

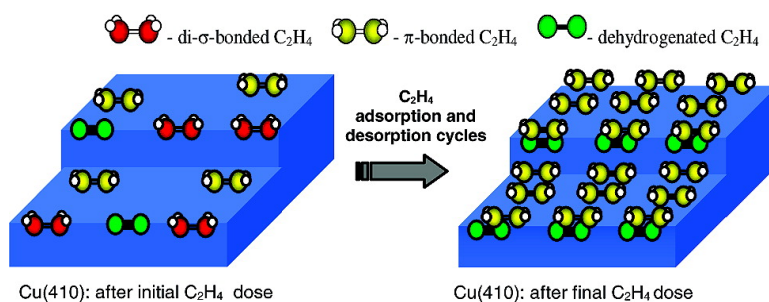
Communication

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Ethylene Decomposition at Undercoordinated Sites on Cu(410)

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Controlling hydrocarbon chemistry on metal surfaces is important for both heterogeneous catalysis and nanotechnology. Formation of C–C bonds and C–H scission is central to carbon nanotube synthesis¹ whereas the inhibition of carbon growth (C–C breaking) is important for preventing the poisoning of industrial catalysts.² Although the importance of special surface active sites for catalysis has been known for many years, only a few investigations deal with the influence of undercoordinated sites on reaction selectivity.^{3,4} In this communication we demonstrate the bond breaking selectivity for molecular ethylene adsorbed on Cu(410). While on terraces ethylene is reversibly π -bonded, the step sites induce not only unexpected di- σ -bonding but also complete dehydrogenation at rather low crystal temperatures, T . The resulting carbon decorates the step edges.

In the steam reforming process, typically on Ni-based catalysts, hydrocarbons dissociate on the surface to form molecular hydrogen, and the remaining carbon reacts to produce carbon monoxide and additional hydrogen.² Thus, a severe problem with Ni catalysts is that carbon accumulates to form graphitic deposits, which ultimately poison the catalyst. For an improved catalyst, carbon removal should be facilitated, a process which would be thermodynamically favored by weaker metal–carbon bonding. Cu-based catalysts may be good candidates for achieving this because the reactivity of Cu exceeds that of other coinage metals, Ag and Au, but is by far lower than that of main group transition metals.

It is known from previous work⁵ that low Miller index surfaces of Cu are unreactive and π -bonded ethylene is reversibly adsorbed. However, recent studies have shown that, even on gold, the presence of defects can cause the decomposition of NO.⁶ Dehydrogenation of ammonia was found on steps of Cu(110)/O₂.⁷ It has been shown that ethylene is stabilized on the open step edges of Ag(410),⁸ its adsorption energy being three times larger than that on (100) terraces.⁹ Density functional theory calculations for C₂H₄–Cu(111) adsorption suggest the coexistence of π - and di- σ -bonded states, depending on the sample preparation conditions.¹⁰ The latter was, however, never observed, except as a result of photoinduced dissociation of CH₂I₂ on Cu(100), where it was identified in temperature-programmed desorption (TPD) by its higher (240 K) desorption temperature relative to that for the π -bonded form.¹¹

Here, we investigate the adsorption of ethylene on Cu(410) at low temperature by high-resolution electron energy loss spectroscopy (HREELS), X-ray photoelectron spectroscopy (XPS), and TPD. Ethylene bonding and reaction products were analyzed as a function of temperature and coverage. Measurements were performed in three different UHV systems, which are described, along with surface preparation procedures, in the Supporting Information (SI). It was found from previous experiments¹² that the sticking

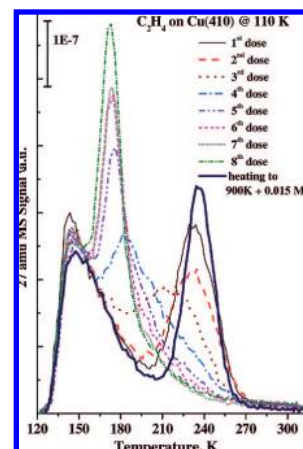


Figure 1. Sequential TPD spectra of 0.015 ML of ethylene desorbing from Cu(410). The heating rate was 3.6 K/s up to a maximum temperature of 390 K. Before the final experiment, the sample was annealed to 900 K.

coefficient of ethylene on Cu(410) is nearly constant at ~ 1 up to a coverage of ~ 0.14 monolayer (ML). The saturation coverage is estimated to be ~ 0.25 ML.

TPD spectra of ethylene ($m/e = 27$) from Cu(410) are presented in Figure 1 for sequential 0.015 ML coverage at 110 K. The heating rate was 3.6 K/s up to a maximum T of 390 K. Experiments were performed by dosing the surface with ethylene, collecting the TPD spectrum, and then dosing the surface again without cleaning the sample. For the first ethylene dose, two well-defined desorption states are detected at ~ 143 and ~ 232 K. The well-separated peaks suggest that two distinct surface species are present. Based on previously published results, the ~ 143 K peak is associated with π -bonded ethylene,⁵ while the feature at 232 K corresponds to di- σ -bonded ethylene.¹¹

Subsequent ethylene doses result in a decrease of the high-temperature peak and in the formation of a peak at lower temperatures. No further changes were observed after 8 cycles where the extra ethylene desorption state appears now at ~ 170 K. The sample was then annealed to 900 K in vacuo, cooled to 110 K, and exposed again to ethylene. The resulting TPD spectrum is very similar to that recorded for the initial, clean surface. It can be concluded that the shift of the high- T peak evidences a gradual occupation of the sites available for a di- σ -bonded ethylene by products of ethylene dehydrogenation. Such products survive annealing up to 390 K, but not to 900 K. Moreover, $m/e = 4$ (D₂) was detected at TPD spectra after dosing C₂D₄, confirming ethylene dehydrogenation. These results will be presented elsewhere. No relevant additional masses were detected by TPD analysis. In addition, the area under the TPD peaks is identical for all spectra

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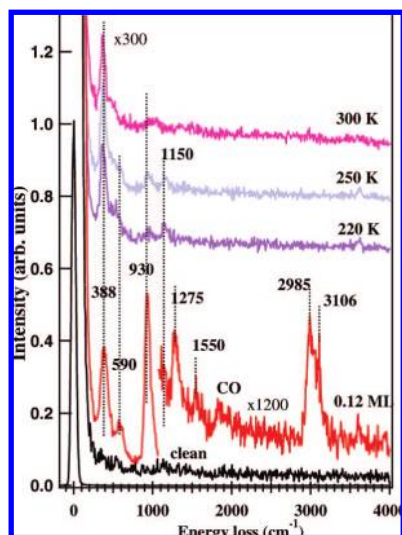


Figure 2. HREELS spectra measured on Cu(410) after exposure to 0.12 ML of ethylene at 145 K, and after annealing to different T . Shown for reference is the spectrum of the clean surface. The loss at 1150 cm^{-1} is the signature for σ -bonded ethylene. The small loss at 930 cm^{-1} after heating results from readsorption from the background during measurement.

presented in Figure 1. The ethylene coverage is thus independent of the amount of ethylene dehydrogenation products present on the surface.

To further investigate ethylene dehydrogenation, HREELS measurements were performed as a function of temperature (see Figure 2). The peaks at $\nu_7(\text{CH}_2) = 930\text{ cm}^{-1}$, $\nu_3(\text{CH}_2) = 1275\text{ cm}^{-1}$, $\nu_1(\text{CH}_2) = 2985\text{ cm}^{-1}$, $\nu_9(\text{CH}_2) = 3106\text{ cm}^{-1}$ are assigned to π -bonded ethylene.⁵ This bonding geometry is expected from the TPD spectra measured for a similar exposure (see SI), which shows a 1:3 ratio between π - and di- σ -bonded moieties. Weaker losses associated with the latter species¹³ are visible at $\nu(\text{CC}) = 1150\text{ cm}^{-1}$ and $\delta(\text{CH}_2) = 1550\text{ cm}^{-1}$ and are still present after annealing to 250 K (at which temperature π -bonded ethylene has desorbed⁵), but not to 300 K in agreement with our TPD results (Figure 1). The CH_2 stretching frequency of di- σ -bonded ethylene (at $\sim 2900\text{ cm}^{-1}$)¹³ is expected to be very weak and is not observable under our conditions. The 388 cm^{-1} loss, on the contrary, is present in all spectra. Since no CH related losses are observed after annealing, we ascribe this mode to either the C- or to the C_2 -substrate vibration, in accord with previous work.^{14,15} Finally the 590 cm^{-1} peak is consistent with adsorbed H.^{16,17} For subsequent adsorption cycles we observe no di- σ -bonded ethylene (see SI), and the desorption temperature of 170 K (see Figure 1) is in accord with π -bonded molecules.

From these experiments, we conclude that C_2H_4 dehydrogenates and leads to carbon decorating the open step edges, even at low temperature. Such C inhibits further dissociation by poisoning the active sites and permits adsorption only in the π -bonded state.¹³ Heating to 900 K leads to a HREEL spectrum of the clean surface (not shown). Since C cannot desorb, it must diffuse into the bulk, where it is no longer detectable by HREELS.

XPS experiments confirm carbon accumulation on the surface. Figure 3 displays the C $1s$ peak measured after exposures to ethylene at 110 K followed by annealing to 300 K for an initial dose (0.15 ML) and after three subsequent cycles (0.15 ML+0.15 ML+0.45 ML). The C $1s$ feature (at $\sim 285\text{ eV}$ binding energy) can be assigned to both ethylene and C_2 , while graphite is expected around 284.2 eV . It could also be due to CH_2 species, which are, however, excluded by HREELS inspection.

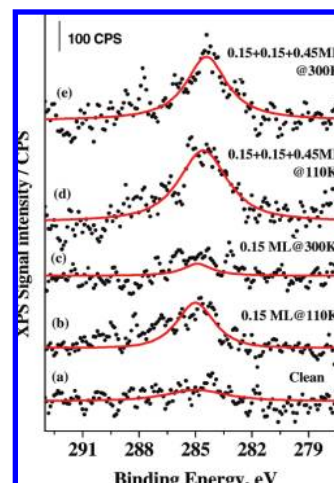


Figure 3. XPS for the clean Cu(410) surface (a), after exposure to 0.15 ML of ethylene at 110 K (b), after subsequently heating to 300 K (c), and after two more dosing (d) and heating (e) cycles (no cleaning or high T annealing was performed between the cycles).

In conclusion, our data demonstrate selective, low-temperature chemistry of ethylene on strongly undercoordinated sites on copper. On the open step edges of Cu(410) such sites promote the dehydrogenation of ethylene. The generated carbon decorates the step edges thereby blocking the active sites for subsequent dissociation and/or adsorption in the di- σ -state. However, these processes can be restored merely by heating the sample to 900 K. A simple thermodynamic calculation (see SI) of Cu–C bonding energy gives an estimate of 170–230 kJ/mol, compared with $\sim 203\text{ kJ/mol}$ for carbon on the Ni(100) surface¹⁸ (and even higher on its steps³). This supports the relevance of copper-based catalysts for the steam reforming process.

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Supporting Information Available: Additional TPD spectra. Thermodynamic estimation of Cu–C bonding energy. Experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Ajayan, P. M. *Chem. Rev.* **1999**, *99*, 1787.
- (2) Bengaard, H. S.; Norskov, J. K.; Sehested, J.; Clausen, B. S.; Nielsen, L. P.; Molenbroek, A. M.; Rostrup-Nielsen, J. R. *J. Catal.* **2002**, *209*, 365.
- (3) Vang, R. T.; Honkala, K.; Dahl, S.; Vestergaard, E. K.; Schnadt, J.; Lægsgaard, E.; Clausen, B. S.; Nørskov, J. K.; Besenbacher, F. *Nat. Mater.* **2005**, *4*, 160.
- (4) Vattuone, L.; Savio, L.; Rocca, M. *Surf. Sci. Rep.* **2008**, *63*, 101.
- (5) Linke, R.; Becker, C.; Pelster, Th.; Tanemura, M.; Wandelt, K. *Surf. Sci.* **1997**, *377–379*, 655.
- (6) Vinod, C. P.; Hans, J. W. N.; Nieuwenhuys, B. E. *Appl. Catal., A* **2005**, *291*, 93.
- (7) Guo, X.-C.; Madix, R. J. *Surf. Sci.* **1996**, *367*, L95–L101.
- (8) Savio, L.; Vattuone, L.; Rocca, M. *Surf. Sci.* **2005**, *587*, 110.
- (9) Kokalj, A.; Dal Corso, A.; de Gironcoli, S.; Baroni, S. *Surf. Sci.* **2004**, *566–568*, 1018.
- (10) Witko, M.; Hermann, K. *Appl. Catal., A* **1998**, *172*, 85.
- (11) Kovacs, I.; Solomosi, F. *J. Phys. Chem. B* **1997**, *101*, 5397.
- (12) Vattuone, L.; Kravchuk, T.; Rocca, M., in preparation
- (13) Chesters, M. A.; Sheppard, N. *Spectroscopy of surfaces*; John Wiley & Sons Ltd: Hoboken, NJ, 1988; Chapter 7.
- (14) Sock, M.; Eichler, A.; Surnev, S.; Andersen, J. N.; Klotzer, B.; Hayek, K.; Ramsey, M. G.; Netzer, F. P. *Surf. Sci.* **2003**, *545*, 122.
- (15) Lin, J.-L.; Bent, B. E. *J. Vac. Sci. Technol., A* **1992**, *10* (4), 2202.
- (16) Lai, W.; Xie, D.; Yang, J.; Zhang, D. H. *J. Chem. Phys.* **1992**, *121* (15), 7434.
- (17) Kolovos-Vellianitis, D.; Kammler, Th.; Kuppers, J. *Surf. Sci.* **2000**, *454–456*, 316.
- (18) Vattuone, L.; Yeo, Y. Y.; Kose, R.; King, D. A. *Surf. Sci.* **2000**, *447*, 1.

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