Electronic Supporting Information (ESI)

Mechanistic Investigations of the Au Catalyzed C-H Bond Activations in on-surface synthesis

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1. Reaction Pathways

Figure S1 shows the reaction pathways of C-H bond activations on Au ad-atoms on the Au(111) and the Au(110), in which the ad-atoms on the surfaces are the active sites towards the C-H bond activations.



Fig. S1. Reaction pathways and the energy profiles in the C-H bond activation reactions, depicting top and side views of initial state (IS), transition state (TS), and final state (FS) on the (a) Au(111) with an ad-atom and (b) Au(110) with an ad-atom. The C, H, Au ad-atoms and Au in surfaces were labeled in grey, white, pale yellow and yellow circles, respectively.

The reaction pathways of the C-H bond activations on the surface steps of the Au(111) and the Au(110)-(1×3) reconstructed surface are shown in Fig. S2. The active site of the surface steps is determined based on the previous study, in which the Au atoms at the step are served as the catalysts towards C-H bond activations.¹ According to the experimental results, the Au atoms in the groove of the Au(110)-(1×3) surface serve as the active sites, as shown in Fig. S2.²



Fig. S2. Calculated reaction pathways and the energy profiles of C-H bond activations, depicting top and side views of initial state (IS), transition state (TS), and final state (FS) on (a) the step of the Au(111) surface and (b) the Au(110)-(1×3) reconstructed structure. The white and the grey circles refer to the C and H atoms in hexane. The first layer, the second layer and the bulk atoms in Au surfaces are presented with pale

yellow, yellow and orange circles, respectively.

The highest activation barrier of the C-H bond in the hexane is observed on the Au(111) terrace. As shown in Fig. S3, the terminal C-H bond in the physisorbed hexane is activated by one Au atom in the Au(111) terrace yielding an activation barrier of 1.98 eV.



Fig. S3. The reaction pathways of C-H bond activation over the bare Au(111) surface, depicting top and side views of initial state (IS), transition state (TS), and final state (FS). The C, H, Au ad-atoms and Au in surfaces were labeled in grey, white, pale yellow and yellow circles, respectively.

Table S1 summarizes distances between C-H, C-Au and H-Au during the process of C-H bond activations and the C-Au-H angles at the transition states. From the initial state to the transition state, the C-H bonds were elongated and the distances between C-Au and H-Au were shortened simultaneously. Passing over the transition states, the C-Au distance was continuously decreasing and finally the C-Au bonds were formed. Table S1. The distances of C-H, C-Au and H-Au during the catalytic process and the C-

Bond Lengths	Surfaces	Au+Au(110)	Au+Au(111)	Au(110)-(1×3)	Step Au(111)	Au(111)
Initial State	C-H/Å	1.12	1.10	1.10	1.10	1.10
	C-Au/Å	3.09	3.25	3.75	3.62	3.72
	H-Au/Å	2.30	2.72	3.33	3.08	2.93
Transition State	C-H/Å	2.95	2.54	2.53	1.75	2.48
	C-Au/Å	2.13	2.16	2.16	2.29	2.26
	H-Au/Å	1.61	1.62	1.75	1.57	3.56
Final State	C-H/Å	4.82	4.15	2.58	2.71	3.30
	C-Au/Å	2.09	2.12	2.17	2.16	2.15
	H-Au/Å	3.26	2.18	1.76	1.80	3.37
C-Au-H Degree at Transition State		103.28	83.25	79.88	49.69	43.59

Au-H angles at the transition state.

The correlation between the catalytic activation barriers and the C-Au-H angles in the transition state is plotted in the Fig. S4. The catalytic activities of the Au catalysts increase with the decrease of the C-Au-H angles at the transition states, indicating that the mechanisms of the catalytic activities are closely related to the electronic structures and the bonding nature of the catalysts.



Fig. S4. The C-H bond activation barriers go up with the increase of the C-Au-H angle

of the transition states. The red, green, blue, cyan and violet cube correspond to the Au ad-atom on the Au(110), the Au ad-atom on the Au(111), the Au(110)-(1×3) surface, the step of Au(111) surface and the Au(111) terrace, respectively.

2. The effective *d*-band center

To obtain a full understanding of the relationship between the *d*-band center and the catalytic activity of Au catalysts, we investigated the influence of the various energy windows on the effective *d*-band centers. As shown in Fig. S5, the catalytic activities increase with the approaching of the *d*-band centers to the Fermi level, which showed an agreement of the previous studies.³ However, such relationship is relative weak because the *d*-band centers of the Au(110)-(1×3) reconstruction surface, the steps of the Au(111) surface and the Au(111) surface are not distinguishable. Similar relation between the catalytic activities and the *d*-band centers is observed, in which the *d*-band center is calculated by integrating the every electrons in Au- $\frac{5d}{z^2}$ orbital. Such weak relationships suggest that the un-hybridized energy levels would decrease the accuracy in the prediction of the catalytic activities based on the conventional *d*-band center model. Thus a more accurate descriptor is highly desired.



Fig. S5. The plots of the C-H activation barriers against the effective *d*-band center (drawn as cube), against the *d*-band center of Au- $\frac{5d}{z^2}$ orbital (drawn as the circle) and against the *d*-band center of Au-5*d* orbital (drawn as the triangle), in which effective *d*-band center exhibits the strongest positive correlation to the C-H bond activation barriers.

3. The Projected Density of States (PDOS) of Au catalysts

The electronic properties were investigated by the PDOS analysis of the Au active sites. Fig. S6 shows that the difference of DOS between the bulk Au atoms and the active sites in surfaces is mainly caused by the $5^{d}z^{2}$ orbital, indicating that the $5^{d}z^{2}$ orbital plays a vital role in the catalysis. Therefore, the effective *d*-band center is calculated by averaging the electronic energy in $5^{d}z^{2}$ orbital in the given energy window (from -6.80 eV to the Fermi level).



Fig. S6. The PDOS of (a) 5*d* orbital and (b) $5^{d}z^{2}$ orbital of the active sites in Au catalysts and bulk Au atoms.

4. The *d*-band width

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Catalysts	5 <i>d</i> -orbital f_d	$5d_{z^2}$ orbital f_d	$5d_{z^2}$ orbital effective f_d
Au ad-atom on Au(110)	0.87	0.86	0.87
Au ad-atom on Au(111)	0.83	0.84	0.84
Au(110)-(1×3)	0.86	0.85	0.87
Step of Au(111)	0.83	0.84	0.83
Terrace of Au(111)	0.83	0.83	0.84

Table S2. The *d*-band fillings (f_d) of active Au sites

Table S2 lists the *d*-band filling in different orbitals and difference energy windows, in which no significant difference in the f_d . Therefore, the *d*-band fillings should have negligible effect on the effective *d*-band width. Thus for the Au based catalysts, the effective *d*-band width is only associated with the value of the effective *d*-band center.

5. The STM analysis

For the experimental evidence, the polymerizations of the linear alkane ($C_{32}H_{66}$) are carried out on Au(110)-(1×3) reconstructed surface and Au(111) surface. Polymerization reactions take place at the steps and the terraces of the Au(111) surface after annealing to 500 K and 540 K, respectively (Fig. S7a and S7b). Of important, at the annealing temperature of 500 K, the polymerization reactions take place at the steps of the Au(111) surface while the self-assembled structures on the terrace remain their integrity, indicating that the Au atoms in the step possess a superior activities towards the terrace atoms. Such sequence of the polymerization temperatures agrees well with the calculated effective *d*-band centers.



Fig. S7. The C₃₂H₆₆ polymerized products (a) at the steps of the Au(111) surface after annealing to 500 K with the self-assembled structure on the terrace of Au(111) and (b) on the terraces of the Au(111) surface after annealing to 550 K. Parameters are V_b = -2.00 V, I_t = 10.00 pA, 85 × 85 nm² for all the images.

6. The C-H activations on the 2D Au-Pc

The C-H bond activations of the hexane on the 2D Au phthalocyanine (Au-Pc) surface are investigated to confirm the validity of the effective *d*-band center model. As seen in Fig. S8, both hexyl radical and hexane molecule are weakly adsorbed on the 2D Au-Pc surface, in which the adsorption heights are as large as 3.81 Å and 4.09 Å, respectively. Such large C-Au distances indicate a weak interaction between the catalyst and the adsorbate. Furthermore, the energy difference between the initial state and the final state are calculated as: $\Delta E = E_{FS} - E_{IS}$, which is given as 3.38 eV. Such energy difference is larger than the energy barriers of the C-H bond activations on the Au surfaces. Therefore, it is reasonable to deduce that the 2D Au-Pc surface exhibits poor activity towards C-H bond activations.



Fig. S8. The calculated adsorption configurations of (a) the hexyl radical and (b) the hexane molecule on the 2D Au-Pc surface. As seen, the corresponding C-Au distances are 3.81 Å and 4.09 Å, respectively. Such large adsorption distance indicates very weak adsorbate-surface interactions (c) The co-adsorption of a H atom and a 1-hexyl radical

on the 2D Au-Pc surface, which can be regarded as the final state (FS) of C-H bond dissociation of hexane. For such H dissociation, the relative energy difference is 3.38 eV, indicating a very large energy barrier. Color codes: Au (yellow), N (blue), H (white), C in the surface (grey) and C in the hexane molecule (brown).

References

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