

Surface Chemistry

Dehydrogenative Homocoupling of Alkyl Chains on Cu(110)

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Abstract: Through the interplay of high-resolution scanning tunneling microscopy imaging and density functional theory calculations, the stepwise dehydrogenative homocoupling of alkyl chains on Cu(110) is demonstrated, proceeding from the intact chain, via the dehydrogenative intermediates, to the formation of the divers final coupling products.

Recently, the construction of nanostructures through covalent interlinking of molecular building blocks on metal surfaces has been among the most active areas of surface science research.^[1-4] Various chemical reactions have been employed on surfaces, including, for example, the Ullmann reaction,^[5-9] Bergman cyclization,^[10,11] decarboxylative polymerization,^[12] azidealkyne click reaction,^[13, 14] Glaser coupling,^[15, 16] imine formation,^[17,18] and dimerization of N-heterocyclic carbenes.^[19] In particular, on-surface synthesis involving hydrocarbons has aroused particular attention due to interest in fabricating novel carbon nanostructures and nanomaterials. In this respect, dehydrogenative or dehalogenated homocoupling of reactants with C–H or C–X (X = halogen) groups has proven a feasible route.^[6, 15, 20-22] Among these on-surface reactions, Ullmann coupling has been the most extensively studied for constructing aromatic molecular structures.^[5-9] In addition, debrominated homocoupling of terminal alkanes, that is, the on-surface Wurtz reaction, was also reported by our group very recently.^[23] Moreover, carbon–carbon coupling through direct C–H activation of hydrocarbons involving different hybridized carbon centers has also been reported as an alternative route.^[15, 20-22] In this manner, linear alkane polymerization, which is of particular scientific and industrial interest, has been achieved on an Au(110) surface where the growth of polymerized alkyl chains is confined in the (1×3) reconstruction grooves of Au(110).^[21] It is nevertheless still of general interest to explore the feasibility of dehydrogenative homocoupling of alkyl chains on other surfaces, especially comparatively simpler surfaces than the reconstructed Au(110).

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to a biphenyl backbone (4-decyl-1,1'-biphenyl, DBP; Figure 1). The Cu(110) substrate was employed because of its relatively high chemical reactivity and there is no surface reconstruction comparing to Au(110).^[24-26] From the interplay of high-resolution scanning tunneling microscopy (STM) imaging and density functional theory (DFT) calculations, we have demonstrated the step-by-step homocoupling of DBP from the intact alkane, via a dehydrogenative intermediate, to the final coupling product on Cu(110). Besides the two typical dimers (products of terminal C-C coupling and terminal/penultimate C-C coupling), which are similar to the coupling products of alkyl chains on Au(110),^[21] other more complicated coupling motifs are also formed, which is probably due to the less constrained nature of the Cu(110) surface in comparison to Au(110). Further DFT calculations on the energy barriers of C-H activation at terminal methyl and penultimate methylene groups have also been performed to verify the experimental results. These findings will complement our understanding of the dehydrogenative coupling of alkanes on metal surfaces, and may provide an alternative way to produce alkanes with higher molecular weight.

In this study, we chose an alkane molecule that is connected

After deposition of the DBP molecules on Cu(110) at room temperature, the molecules self-assembled into well-ordered chain structures (Figure 1a), from which two specific growth directions could be identified. From the high-resolution STM image shown in Figure 1b, we could further distinguish the submolecular details as indicated by the equally scaled molecular models. It is seen that the DBP molecules adopt a closepacked fashion with their alkyl chains interdigitating with each other to maximize their intermolecular van der Waals forces, which is similar to the previous studies on the self-assembly of



Figure 1. Large-scale (a) and close-up (b) STM images showing the formation of the self-assembled interdigitated structure after deposition of DBP molecules on Cu(110) at room temperature. The blue arrows in (a) indicate the deviation of the self-assembled molecular chain from the white dashed line. The optimized molecular models are superimposed on the STM image for clear presentation in (b). c) Top view (upper panel) and side view (middle panel) of the DFT-relaxed model of the DBP molecule on Cu(110) and its corresponding STM image simulation (lower panel). Scanning conditions: l_t =0.7 nA; V_t = -2000 mV.

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alkyl chain groups on surfaces.^[27–28] Moreover, DFT calculations were performed on the adsorption geometry of DBP on Cu(110) (Figure 1 c), which showed a flat-lying geometry. Based on this configuration, an STM image simulation (lower panel of Figure 1 c) was calculated at the bias voltage of the experimental condition where good agreement was also achieved with the experimental results.

After annealing the DBP-covered sample to about 400 K, interestingly, we found that the self-assembled chain structures dissociate into isolated monomers (Figure 2a). As demonstrat-



Figure 2. Large-scale (a) and close-up (b) STM images showing the formation of dehydrogenated intermediates (DBP*) on Cu(110) after annealing the sample at approximately 400 K. c) Top view (upper panel) and side view (middle panel) of the DFT-relaxed model of one DBP* dehydrogenated at the terminal methyl group on Cu(110) and the corresponding STM image simulation (lower panel).Scanning conditions: I_t =0.85 nA; V_t =-1250 mV.

ed in our previous study, the debrominated alkyl radicals could be stabilized on metal surfaces by forming chemical bonds with the substrate atoms,^[23] and the radicals distributed on surfaces are very similar to the case here. Thus we infer that the isolated monomers (Figure 2b) should be assigned to the dehydrogenative intermediates (DBP*), which are bonded to the Cu(110) surface. To afford further insight into this intermediate state, we performed DFT calculations on the adsorption geometries of DBP* on Cu(110) and the corresponding STM image simulations, and the energy barriers of dehydrogenation from the terminal methyl and penultimate methylene groups on Cu(110). As shown in Figure 3, the activation barrier for the C-H bond dissociation from the terminal methyl group was calculated to be approximately 1.5 eV, and that from the penultimate methylene group approximately 1.6 eV, which are slightly higher than those on Au(110) (ca. 1.33 eV).^[21]

Considering the similar chemical environments and registries with respect to the substrate, the activation barriers for the C–H bond dissociation from the other methylene groups should be similar to that from the penultimate methylene group. Therefore, the dehydrogenative intermediates shown in Figure 2 could be assigned to various alkyl radicals bonding to the Cu(110) surface. As an example, a DFT-relaxed model of one DBP* molecule dehydrogenated at the terminal methyl group is shown in Figure 2c, and the other possible dehydrogenative intermediates are listed in Figure S1 (see the Supporting Information). From the STM image simulations shown in Figure S1, we conclude that the very similar electronic charac-



ommunication

Figure 3. DFT-calculated energy diagrams for C–H activation of the simplified molecule at the terminal (deH-1) methyl and penultimate (deH-2) methylene groups on Cu(110). The structural models of the initial state (IS), the transition states (TS-deH-1 and TS-deH-2), and the final states (FS-deH-1 and FS-deH-2) are shown below.

teristics of these dehydrogenative intermediates make them indistinguishable from the STM image (Figure 2 b).

After further annealing the sample to approximately 430 K, we detected a series of coupling products (Figure 4). In particular, two typical dimer structures could be identified (Figure 4b, c) that are analogous to those formed on Au(110), where these two dimers were attributed to terminal C–C coupling and terminal/penultimate C–C coupling, respectively.^[21] More interestingly, we also observed other, more complicated, coupling products including different dimers, trimers, and tetramers (with the proposed models; Figure 4d–j). However, the exact coupling positions are difficult to assign. From the comparison of the comparatively smooth Cu(110) surface with the reconstructed Au(110) surface, we conclude that, besides the



Figure 4. a) STM image showing the formation of various coupling products on Cu(110) after annealing the sample at approximately 430 K. Two typical dimer structures: b) Terminal C–C coupling; c) terminal/penultimate C–C coupling, together with their corresponding DFT-relaxed geometries on Cu(110) and STM image simulations. d–j) Other, more complicated, products with the newly formed C–C bonds highlighted in red: d, e) dimers; f–i) trimers; j) tetramer, together with the proposed structural models. Scanning condition: I_t =0.85 nA; V_t =-1250 mV.

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intrinsic chemical nature of the surface, the surface geometry also plays an important role in the process of on-surface dehydrogenative coupling of alkyl chains. Moreover, from our experiments, we identified that the final coupling process is the rate-limiting step for the homocoupling of alkane molecules, which allows us to observe the dehydrogenative intermediates. As shown by the STM images, some alkyl groups were covalently linked to the biphenyl moieties. To afford a comprehensive pictures of homocoupling of alkane molecules on metal surfaces, we also performed the experiments on other two surfaces, Cu(100) and Ag(110). We observed similar coupling products on Cu(100) (see the Supporting Information, Figure S2), whereas for the case of Ag(110), the alkane molecules desorbed after annealing the sample at approximately 400 K and no coupling process was detected (see the Supporting Information, Figure S3).

In conclusion, through high-resolution UHV-STM imaging and DFT calculations, we have demonstrated the dehydrogenative homocoupling of alkyl chains on the Cu(110) surface. In comparison to the reconstructed Au(110) surface, a step-bystep reaction pathway from the intact molecules, via the dehydrogenative intermediates, to the final diverse coupling products was observed on Cu(110), whereas the homocouplings of alkene and alkyne molecules were proposed to follow a different pathway.^[15,20] In comparison to the selectively dehydrogenative coupling of quaterphenyl molecules,^[22] there is no preferential C site with respect to C-H activation of alkyl chains on Cu(110), which results in the formation of diverse coupling products of alkane molecules on Cu(110). These findings complement our understanding of the dehydrogenative coupling of alkanes on different metal surfaces, which may shed light on the preparation of low-dimensional carbon nanomaterials or novel hydrocarbons with high molecular weight.

Experimental Section

All STM experiments were performed in a UHV chamber (base pressure 1×10^{-10} mbar) equipped with a variable-temperature "Aarhus-type" STM,^[29,30] a molecular evaporator, and standard facilities for sample preparation. The DBP molecules (purchased from Alfa Aesar, purity >98%) were deposited by thermal sublimation onto the metal substrates after the substrates were well prepared. The STM measurements were performed in a typical temperature range of 100–150 K. All calculations were performed based on periodic density functional theory (DFT) by using VASP code.^[31,32] The projector-augmented wave method was used to describe the interaction between ions and electrons,^[33, 34] and the PBE exchange-correlation functional was employed,^[35] van der Waals (vdW) corrections to the PBE density functional were also included using the DFT-D2 method reported Grimme.^[36] The energy cut-off for the plane-wave basis was set to 400 eV, and a 2×1×1 k-point grid determined by the Monkhorst-Pack method was used. The simulated STM image was obtained by using the Tersoff–Hamann method.^[37] The climbing-image nudged elastic band was applied to locate the transition state.^[38] The atomic structures were relaxed until the forces on all unconstrained atoms were \leq 0.03 eVÅ⁻¹ for both geometry optimization and transition-state search.

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