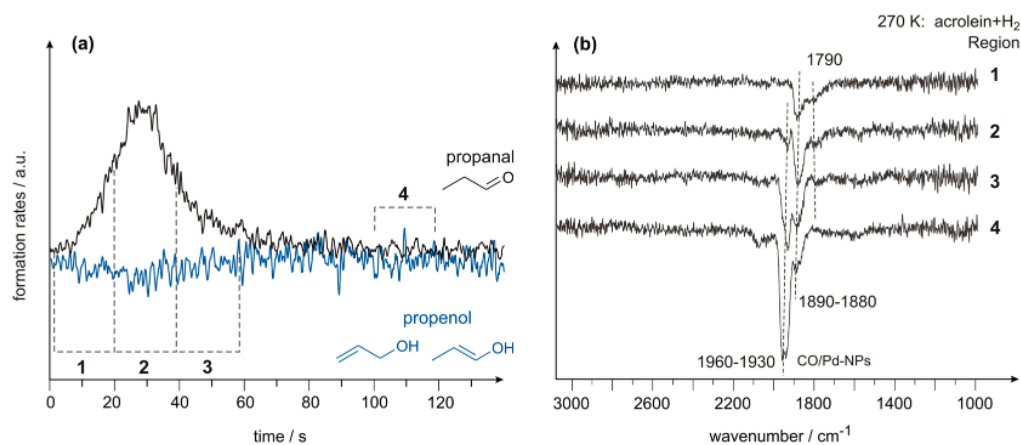


Figure 4. (a) Formation rate of propanol (blue line) and propanal (black line) on 12 nm sized supported Pd nanoparticles at 270 K under continuous exposure of  $H_2$  and acrolein. (b) IR spectra obtained on Pd nanoparticles turning over. Spectra 1–4 correspond to the regions 1–4 indicated in (a).

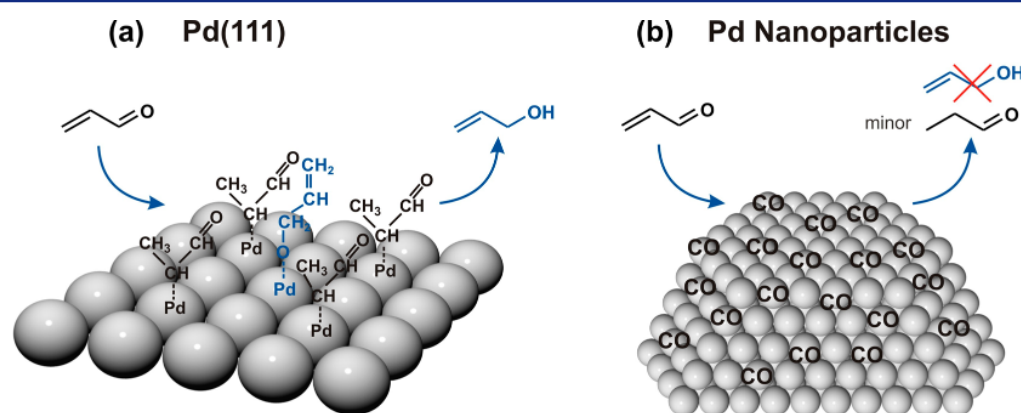


Figure 5. Model of the chemical composition of the surfaces turning over (a) Pd(111) and (b) Pd nanoparticles. On Pd(111), a dense overlayer of spectator (oxopropyl) species is formed at the initial stages of reaction, which allows activation of  $C=O$  double bond and renders the surface chemoselective toward unsaturated alcohol formation. In contrast, on Pd nanoparticles acrolein readily decarbonylates forming CO molecules, which prevent hydrogenation of  $C=O$  bond and result in formation of the undesired product propanal.

carried out an identical spectroscopic investigation on the evolution of surface species during the reaction over oxide supported Pd model catalyst with the simultaneous monitoring the gas phase products. Figure 4a shows the results of these experiments; for a detailed description we refer the reader to the Supporting Information. The IR spectra obtained on the Pd nanoparticles turning over are dominated by the features in the range  $1800\text{--}1960\text{ cm}^{-1}$ , which can be clearly related to an accumulation of CO molecules on the surface. Note that CO cannot desorb from Pd nanoparticles at our low reaction temperatures.<sup>33</sup> This observation suggests that acrolein undergoes decarbonylation on Pd nanoparticles, which was also observed previously on powdered catalysts.<sup>11,12</sup> Thus, the observed behavior strongly suggests that acrolein decomposes on Pd nanoparticles under the reaction conditions forming CO molecules that block the surface and prevent formation of well-ordered spectator I overlayers required for selective acrolein hydrogenation to propanol. Since the Pd clusters are mostly terminated by (111) facets<sup>20</sup> that are not active in acrolein decomposition as observed for Pd(111), most likely edges, corners, (100) facets, and the other low-coordinated surface sites of Pd nanoparticles are responsible for acrolein decarbonylation. Note that these low coordinated surface sites represent

only 20% of the surface sites, while the rest of the surface is (111) facets. Since the entire particle becomes covered by CO in the course of the reaction, strong coupling between the (111) facets and the low coordinated sites by CO surface diffusion must be inferred to explain the observed CO accumulation. Interestingly, not only alcohol formation but also hydrogenation of the  $C=C$  bond, which is generally discussed to be easy even over carbon-containing surfaces, is prevented on the surface covered by CO.

## CONCLUSIONS

Summarizing, the mechanisms of selective partial hydrogenation of acrolein over two model surfaces—Pd(111) and Pd nanoparticles supported on  $Fe_3O_4/Pt(111)$  film—were investigated using a combination of molecular beam techniques with *in situ* IRAS under well-defined UHV conditions. The desired reaction pathway—selective hydrogenation of the  $C=O$  bond in acrolein to form propanol—was observed over Pd(111) surface with nearly 100% selectivity, while only  $C=C$  bond hydrogenation occurred over oxide supported Pd nanoparticles. The selectivity in hydrogenation of the  $C=O$  bond was found to critically depend on the presence of an overlayer of spectator species formed at the initial stages of the

reaction (Figure 5a). Most likely, the spectator, rendering the surface chemoselective, results from the addition of one H atom to the C=C bond of acrolein to form oxopropyl species. After a dense overlayer of the spectator is formed, acrolein adsorbs on this modified surface via the C=O bond and can be selectively hydrogenated to an unsaturated alcohol propenol. The nature of the corresponding surface reaction intermediate was established spectroscopically. By monitoring the surface species during the course of the reaction via IRAS, we were able for the first time to experimentally follow the simultaneous evolution of the reactive intermediate on the surface and formation of the product in the gas phase. With this a direct assignment of one of the surface species to a reaction intermediate was achieved, while the other surface species were identified as spectators. On supported Pd nanoparticles, formation of a spectator overlayer was found to be prevented by strong acrolein decarbonylation, and the surface was observed to be active only for hydrogenation of the C=C bond (Figure 5b).

Obtained atomistic-level insights into chemoselective hydrogenation chemistry of acrolein highlight the exceptional importance of spectator species which are usually formed on the catalytically active surface under reaction conditions. Related effects are expected to play a key role in controlling chemoselectivity in hydrogenation of all types of  $\alpha,\beta$ -unsaturated aldehydes and ketones and hold a great potential for further development of new chemo- and enantioselective powdered catalysts such as e.g. ligand-modified nanoparticles.

## ASSOCIATED CONTENT

### \* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b04363.

Further details on the preparation procedure of supported model catalysts, the scanning tunneling microscopy image of the resulting surface, and more detailed discussion on of the reactivity on Pd nanoparticles (PDF)

## AUTHOR INFORMATION

Corresponding Author

\*E-mail [schauermann@fhi-berlin.mpg.de](mailto:schauermann@fhi-berlin.mpg.de).

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

Support from the European Research Council (ERC Starting Grant ENREMOS, project number 335205) is gratefully acknowledged. S.S. thanks the Fonds der Chemischen Industrie for the Chemiedozentenstipendium.

## REFERENCES

- (1) Gallezot, P.; Richard, D. *Catal. Rev.: Si. Eng.* 1998, 40, 81.
- (2) Maki-Arvela, P.; Hajek, J.; Salmi, T.; Murzin, D. *Y. Appl. Catal., A* 2005, 292, 1.
- (3) Pradier, C. M.; Birchem, T.; Berthier, Y.; Cordier, G. *Catal. Lett.* 1994, 29, 371.
- (4) Birchem, T.; Pradier, C. M.; Berthier, Y.; Cordier, G. *J. Catal.* 1996, 161, 68.
- (5) Marinelli, T. B. L. W.; Nabuurs, S.; Ponec, V. *J. Catal.* 1995, 151, 431.
- (6) Hutchings, G. J.; King, F.; Okoye, I. P.; Padley, M. B.; Rochester, C. H. *J. Catal.* 1994, 148, 453.

- (7) Englisch, M.; Ranade, V. S.; Lercher, J. A. *J. Mol. Catal. A: Chem.* 1997, 121, 69.
- (8) Kliewer, C. J.; Bieri, M.; Somorjai, G. A. *J. Am. Chem. Soc.* 2009, 131, 9958.
- (9) Haubrich, J.; Loffreda, D.; Delbecq, F.; Sautet, P.; Krupski, A.; Becker, C.; Wandelt, K. *J. Phys. Chem. C* 2009, 113, 13947.
- (10) Kennedy, G.; Baker, L. R.; Somorjai, G. A. *Angew. Chem., Int. Ed.* 2014, 53, 3405.
- (11) de Jesús, J. C.; Zaera, F. *Surf. Sci.* 1999, 430, 99.
- (12) Murillo, L. E.; Chen, J. G. *Surf. Sci.* 2008, 602, 919.
- (13) Loffreda, D.; Delbecq, F.; Vigne, F.; Sautet, P. *Angew. Chem., Int. Ed.* 2005, 44, 5279.
- (14) Ide, M. S.; Hao, B.; Neurock, M.; Davis, R. J. *ACS Catal.* 2012, 2, 671.
- (15) Gross, E.; Liu, J. H.-C.; Toste, F. D.; Somorjai, G. A. *Nat. Chem.* 2012, 4, 947.
- (16) Marshall, S. T.; O'Brien, M.; Oetter, B.; Corpuz, A.; Richards, R. M.; Schwartz, D. K.; Medlin, J. W. *Nat. Mater.* 2010, 9, 853.
- (17) Libuda, J.; Meusel, I.; Hartmann, J.; Freund, H.-J. *Rev. Sci. Instrum.* 2000, 71, 4395.
- (18) Weiss, W.; Ranke, W. *Prog. Surf. Sci.* 2002, 70, 1.
- (19) Lemire, C.; Meyer, R.; Henrich, V. E.; Shaikhutdinov, S.; Freund, H. J. *Surf. Sci.* 2004, 572, 103.
- (20) Schalow, T.; Brandt, B.; Starr, D. E.; Laurin, M.; Shaikhutdinov, S. K.; Schauer mann, S.; Libuda, J.; Freund, H. J. *Phys. Chem. Chem. Phys.* 2007, 9, 1347.
- (21) Schalow, T.; Brandt, B.; Starr, D. E.; Laurin, M.; Schauer mann, S.; Shaikhutdinov, S. K.; Libuda, J.; Freund, H. J. *Catal. Lett.* 2006, 107, 189.
- (22) Ponec, V. *Appl. Catal., A* 1997, 149, 27.
- (23) Bournel, F.; Laffon, C.; Parent, P.; Tourillon, G. *Surf. Sci.* 1996, 359, 10.
- (24) Hamada, Y.; Nishimura, Y.; Tsuboi, M. *Chem. Phys.* 1985, 100, 365.
- (25) Akita, M.; Osaka, N.; Itoh, K. *Surf. Sci.* 1998, 405, 172.
- (26) Colthup, N. B.; Daly, L. H.; Wiberley, S. E. In *Introduction to Infrared and Raman Spectroscopy*, 3rd ed.; Colthup, N. B., Daly, L. H., Wiberley, S. E., Eds.; Academic Press: San Diego, CA, 1990; p 289.
- (27) Mecke, B.; Noack, K. *Spectrochim. Acta* 1958, 12, 391.
- (28) Mitchell, W. J.; Xie, J.; Jachimowski, T. A.; Weinberg, W. H. *J. Am. Chem. Soc.* 1995, 117, 2606.
- (29) Weldon, M. K.; Friend, C. M. *Chem. Rev.* 1996, 96, 1391.
- (30) Hoffmann, F. M. *Surf. Sci. Rep.* 1983, 3, 107.
- (31) Zaera, F. *Langmuir* 1996, 12, 88.
- (32) Ludwig, W.; Savara, A.; Brandt, B.; Schauer mann, S. *Phys. Chem. Chem. Phys.* 2011, 13, 966.
- (33) Sandell, A.; Libuda, J.; Bruhwiler, P. A.; Andersson, S.; Maxwell, A. J.; Bäumer, M.; Martensson, N.; Freund, H. J. *J. Vac. Sci. Technol., A* 1996, 14, 1546.