

Acetylene Coupling on Cu(111): Formation of Butadiene, Benzene, and Cyclooctatetraene

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Acetylene trimerizes to benzene on the (111) face of copper, as it does on the (100) and (110) planes. However, Cu(111) also yields butadiene and cyclooctatetraene, the latter never previously found with Cu or any other material. No coverage threshold is observed for the onset of these coupling reactions, implying high adsorbate mobility: gaseous benzene is formed by a surface reaction rate-limited process, whereas butadiene and cyclooctatetraene are formed by desorption rate-limited processes. H/D isotope tracing shows that benzene formation proceeds via a statistically random associative mechanism, whereas butadiene formation is associated with strong kinetic isotope effects, probably associated with C–H cleavage. A pericyclic mechanism involving dimerization of C_4H_4 metallocycles is proposed to account for the formation of cyclooctatetraene. We also found that ~ 45 nm α -alumina supported copper particles operated under catalytic conditions at atmospheric pressure yield the same principal reaction products as those found with Cu(111) under vacuum conditions. It therefore seems likely that the elementary reaction steps that describe the surface chemistry of the model system are also important under practical conditions. Comparison of the structure, bonding, and reactivity of acetylene on Cu(111) and Pd(111) indicates that the effectiveness of copper in promoting C–H cleavage in adsorbed acetylene is associated with greater rehybridization of the C–C bond with concomitant weakening of the C–H bond.

1. Introduction

Acetylene trimerization to benzene has been studied under ultrahigh vacuum (UHV) conditions on a variety of metallic and bimetallic single-crystal surfaces (Pd(111),^{1,2} Cu(110),^{3,4} Cu(100),⁵ Au(111)/Pd,⁶ Au/Pd(111),⁷ Pt(111)/Sn,⁸ Pd(111)/Sn⁹) and also on TiO₂(001).^{10,11} The reaction on Pd(111) has received the most attention having been explored by means of both experiment and theory in regard to structural, kinetic, and mechanistic aspects.^{12,13,14} A few complementary studies have also been carried out at atmospheric pressure with dispersed Pd,¹⁵ Pd/Au,¹⁶ and Pd/Sn¹⁷ catalysts operated under steady-state conditions. All the data are consistent with initial formation of a tilted C_4H_4 metallocycle intermediate that undergoes reaction with a third acetylene molecule to form benzene. This C_4 intermediate may also react with other surface species such as O_a, S_a to yield furan¹⁸ and thiophene,¹⁹ respectively. An interesting aspect of the prototypical trimerization reaction is its apparent structure sensitivity on palladium surfaces—only the (111) plane is effective for benzene formation.²⁰ In this regard, copper is different. The (110)⁴ and (100)⁵ surfaces convert $\sim 75\%$ and $\sim 30\%$ of the originally adsorbed acetylene to benzene, respectively, under temperature-programmed reaction (TPR) conditions. And, as we shall see, the (111) surface is also effective.

Here we report TPR results for acetylene coupling on the Cu(111) surface, previously not studied, along with complementary data obtained at atmospheric pressure using Cu/Al₂O₃ dispersed catalysts. On Cu(111), in addition to benzene formation, we observe butadiene and cyclooctatetraene (COT): the latter has never been previously reported as a reaction product

of acetylene coupling on any surface; butadiene production from acetylene has been observed on Pd(111), though in very small amounts and only under conditions of laser induced thermal desorption (LITD).²¹ The formation of butadiene provides a clear and direct chemical confirmation of the formation and participation of the C_4H_4 intermediate, previously identified by spectroscopic²² and indirect chemical methods.^{23,24} The observation of COT raises the question of whether this molecule is an intermediate to benzene formation via ring contraction ($C_8 \rightarrow C_6 + C_2$).²⁵ With the dispersed catalyst, whose surfaces are dominated by (111) planes, we find the same C₂, C₄, C₆, and C₈ products, along with much higher oligomers, indicating that in this case the reactive behavior under vacuum conditions does mimic that which occurs at elevated pressure under conditions of turnover.

2. Experimental Methods

UHV experiments were performed in an apparatus that has been described in detail elsewhere.²⁶ Briefly, this incorporated facilities for XPS and TPR measurements (1.3 K s^{-1}). With respect to the latter, the mass spectrometer collimator was positioned ~ 10 mm from the center of the front face of the Cu(111) crystal so that only species desorbing from the front face of the sample were detected. The crystal could be resistively heated to 850 K and cooled to 120 K. It was cleaned by cycles of Ar⁺ sputtering (1 keV, 4 μ A) and annealing (800 K) until no impurities were detectable (XPS). C₂H₂, C₂D₂, and COT were dosed by means of by a 6 mm diameter collimator tube directed at the sample; exposures, after correction for the doser gain factor, are quoted in Langmuirs ($1 \text{ L} = 1 \times 10^{-6} \text{ Torr s}$). Relative desorption yields of products are referred to a maximum ethylene yield of 1.0. They were obtained by first calibrating the quadrupole mass spectrometer's mass-dependent instrumen-

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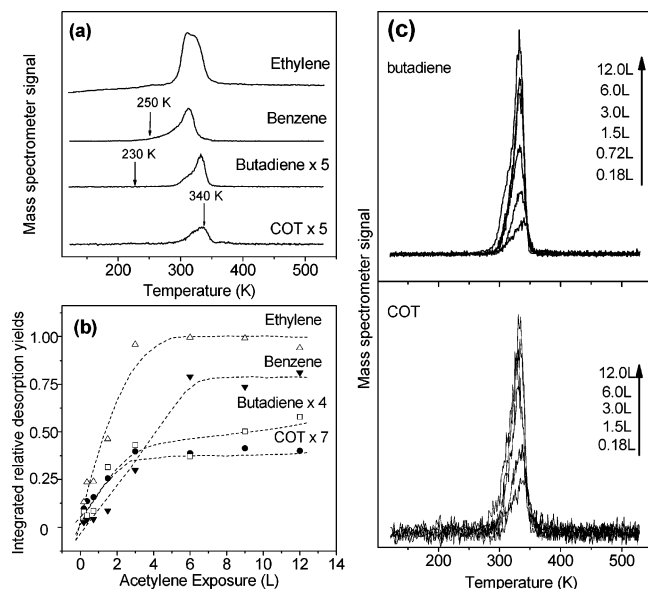


Figure 1. (a) TPR spectra showing reactively formed COT, butadiene, benzene, and ethylene after an exposure of 12 L of acetylene to Cu(111) at 120 K, (b) integrated relative desorption yields of all gaseous products as a function of acetylene exposure, and (c) TPR spectra of relatively formed COT (m/z 104) and butadiene (m/z 54) as a function of acetylene exposure.

tal response function, using known pressures of H_2 , N_2 , O_2 , Ar, and Xe, allowing for differences in ionization gage sensitivities.^{27,28} Then, by using this calibration and the measured intensities, and making allowances for fragmentation patterns by subtracting contributions from the raw data as appropriate, corrected intensities proportional to product yields were obtained. Catalytic tests were performed with a single pass quartz tubular plug flow reactor, using 100 mg of Cu/Al_2O_3 catalyst in which the average copper particle size was ~ 45 nm (XRD). The catalyst was prepared by incipient wetness impregnation with an aqueous solution of copper nitrate so as to achieve a 10% w/w metal loading. After drying at 373 K overnight and calcining in air at 573 K the catalyst was reduced in hydrogen at 550 K for 2 h. Reaction gases (acetylene (Linde), 20% H_2/He (BOC), He (BOC)) were delivered by mass flow controllers, at a total flow rate of $50\text{ cm}^3\text{ min}^{-1}$. The reactor output was analyzed by quadrupole mass spectrometry (Hiden RGA 301).

3. Results and Discussion

Figure 1a shows TPR data acquired after exposing the Cu(111) sample to a saturation dose of acetylene at 120 K. The gaseous products observed were COT (m/z 104), benzene (m/z 78), butadiene (m/z 54), and ethylene (m/z 28) along with unreacted acetylene (m/z 26). The identification of butadiene and COT was confirmed by measuring the m/z 54:53:39 and 51:78:103:104 fragmentation patterns, respectively, after correcting the corresponding desorption spectra for interferences from ethylene and benzene. These fragmentation patterns were in good agreement with NIST standards.²⁹

The observation of COT as a product of acetylene coupling is unprecedented. Although trace amounts of butadiene (though not COT) formed from acetylene on Pd(111) under LITD²¹ conditions have been found “such reactions are very sensitive to the details of the laser heating” so that the implications of such observations for the ordinary thermal chemistry are unclear.³⁰ Mechanistic aspects of C_4 , C_6 , and C_8 product formation are discussed below. Production of butadiene implies some C–H scission in the originally adsorbed acetylene to yield

H_a that subsequently reacts with the C_4H_4 metallocycle intermediate. (The availability of H_a is confirmed by the appearance of ethylene, resulting from acetylene hydrogenation.) When directly adsorbed onto Cu(111), benzene, butadiene and COT (see below) are characterized by desorption peak temperatures of ~ 250 ,³¹ 230 ,³² and ~ 340 K, respectively. Comparison of these peak temperatures with those shown in Figure 1a indicates that in the present case gaseous reactively formed benzene and butadiene result from surface reaction rate-limited processes. On the other hand, comparison of Figure 1a and Figure 4, the latter to be discussed in detail later, suggests that appearance of gaseous reactively formed COT is desorption rate limited.

Figure 1b shows the integrated relative desorption yields for all gaseous products, corrected for instrumental sensitivity, as a function of acetylene exposure at 120 K. Figure 1c shows raw data as a function of acetylene exposure for the cases of butadiene and COT. The results shown in Figure 1b correspond to $\sim 15\%$ of the initially adsorbed acetylene having been converted to gaseous products. C 1s XP spectra acquired after a TPR sweep showed no detectable carbon deposition, consistent with the relatively small amounts of C–H cleavage that would have been necessary to produce enough H_a to account for the observed yields of ethylene and butadiene ($\sim 7\%$ of the initially adsorbed acetylene, which would correspond to ~ 0.02 monolayers of carbon). Note that there is no acetylene coverage threshold associated with any of the products, which stands in contrast to the behavior found on Pd(111)¹ where benzene is the sole gaseous product and appears only above an acetylene coverage threshold of $1/3$, coincident with the onset of a $(\sqrt{3} \times \sqrt{3})R30^\circ$ LEED pattern. It therefore seems that adsorbate mobility is higher on Cu(111) than on Pd(111). This conclusion is also consistent with the reported observation³³ of a $[2,0;1,4]$ LEED pattern on Cu(111) from the lowest acetylene exposures, possibly formed via a precursor-trapping mechanism. Note that this structure corresponds to a local coverage of 0.25 monolayer, in reasonable agreement with the saturation acetylene coverage of 0.3 monolayer estimated from our XPS data with the method of Carley and Roberts.³⁴ That is, low exposures of acetylene to Cu(111) lead to island formation on an otherwise bare surface, thus enabling reactions to occur without a coverage threshold. This greater mobility of acetylene on copper compared to palladium contrasts with the substantially stronger interaction of the molecule with Cu(111) relative to Pd(111). Thus photoelectron diffraction^{35,36} and HREELS^{37,38} measurements for acetylene on these two surfaces clearly indicate a significantly stronger perturbation of the C=C bond on the copper surface ($r_{C-C} = 1.48 \pm 0.10$ Å and $\nu_{C-C} = 1307\text{ cm}^{-1}$ for Cu(111); $r_{C-C} = 1.34 \pm 0.10$ Å and $\nu_{C-C} = 1402\text{ cm}^{-1}$ for Pd(111)).

To characterize further the mechanism of benzene formation, isotope tracing experiments were carried out with mixtures of C_2D_2 and C_2H_2 . Figure 2 shows the product distribution obtained after sequential dosing of the surface first with 0.5 L of C_2D_2 and then with 0.5 L of C_2H_2 (black bars); the result of using the reverse dosing sequence is illustrated by the white bars. Notice that in both cases no “odd” benzenes were observed and that the relative yields of the “even” benzenes were close to $C_6H_6:C_6H_4D_2:C_6H_2D_4:C_6D_6 = 1:3:3:1$. This is clear evidence that the reaction proceeds via a purely associative mechanism, without any C–H scission, via statistically random coupling of the adsorbed acetylene molecules. Closer inspection of the results shows that when C_2D_2 was dosed first the deuterium-rich products were slightly favored; the converse is true for the case in which C_2H_2 was dosed first. This reflects the fact that

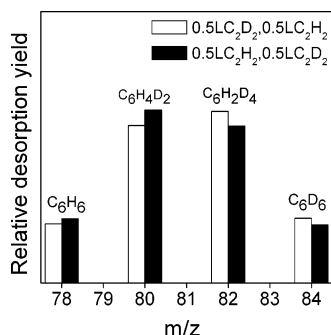


Figure 2. Observed relative desorption yields of benzene isotopomers showing product distribution after sequential dosing of 0.5 L of C₂H₂ then 0.5 L of C₂D₂ (black bars), and vice versa (white bars) on Cu(111) at 120 K.

the sticking probability of acetylene decreases with coverage so that equal exposures necessarily result in a lower coverage of the molecule that was dosed second.

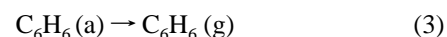
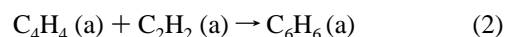
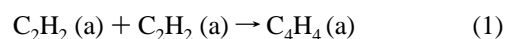
The isotope distribution in the butadiene product was similarly examined and the corresponding results are shown in Figure 3a, along with the distribution calculated on the basis of random coupling of pairs of acetylene molecules to yield C₄H₄, C₄H₂D₂, and C₄D₄, followed by reaction with H_a and D_a, these atoms assumed to be present in equal concentrations (Figure 3b). The experimental results shown in Figure 3a have been approximately corrected for mass interferences due to isotopomers (for example, the *m/z* 58 signal, mainly due to C₄H₂D₄, also contains a contribution from C₄D₆). This was done by assuming that the fragmentation patterns of all isotopomers were identical with that of ordinary butadiene (C₄H₆). This is of course a crude procedure because the actual fragmentation patterns are likely to be affected by isotope effects, and this to an unknown degree. Nevertheless, the corrections so introduced are relatively small so that Figure 3a should provide a reasonable approximation to the true distribution of butadiene isotopomers. In marked contrast to the benzene case, it is clear that the experimental and calculated distributions are very different.

The obvious difference between the two cases is that benzene formation does not require any C–H cleavage in the adsorbed acetylene, as demonstrated by Figure 2, whereas butadiene formation does. This suggests that the divergence between the observed and calculated distributions of butadiene isotopomers is due to strong primary kinetic isotope effects, likely due to the substantially greater strength of the C–D bond compared to the C–H bond which, at ~300 K, would correspond to a difference in dissociation rate constants of $k_H/k_D \sim 7$.³⁹ A closer inspection of the experimental results supports this interpretation.

Thus the yield of C₄H₆ is much greater than the simple statistical expectation, whereas the yield of C₄D₆ is smaller than expectation and much smaller than the yield of C₄H₆. This is consistent with a much scarcer supply of D_a compared to H_a. Similarly, all other products that incorporate an odd number of D atoms, thus requiring one C–D cleavage, appear with much lower intensities than the simple expectation. We cannot provide an explanation for some of the subtler apparent differences, for example, the way in which the yields of C₄H₅D and C₄D₅H change with the dosing sequence. It seems possible that, at least in part, these anomalies reflect our crude treatment of the raw data.

Attempts to examine the distribution of COT isotopomers in a similar way were unsuccessful: the signals were too weak to measure reliably. This was due to the rather low yield of this product (Figure 1b) and the fact that the total yield would have been distributed over five different isotopomers. The importance of isotope effects in determining product yields where C–H cleavage is a prerequisite was confirmed by experiments in which pure C₂D₂ was used. In this case, the yields of ethylene and butadiene were reduced by factors of 12 and 8, respectively, compared to the corresponding C₂H₂ experiments. This does leave open the question of why C–H cleavage is significant on Cu(111), whereas it is negligible on Pd(111). As noted above, experiment shows that acetylene is substantially more strongly re-hybridized when adsorbed on Cu(111) (C–C bond length intermediate between sp² and sp³) compared to its behavior on Pd(111) (bond length very close to sp²). For gaseous ethylene and ethane, the corresponding sp³ and sp² C–H bond strengths are 423 and 448 kJ/mol, respectively.⁴⁰ Therefore it seems possible that the relative ease of C–H cleavage on Cu(111) is due to a significantly weaker C–H bond in the adsorbed molecule.

It has been established^{23,24,41} that benzene formation on Pd(111) occurs as follows



with step 3 being rate limiting for the appearance of gaseous benzene. The present results are consistent with a similar sequence of steps, except that either step 1 or step 2 is rate limiting (benzene formation is surface reaction rate limited—see Figure 1a). And in the present case formation of butadiene

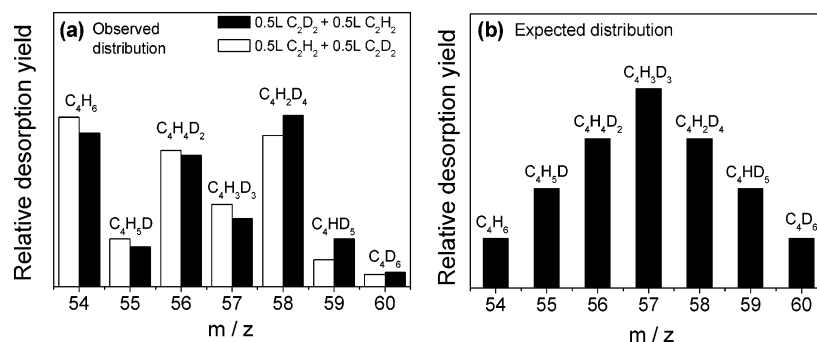


Figure 3. Observed relative desorption yields showing the product distribution of butadiene isotopomers following sequential dosing of 0.5 L of C₂D₂ then 0.5 L of C₂H₂ (black bars), and vice versa (white bars) on Cu(111) at 120 K. (b) Expected isotopomer distribution for random coupling of pairs of acetylene molecules to yield C₄H₄, C₄H₂D₂, and C₄D₄, followed by reaction with H_a and D_a.

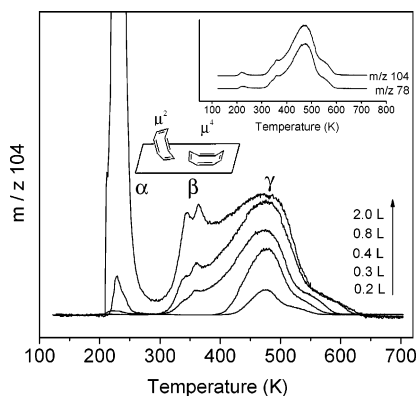


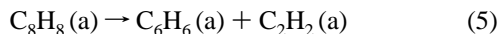
Figure 4. Temperature-programmed desorption of COT (m/z 104) from Cu(111) following adsorption at 120 K, as a function of initial exposure. Insets show superimposability of m/z 104 and 78 spectra for the case of 0.4 L of COT, and two possible configurations corresponding to the β state.

provides direct chemical evidence for the initial formation of a C4 metallocycle:



Figure 1a shows that benzene and butadiene, both of which are surface reaction rate limited, appear at distinctly different temperatures. Therefore reaction 1 cannot be rate limiting for both channels. The simplest rationalization, though not the only one, would be that (1) is fast, with (2) and (4) being rate limiting for benzene and butadiene, respectively. Note that the line shapes for butadiene and COT, though somewhat similar, are not identical (Figure 1a). Identical line shapes would of course imply (4) cannot be the rate-limiting step for butadiene formation.

The observation of COT shows that the catalytic coupling chemistry of copper is richer than that of palladium and its alloys with Au and Sn. Its formation also raises the possibility that in the present case an alternative pathway to benzene formation exists, via ring contraction.



This process is known to occur on Pt(111).²⁵ To examine this possibility, we performed TPR experiments by directly adsorbing COT on Cu(111) and Figure 4 shows a series of COT desorption spectra obtained following adsorption at 120 K. Note that m/z 78 is an important ion in the mass spectra of both benzene and COT. Control experiments showed that the m/z 78 desorption spectra always mirrored the m/z 104 spectra exactly, with an intensity ratio corresponding to that of COT, and an example is shown in the inset to Figure 4. The key conclusion is that no benzene was formed, nor were any other reaction products observed—COT adsorbed and desorbed reversibly. Therefore we may discard reaction 5. The population of the weakly bound α state increased without limit, indicating that it was a physisorbed species—confirmed by the activation energy to desorption (~ 60 kJ/mol) which is close to that reported by Hostetler et al. for desorption of COT multilayers from Pt(111).²⁵ As to the γ state, comparison with earlier studies of COT adsorption on Ag(110)⁴² and on Pt(111)²⁵ suggests that it corresponds to flat-lying COT with D_{8h} symmetry. The β state comprises two components with the onset of desorption occurring at ~ 300 K. This coincides with the onset temperature for reactively formed COT (Figure 1b) implying that appearance of gaseous reactively formed COT is a desorption rate-limited process.

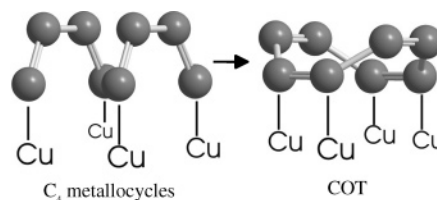


Figure 5. Formation of μ^4 COT via cycloaddition of two C_4 metallocycles.

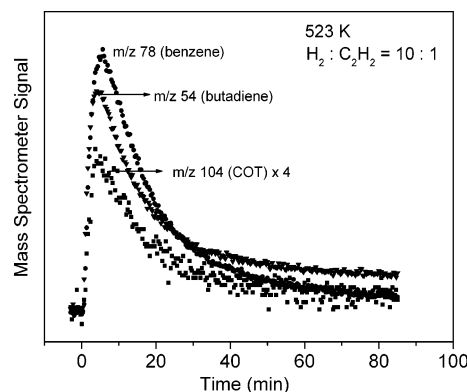


Figure 6. Single pass catalytic reactor data. Time dependence of principal products.

Gaseous COT adopts a tub conformation;⁴³ HREEL spectra show that COT multilayers are also characterized by tub geometry.⁴² Therefore a plausible explanation for the two components of β adsorbed COT is that they correspond to tub COT adsorbed with μ^2 and μ^4 geometries (see Figure 4). In regard to reactively formed COT, a possible mechanism based on a concerted pericyclic [4+4] cycloaddition reaction⁴⁴ between two tilted C_4 metallocycles is illustrated in Figure 5. The product of this reaction is a μ^4 adsorbed COT molecule.

Catalytic Measurements at Atmospheric Pressure. Acetylene coupling has been previously studied at atmospheric pressure over dispersed metal catalysts consisting of pure Pd,¹⁵ Pd/Au,¹⁶ and Pd/Sn.¹⁷ In every case, it was found that the behavior paralleled that observed with the corresponding single-crystal model systems studied by TPR in UHV—strongly suggesting that in these cases the UHV data do indeed shed light on the reaction mechanisms that operate at elevated pressure. The measurements were carried out in the presence of added H_2 (to inhibit carbon deposition) and the products were benzene, cyclohexene, and cyclohexane accompanied by much smaller amounts of butenes. These are in good accord with initial formation of C_4H_4 and C_6H_6 , followed by some hydrogenation of both. It was therefore of interest to carry out corresponding measurements with a Cu catalyst at atmospheric pressure to determine whether the significantly different chemistry found under UHV conditions for Cu compared to Pd and Pd-based systems was reflected in the behavior of the practical dispersed catalyst. The $\alpha\text{-Al}_2\text{O}_3$ supported catalyst consisted of large particles of Cu (~ 45 nm) whose external surfaces are likely to be dominated by (111) facets. As in the earlier studies, H_2 was co-fed along with the acetylene to moderate carbon deposition, which, as we shall see, was considerable. Figure 6 shows the time dependence of the principal products obtained (benzene, butadiene, COT) at 523 K in the case of a 10:1 hydrogen:acetylene mixture. In addition to these, much smaller amounts of butene, ethylene, and C_n ($n = 10, 12, 14$) hydrocarbons were detected, although we were unable to determine the identity of the latter. The rapid falloff of the initial activity to a lower quasi steady state value is consistent with extensive deposition of

hydrocarbonaceous species. The principal point is that the main features of the overall behavior of a practical Cu catalyst at atmospheric pressure were in good agreement with the model system operated under UHV conditions. They also differ markedly from that of Pd-based catalysts which themselves are mimicked by the corresponding model systems in a vacuum. In the present instance, the chief qualitative difference between the UHV and atmospheric pressure data is that in the latter case the relative yield of butadiene is much higher. This is unsurprising—one would expect much more hydrogenation of the C_4H_4 intermediate in the presence of a high pressure of hydrogen. Clearly, copper is a much more versatile acetylene coupling catalyst than palladium, and it seems likely that the formation of high molecular weight oligomers was responsible for the rapid deactivation that occurred under the chosen conditions.

Conclusions

1. Under UHV conditions, acetylene trimerization on Cu surfaces is far less structure sensitive than it is on Pd surfaces. On Cu(111), in addition to benzene, acetylene yields butadiene and cyclooctatetraene as new coupling products—these are not found on Cu(100) and Cu(110).

2. No coverage threshold is observed for the onset of the coupling reactions, implying high adsorbate mobility; the appearance of gaseous benzene and butadiene is surface reaction rate limited, whereas COT is formed by a desorption rate-limited process.

3. Isotope tracing experiments show that benzene formation proceeds via a statistically random associative mechanism, whereas butadiene formation is associated with strong kinetic isotope effects, probably associated with C–H cleavage. Compared to Pd(111), the effectiveness of Cu(111) in promoting C–H cleavage is ascribed to greater rehybridization of the C–C bond in adsorbed acetylene resulting in weakening of the C–H bond.

4. The catalytic behavior at atmospheric pressure of ~ 45 nm copper particles dispersed on α -alumina is consistent with the reactive properties of the (111) crystal face in a vacuum. It therefore seems likely that the elementary reaction steps that describe the surface chemistry of the model system are also important under practical conditions.

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