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Article

Hydrogenation of Cinnamaldehyde on Cu(110) Single-Crystal Surfaces

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ABSTRACT: Temperature-programmed desorption experiments in two modalities, namely, using linear temperature ramping (TPD) and under isothermal conditions (IsoTPD), were performed to characterize the chemical reaction between cinnamaldehyde and hydrogen on Cu(110) single-crystal surfaces. It was found that hydrogenation can only take place if atomic hydrogen is used, as reactivity with H_2 was not detectable, and that it occurs selectively at the carbonyl moiety to produce the cinnamyl alcohol, the desired product. That molecule accounts for more than two-thirds of all the products, with the rest corresponding to the more extensively hydrogenated hydrocinnamyl alcohol. Interestingly, the production of hydrocinnamaldehyde (the undesired product) via the hydrogenation of the C═C bond is negligible. The same chemistry was observed on clean and oxygen-pretreated surfaces, indicating that the oxidation state of the Cu atoms may not be significant in determining selectivity for this conversion. Also, both types of experiments, TPD and IsoTPD, led to the same results, an observation that points to a Langmuir−Hinshelwood mechanism between two adsorbed species (the unsaturated aldehyde and atomic hydrogen). These results provide molecular-level confirmation of the intrinsic hydrogenation selectivity of Cu surfaces in single-atom alloy catalysts.

1. INTRODUCTION

One reason platinum-group metals are extensively used in heterogeneous catalysis is because they can easily promote the activation of relevant diatomic molecules. These include O_2, used in many oxidation processes, and, more relevant to this report, H_2, a key reactant in hydrogenation reactions. Hydrogenation catalysis is central to many industrial processes such as oil refining, petrochemical conversions, food processing, and the organic synthesis of pharmaceuticals and other fine chemicals.[1−3] Once the H−H bond is broken on the surface of platinum-group metals and adsorbed atomic H atoms are formed, those can be easily incorporated into the unsaturations (i.e., double and triple bonds) of organic molecules to produce saturated products.

Platinum has proven to be a particularly good general hydrogenation catalyst, and is therefore used extensively in industry for this purpose. As long as the target products are fully saturated molecules, the performance of Pt as a catalyst is hard to beat. However, one limitation with Pt and other related metals such as Rh and Pd is that they are not always very selective: it is difficult to target the hydrogenation of one specific unsaturated bond in molecules with multiple double or triple bonds with these metals.[4] Selectivity is critical in many modern chemical industrial processes, for the production of fine chemicals in particular, because selective catalysts reduce the amount of feedstocks consumed, minimize the need for additional separation and purification steps, and avoid the production of potentially polluting byproducts.[5−9] A commonly cited case where this is the case is the hydrogenation of unsaturated aldehydes, where Pt preferentially promotes the hydrogenation of the C═C bond to produce the saturated aldehyde rather than the C═O bond to yield the more desirable unsaturated alcohol.[10−12]

Several approaches have been tested to improve selectivity in unsaturated aldehyde hydrogenation processes.[10−12] We have, for instance, explored the possibility of increasing unsaturated

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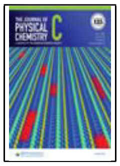

alcohol production via the appropriate selection[13,14] or modification[15,16] of the support, and also by tuning the metal nanoparticle size.[17] One particularly promising way to modify selectivity in hydrogenation processes that has gained great interest in recent years is the use of single-atom alloy (SAA) catalysts, where a highly active minority metal such as Pt is diluted within a matrix of a second majority element such as Cu.[18,19] The premise behind the expected improvement in selectivity with SAAs is that one type of surface sites within the majority Cu metal may selectively promote the H atom incorporation steps into the unsaturations of the organic reactants but may need to be aided by a second type of site, individual Pt atoms highly diluted within the alloy, to promote the initial H_2 activation.

The fact that SAA catalysts can be used to improve selectivity in hydrogenation reactions has been proven with a number of reactants, including phenylacetylene,[20] butadiene,[21] and NO.[22] SAA catalysts have also been successfully tested with unsaturated aldehydes, with both acrolein[23] and cinnamaldehyde.[24,25] However, a full understanding of how these catalysts work is still being developed. A series of beautiful surface-science experiments with model systems and under vacuum conditions have provided support for the basic components of the model mentioned above, in particular the ability of isolated Pt atoms to dissociate H−H bonds and to spillover the resulting H atoms onto the main Cu surface.[26,27] However, we have recently questioned the relevance of some of those observations to catalysis taking place under highly reactive environments, as Cu surfaces are easily oxidized in the presence of even traces of O_2 or water, Pt atoms are quite mobile and can segregate in and out of the surface driven by the adsorbed species, and Cu−Pt alloys display different electronic properties than the pure elements even if one of them (Pt) is highly diluted.[24] Then there is the issue of evaluating and understanding the selectivity of hydrogenation steps on pure Cu surfaces. This is difficult to test directly because Cu catalysts show poor activity (given that they cannot activate H−H bonds). Here we report results from surface-science studies on a model Cu(110) single-crystal surface where the hydrogenation of cinnamaldehyde was performed with H atoms produced in the gas phase to address this issue. Both regular temperature-programmed desorption (TPD) and isothermal (IsoTPD) kinetic experiments indicated that, indeed, Cu surfaces are quite selective toward the hydrogenation of the C═O bond. The differences in hydrogenation selectivity between Pt and Cu are explained by differences in the adsorption geometry of the unsaturated aldehyde[28−30] and by the high activation barrier for the H addition to the C═C bonds on Cu.[24]

2. METHODS

The experiments reported here were all performed in an ultrahigh-vacuum (UHV) apparatus described in previous publications.[31,32] A UTI quadrupole mass spectrometer was used for the TPD and IsoTPD experiments. Up to 15 different masses were monitored in each single TPD or IsoTPD run by using a personal computer interfaced to the mass spectrometer. X-ray photoelectron spectroscopy (XPS) data to certify the cleanliness of the surface were acquired by using a 50 mm radius hemispherical electron energy analyzer (VSW HAC 5000) and an aluminum-anode ($h\nu = 1486.6$ eV) X-ray source. Gas dosing was done by backfilling of the chamber using a leak valve and is reported in langmuirs (1 langmuir = 1×10^{-6} Torr s), uncorrected for differences in ion gauge sensitivities. The pressure in the main UHV chamber was measured by using a nude ion gauge.

A polished Cu single-crystal disk, 10 mm in diameter and 2 mm in thickness and cut to expose a (110) facet, was mounted on a manipulator capable of x−y−z−θ motion and of liquid-nitrogen cooling and resistive heating by wedging it in between thin tantalum wires attached to copper rods, which were in turn connected to the main body of the manipulator. The temperature of the crystal was followed by using a K-type thermocouple wedged into a hole drilled on the side of the crystal and controlled by a homemade proportional-integral-derivative (PID) circuit. A constant heating rate of 4 K/s was used for the TPD experiments. The surface of the crystal was cleaned before each TPD or IsoTPD experiment by sequential cycles of Ar^+ ion sputtering (using a PerkinElmer PHI 04-300 ion gun and an ion energy of 2 kV) and annealing at 1100 K until the surface was deemed free of impurities by XPS and CO TPD. For the experiments on oxidized samples, the surface was exposed to 30 langmuirs of O_2 at 500 K prior to the adsorption of the unsaturated aldehyde. For the regular TPD experiments, the surface was presaturated with atomic hydrogen by flowing H_2 (3×10^{-6} Torr × 300 s) through a hot W filament (resistively heated with 11 V × 14 A ∼ 150 W) placed in front of the Cu(110) crystal, about 5 cm away. Cinnamaldehyde (CMA, Sigma-Aldrich, ≥95% purity) was placed in a glass container, mounted in a gas manifold, distilled via repeated freeze−pump−thaw cycles, and fed into the UHV chamber as a gas, relying on its high vapor pressure; 5000 langmuirs of CMA was dosed at 325 K to ensure monolayer saturation. In the case of the IsoTPD experiments, the CMA-dosed Cu surface was first heated to the reaction temperature, 325 K, and then the W filament was turned on and the reaction was initiated by opening the leak valve used to introduce the H_2 gas ($P = 3 \times 10^{-6}$ Torr).

3. RESULTS

The thermal chemistry of CMA adsorbed on the Cu(110) surface, clean and oxygen-predosed, with hydrogen was explored by both regular TPD and isothermal (IsoTPD) kinetic experiments. Because of the complexity and similarities of the cracking patterns of the mass spectra of the reactants and products involved in the hydrogenation of cinnamaldehyde, the signals for a large range of amu's were followed by carrying out the same experiments several times. Some amu values were used repeatedly to employ them as reference, to compare the results from different runs, and to calibrate and quantitatively scale the results from separate experiments as the resolution and sensitivity parameters of the mass spectrometer needed to be varied to record data within different ranges of amu values (as the detection limit of quadrupole mass spectrometers decreases exponentially with amu). In total, ∼60 amu values were followed, not only to facilitate the deconvolution of the signals into its constituent contributing molecules[33] but also to rule out other possible products such as phenyl-containing (benzene, toluene, ethylbenzene, and styrene) and oxygen-containing (propenal, propenol, and propanol) fragments. It should be noted that in these experiments it was possible to detect the molecular peaks of both the reactant (3-phenylprop-2-enal, or cinnamaldehyde, CMA, 132 amu) and the main hydrogenation products: 3-phenylprop-2-en-1-ol (cinnamyl alcohol, CMO, 134 amu, the desired unsaturated alcohol product), 3-phenylpropanal (hydrocinnamaldehyde, HCMA, 134 amu, a competing and less valuable saturated aldehyde byproduct), and 3-phenyl-1-propanol (hydrocinnamyl alcohol, HCMO, 136 amu, the saturated alcohol resulting from hydrogenation of both C═C and C═O bonds).

Representative raw data from regular TPD experiments with Cu(110) surfaces saturated sequentially with hydrogen atoms and CMA are reported in Figure 1. The focus in that figure is on the high amu values, all the way to 136 amu, to follow the evolution of the CMA hydrogenation products. A low-temperature peak seen around 325 K is likely to come from condensed CMA and is therefore not relevant to the surface chemistry addressed here, but additional CMA molecular desorption is seen at 420 K, as indicated by the prominent peaks in the 51, 77, 78, 91, 103, 115, 116, 131, and 132 amu traces. In addition, the formation of hydrogenation products is clearly evidenced by the signals seen in the 134 and 136 amu traces: the somewhat broader feature seen between 420 and 460 K, the most prominent in the 117 and 118 amu signals, are identified with HCMO, whereas the intermediate peaks around 430 K correspond to a combination of CMO and HCMA. Moreover, the fact that this latter desorption is detected in the 115 amu trace indicates that CMO may be the majority component. Two more general observations can be highlighted at this point: (1) there is no clear evidence of the formation of other products (a small amount of styrene is detected at 540 K in the absence of coadsorbed H, data not shown), and (2) no reactivity at all was observed in blank experiments with H_2 (with the filament off), presumably because of the inability of Cu to dissociate the H−H bond.

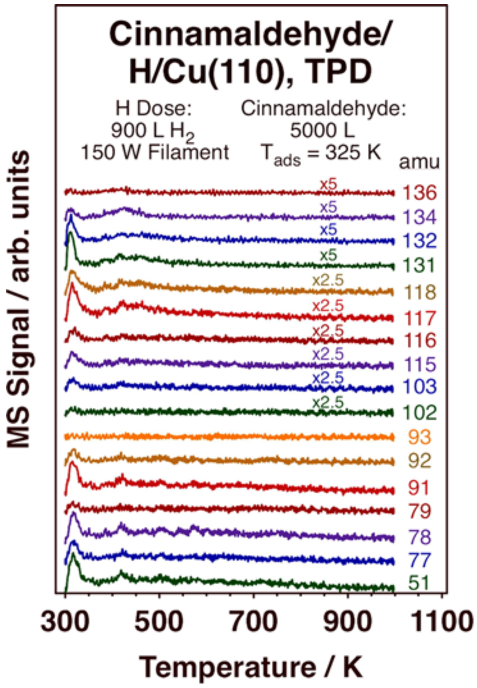

Figure 1. TPD traces for cinnamaldehyde adsorbed on a Cu(110) surface presaturated with atomic hydrogen.

Comparative TPD studies were performed on a Cu(110) surface pretreated with oxygen. The rationale for this is twofold: (1) many oxygen-containing molecules such as alcohols and aldehydes adsorb only weakly on clean Cu surfaces but can be stabilized by coadsorbed oxygen,[34,35] and (2) Cu can be easily oxidized by trace amounts of O_2 or water in reaction mixtures under atmospheric pressures and may be the active phase in at least some hydrogenation catalysis.[36,37] Representative TPD data for CMA adsorbed on Cu(110) saturated sequentially with oxygen and hydrogen atoms are displayed in Figure 2. The uptake of CMA on the Cu surface was found to indeed be enhanced by the presence of oxygen atoms on the surface, as indicated by the increase intensity of the corresponding peaks at 420 K; this is seen the most clearly in the traces for 51, 77, 78, and 91 amu but is corroborated by the data for the heavier fragments. Interestingly, though, the addition of surface oxygen does not seem to alter the basic kinetics of the CMA hydrogenation, as rest of the desorption peaks are associated with the same products and appear at the same temperatures.

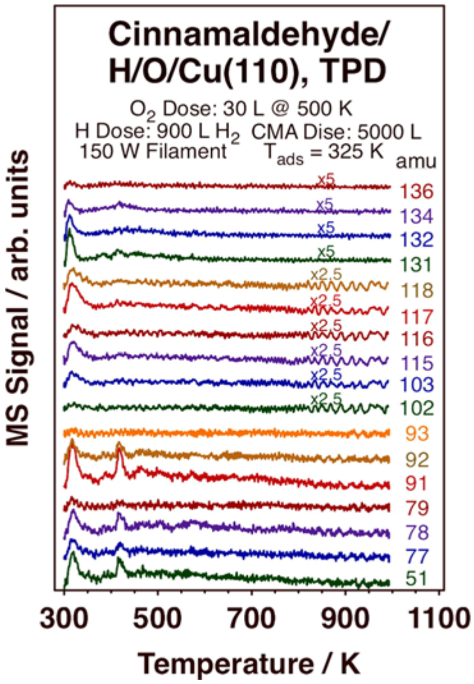

Figure 2. TPD traces for cinnamaldehyde adsorbed on a oxygen-pretreated Cu(110) surface presaturated with atomic hydrogen.

Complementary experiments were performed isothermally by holding the temperature of the CMA-saturated Cu(110) surface constant at 325 K and exposing it to atomic hydrogen produced in the gas phase; the desorbing products were analyzed as a function of time with the same mass spectrometer used for the TPD studies. The results for the cases of the clean and oxygen-pretreated surfaces are reported in Figures 3 and 4, respectively. It can be seen there that signals are detectable for many amu's at the start of the atomic-hydrogen exposure (t = 0 min), as indicated by sudden signal intensity jumps within the first minute followed by slow decays over the following 10−20 min (presumably because of the consumption of the adsorbed CMA). To check that these changes originate from reaction between the adsorbed CMA and the H atoms provided from the gas phase, appropriate blank experiments were performed as well. Dosing of the surface with H_2 while keeping the filament (used to dissociate the H−H bonds and produce atomic hydrogen) off led to no detectable changes in the mass spectrometer signals. On the other hand, turning the filament on in the absence of any gas-

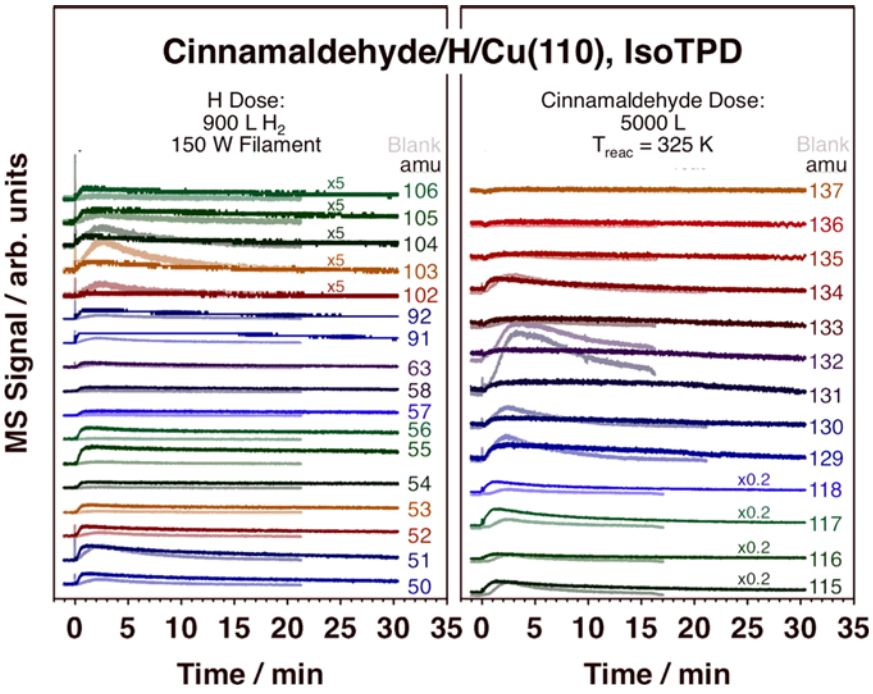

Figure 3. IsoTPD traces for cinnamaldehyde adsorbed on a Cu(110) surface presaturated with atomic hydrogen. Data for the desorbing species are reported as a function of the time of exposure to the gas-phase H atoms. The light-colored traces correspond to blank experiments performed with the hot filament used for H production on but without any gas-phase H_2.

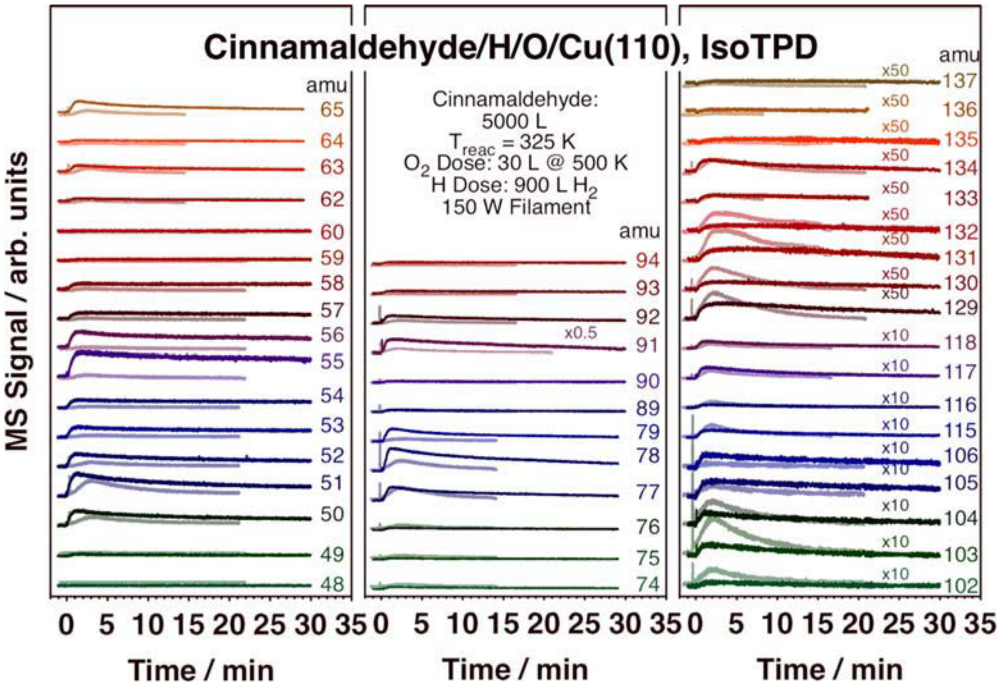

Figure 4. IsoTPD traces for cinnamaldehyde adsorbed on an O_2-pretreated Cu(110) surface presaturated with atomic hydrogen. As in Figure 3, the light-colored traces correspond to blank experiments performed with the hot filament used for H production on but without any gas-phase H_2.

phase H_2 does lead to reactivity and desorption from the surface, as indicated by the light-colored traces in Figures 3 and 4. The mass spectrometer signals evolve in a longer time frame than with atomic hydrogen, peaking after ~5 min, and point to a different product distribution and to higher yields: the large signals in the 50, 51, 91, 102, 103, 104, 115, 116, 131, and 132 amu traces indicate that the main event taking place is CMA molecular desorption, but the clear peak seen in the trace for 134 amu also identifies a partial hydrogenation product, most likely CMO. It is possible that due to its proximity, the hot filament causes the slow local heating of the surface, although no significant changes in the temperature of the Cu(110) crystal were measurable with the thermocouple attached to it. Alternatively, the excitation may come from electron bombardment. It is important to note, however, that no evidence of this type of excitation is seen in the results from experiments with

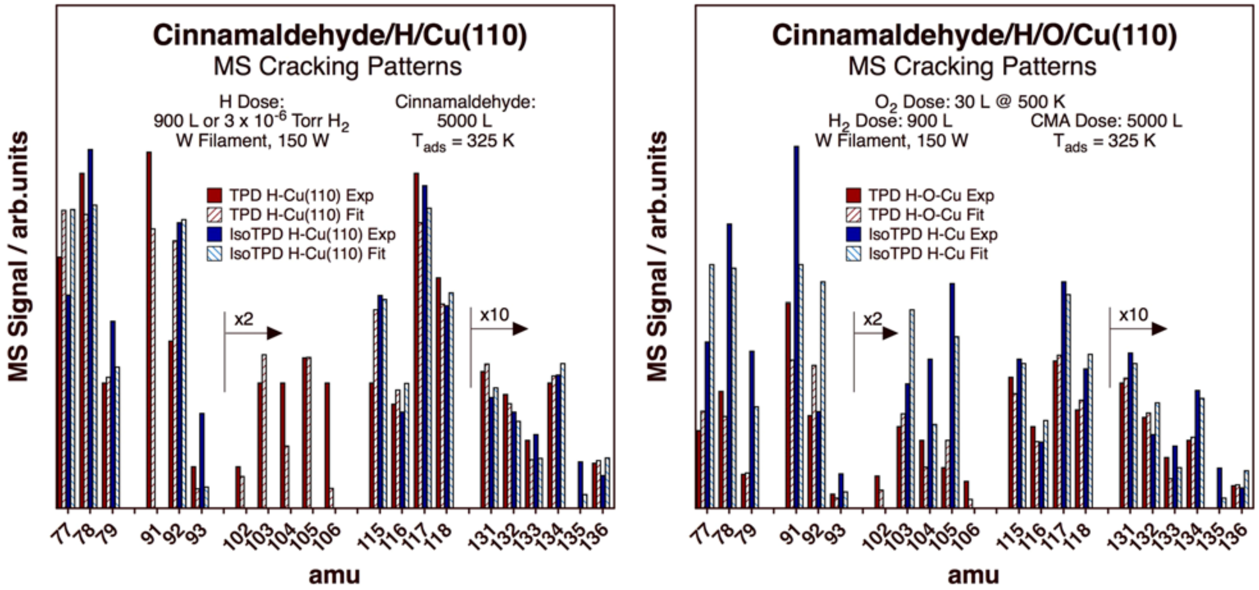

Figure 5. Measured (solid bars) and calculated (hashed bars) cracking patterns from TPD (left-slanted hashed and red bars) and IsoTPD (right-slanted hashed and blue bars) experiments with CMA adsorbed on clean (left panel) and oxygen-pretreated (right) Cu(110) surfaces and atomic hydrogen.

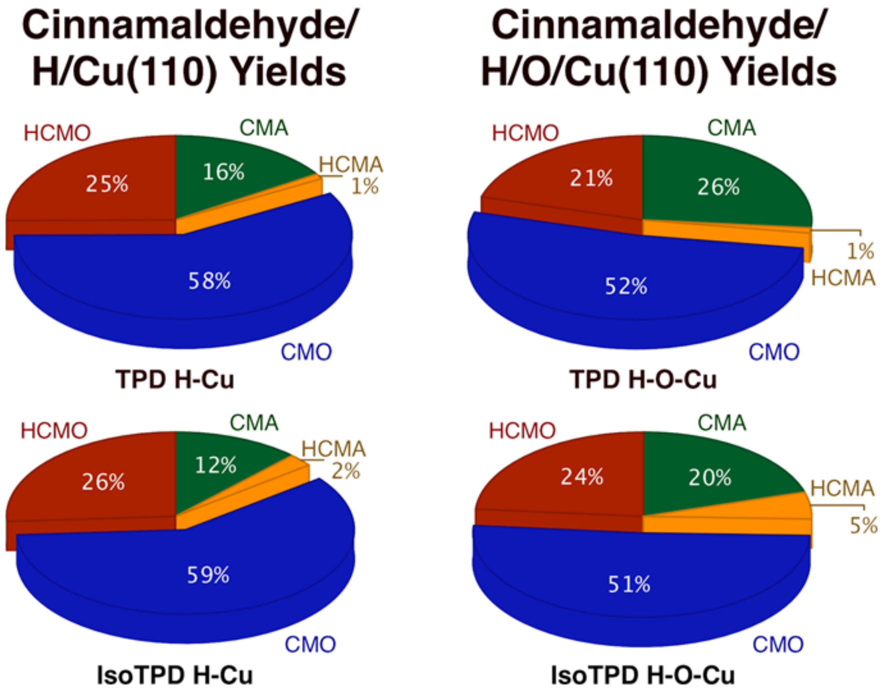

Figure 6. Yields calculated from the deconvolution process reported in Figure 5. Results are shown for the TPD (top row) and IsoTPD (bottom row) experiments with CMA adsorbed on clean (left column) and oxygen-pretreated (right column) Cu(110) surfaces and atomic hydrogen. Four desorbing species were detected in all cases: CMA, CMO, HCMA, and HCMO.

atomic hydrogen, since the desorption traces do not show any additional kinetic component with the time frame (~5 min) of the results from the blank experiments. It is possible that the introduction of H_2 into the UHV chamber leads to some filament cooling.

Next, we briefly discuss and interpret the data from the isothermal desorption experiments in Figure 3, the dark-color traces. Here too there is evidence for CMA molecular desorption, as signals are clearly seen in the traces for 50, 51, 52, 91, 102, 103, 104, 115, 116, 131, and 132 amu. However, it is also clear that significant amounts of products from hydrogenation are detected as well, possibly in larger yields than the molecular CMA. For one, large peaks are observed in the 105, 106, 117, 118, and 134 amu traces, likely indicative of CMO production with perhaps a minor contribution from HCMA. Other minor peaks, in particular for 136 amu, also suggest the formation of HCMO.

Similar IsoTPD experiments were again performed on an oxygen-pretreated Cu(110) surface, as reported in Figure 4. The results do not differ much from those obtained from the clean Cu(110). For one, slow desorption is seen in the blank experiments, mainly molecular CMA, with a time constant on the order of several minutes. Also, when atomic H is dosed, the response is faster and the CMA yield lower, as more hydrogenated molecules are produced. On the other hand, an enhancement in initial CMA coverage and total desorption yield, as seen in the regular TPD experiments, is not as evident in the IsoTPD results.

More detailed analysis and quantitation of the results from these studies required deconvolution of the raw data. This was performed by by using a procedure developed in our lab and described in detail elsewhere,[32,33] together with the mass spectra cracking patterns of the individual molecules considered (CMA, CMA, HCMA, and HCMO) reported in the NIST website.[38] The results are shown in Figure 5 in the form of the relative intensities of the TPD and IsoTPD peaks for different amu's, comparing the experimental numbers to those estimated by our fits. They are fairly similar for the clean and oxygen-pretreated Cu(110) surfaces, and the fits are in general good.

The composition of the desorbing gases calculated from this deconvolution process is reported in Figure 6. Although there are some subtle differences across the four pie charts in that figure, the general trends are similar in all cases, indicating that neither the style of experimentation (temperature-ramped or isothermal) nor the presence of oxygen on the Cu(110) surface appears to affect the basic mechanistic details that define selectivity in the CMA hydrogenation reaction. In all cases, there is limited CMA molecular desorption, amounting to approximately one-quarter of the saturated monolayer. The addition of oxygen to the surface appears to passivate the surface somewhat as a larger fraction of the CMA desorbs intact (26 and 20% versus 16 and 12%), although this may be the result of an overall increase in saturation absolute coverage. It is also clear that the isothermal kinetic experiments lead to higher reactivity, an observation that relates to experimental details and can be interpreted as the result of a higher activation barrier for CMA desorption versus hydrogenation (so, as the temperature increases during regular TPD, molecular desorption is favored).

In terms of selectivity, the data in Figure 6 show that the main product in all cases is, by far, the unsaturated alcohol, CMO, which is the desired product. Some fully hydrogenated saturated alcohol is made as well, but the yield for the saturated aldehyde, HCMA, is quite small regardless of the oxidation state of the surface or the experimental method used. Selectivities are perhaps best expressed in terms of percentages referred to the total amount of products, as done in Table 1. Again, the numbers in all cases are quite close, and the variations in most cases are within the error margin of the experiments. CMO constitutes more than two-thirds of the detected products, and most of the rest is ascribed to HCMO; only 1−2% of the total products correspond to the undesirable partially hydrogenated HCMA.

Table 1. Selectivities for the Hydrogenation of CMA Adsorbed on Cu(110) Surfaces

		selectivity/%		
surface	method	CMO	HCMA	HCMO
H−Cu(110)	TPD	69 ± 2	1 ± 2	30 ± 2
	IsoTPD	68 ± 2	2 ± 2	30 ± 2
H−O−Cu(110)	TPD	70 ± 2	1 ± 2	29 ± 2
	IsoTPD	64 ± 2	6 ± 2	30 ± 2

4. DISCUSSION

The intrinsic selectivity of Cu surfaces for the hydrogenation of C═O bonds in the presence of C = C bonds in unsaturated aldehydes was probed here by carrying out kinetic measurements, both regular temperature-programmed (TPD) and isothermal (IsoTPD) desorption experiments, with cinnamaldehyde (CMA) on a model Cu(110) surface and under controlled (UHV) conditions. The results from these studies, summarized in Table 1, indicate that, as expected and desired, Cu appears to indeed favor the hydrogenation of C═O bonds to produce unsaturated alcohols.

A few additional observations from the data may also be of relevance to the understanding of hydrogenation reactions with Cu-based catalysts. First, it should be emphasized that hydrogenation products could only be detected in these experiments when using atomic hydrogen; exposure of the Cu(110) surface to molecular H_2 either before or after CMA adsorption resulted in no detectable hydrogenation at all. This was expected, as Cu surfaces are highly inefficient in promoting the dissociation of H−H bonds,[39,40] the reason pure Cu is seldom used as a hydrogenation catalyst. On the other hand, our experiments confirm that if atomic hydrogen becomes available on the surface, Cu can indeed promote the incorporation of those into the double (and triple) bonds of unsaturated organic reactants and does that selectively. This has been part of the rationale for designing single-atom alloy (SAA) catalysts with this metal;[10,19,41] we have already shown that $CuPt_x$/SBA-15 catalysts are active and highly selective for the hydrogenation of CMA.[24,25] Importantly, the catalytic results with SAAs are not in themselves proof that Cu is selective in unsaturated aldehyde hydrogenations, as the formation of alloys is likely to modify the electronic properties of bimetallic catalysts and perhaps produce new surfaces with unique chemistry, different from those of the pure metals. Only with experiments such as those reported here can the intrinsic hydrogenation chemistry of Cu be probed.

The answer appears to be that, indeed, Cu surfaces hydrogenate C═O bonds preferentially in the presence of C═C bonds within the same reacting molecules. An explanation for this has come from infrared absorption spectroscopy experiments and quantum mechanics calculations[24,30] and relates to the adsorption mode of the reactant on the surface. Whereas on Pt unsaturated aldehydes prefer to form multiple bonds with the surface, with a predominant interaction via the C═C bond,[28,42,43] on Cu adsorption is primarily via the oxygen end of the molecule.[24,30] Because of this difference, the incorporation of hydrogen atoms into the C═C bond of the unsaturated aldehyde exhibits a large activation barrier on Cu, much higher than that for the addition of H to the carbon atom of the carboxyl moiety.[24] There is a clear kinetic limitation for C═C bond hydrogenation on Cu that does not exist on Pt.

As a consequence, according to our results, more than two-thirds of the CMA that reacts with hydrogen on Cu(110) yields the desired unsaturated alcohol, CMO. In fact, the formation of the competing and undesirable saturated aldehyde, HCMA, is negligible, amounting to only a couple of percent of the total hydrogenation products. What is interesting is that the rest of the products, ∼30%, are composed of the saturated alcohol, HCMO. Because the making of HCMO requires more extensive hydrogenation, its production has traditionally been considered the result of secondary reactions. On the other hand, we have recently shown, using molecular beam experiments, that this type of product can originate from chemical steps that take place directly on the adsorbed reactant, without invoking subsequent desorption and readsorption of intermediate products (at least on Pt).[44] A similar argument can be made to conclude that HCMO is a primary, not secondary, product of the hydrogenation process reported above, as here too the products that desorb from the surface do not have the option of readsorbing and reacting further. We have previously argued that the full incorporation of four H atoms into the unsaturated aldehydes without the loss of partially hydrogenated products can be explained by the formation of allylic surface intermediates after the first H addition.[44] This possibility needs to be explored further by quantum mechanics calculations.

Another consideration of relevance to hydrogenation catalysis that we explored explicitly in these studies is the potential role of the oxidation state of the surface. Cu surfaces are easily oxidized upon exposure to air, or even to traces of O_2 or water, and are not easily reduced by H_2 (because of the difficulty in activating that molecule in the first place).[24] Also, as mentioned before, oxygen is known to aid with the stabilization of oxygen-containing organic adsorbates such as alcohols.[34,35] In the experiments reported here, predosing of oxygen does appear to increase the surface coverage of the initial CMA reactant. However, this does not seem to translate into any significant variations in reactivity or selectivity during the subsequent hydrogenation steps. In particular, Table 1 clearly shows that the selectivities toward CMO, HCMA, and HCMO are all the same, within experimental errors, on the H−Cu(110) and H−O−Cu(110) surfaces. This lack of effect of Cu oxidation state on hydrogenation conversions may very well extend to real catalysts, in which case it may not be so critical to be able to fully reduce the Cu-based catalysts before reaction. It is certainly an aspect of this catalysis worth exploring further, perhaps by carrying out *in situ* or *operando* experiments during hydrogenation catalysis using X-ray photoelectron or X-ray absorption spectroscopies to follow the oxidation state of the surface atoms. We are already engaged in such experiments at the present time.

Finally, there is the issue of the dynamics of hydrogen incorporation into the organic unsaturations on the adsorbed reactants. The general assumption in catalysis is that most surface steps involve two adsorbed species, following the so-called Langmuir−Hinshelwood (LH) mechanism, but there have been a few instances where evidence has been provided for direct reactions between an adsorbate and a gas-phase species, via an alternative Eley−Rideal (ER) pathway.[45−50] Given the unstable nature of hydrogen atoms, they tend to react readily with other molecule upon contact, and because in these experiments the hydrogen atoms are produced in the gas phase, it may be tempting to conclude that the unsaturated aldehyde reactions may follow the latter ER route. However, basically the same results were obtained here with TPD and IsoTPD experiments, and in the first type the hydrogen atoms are preadsorbed on the surface before the CMA uptake. The lack of any discernible additional features in the IsoTPD data strongly suggests that there is no significant ER contribution to the hydrogenation reactions reported above.

5. CONCLUSIONS

The mechanistic details of the hydrogenation of unsaturated aldehydes on Cu surfaces were explored by using cinnamaldehyde, a model system (a Cu(110) single crystal), and temperature-programmed desorption (TPD) experiments performed under UHV conditions. Reactivity is only possible with atomic hydrogen, which was provided via the gas-phase activation of the H−H bond using a hot filament; no detectable products were seen with H_2, as Cu is known to be quite inefficient for the promotion of molecular hydrogen dissociation. The main conclusion from this work is that copper surfaces show an intrinsic preference for the hydrogenation of C═O bonds when in competition with C═C bonds. This is explained by an adsorption mode with binding to the surface via the terminal carbonyl oxygen atom and a high barrier for the incorporation of hydrogen atoms to the C═C bond. The role of adsorbed oxygen on the Cu surface was explored as well, to account for the possibility of the presence of partially oxidized surfaces during catalysis, but similar results were obtained with clean versus oxygen-covered Cu(110) substrates, suggesting that this is not an important factor in determining catalytic activity or selectivity. Finally, comparable results were also obtained from the TPD versus IsoTPD experiments, an indication that the hydrogenation steps involve adsorbed, not gas-phase, hydrogen atoms, and follow a Langmuir−Hinshelwood mechanism.

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Notes

The authors declare no competing financial interest.

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