

苯乙烯在 Ag(111)和 Ag(110)表面环氧化反应结构敏感性的 理论研究

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Theoretical Investigation of Structure-Sensitivity of Styrene Epoxidation on Ag(111) and Ag(110) Surfaces

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Micro-kinetic model

To make a quantitative analysis and compare with the experimental findings more directly, the micro-kinetic analysis of the styrene epoxidation has been also performed. Here the favorable reaction path via linear oxametallacycle is chosen to perform the micro-kinetic analysis, and thus the simulation explicitly contains the reaction steps of M1, M5~11 (Table 2) and the reverse reaction process is not considered because the corresponding reaction rates are about nine orders of magnitude smaller than the forward reaction. The reaction step of styrene adsorption (M1) was assumed to be pre-equilibrium, and other steps were treated by steady-state approximation.

During the styrene epoxidation process, the catalyst surface will be covered by different species, which can be represented by the formulas: $\theta_{C_8H_8} = K_1 \times P_{(C_8H_8)} \times \theta_*$,

$\theta_{OMMS(2)} = \frac{k_5 \times \theta_{C_8H_8} \times 0.375}{k_6 + k_7 + k_8}$, where 0.375 is the oxygen coverage on both Ag(111) and

Ag(110) surfaces. The coverage of different products can be calculated by the

formulas: $\theta_{C_8H_8O} = \frac{k_6 \times \theta_{OMMS(2)}}{k_{10}}$, $\theta_{C_6H_5CH_2CHO} = \frac{k_7 \times \theta_{OMMS(2)}}{k_{11}}$,

$\theta_{C_6H_5CHCHO} = \frac{k_8 \times \theta_{OMMS(2)}}{k_9}$. The total surface coverage is defined to 1, so we can obtain

the free site of the surface. So the free active site is $\theta_* = 1 - \theta_{C_8H_8} - \theta_{OMMS(2)} - \theta_{C_8H_8O} - \theta_{C_6H_5CH_2CHO} - \theta_{C_6H_5CHCHO} - 0.375$. Finally, the formation

rate of different products can be obtained by: $R_{(C_8H_8O)} = k_{10} \times \theta_{C_8H_8O}$,

$R_{(C_6H_5CH_2CHO)} = k_{11} \times \theta_{C_6H_5CH_2CHO}$, $R_{(C_6H_5CHCHO)} = k_8 \times \theta_{OMMS(2)}$. The relative selectivity is

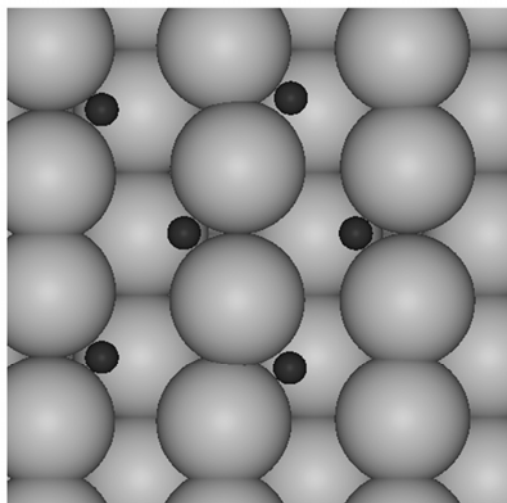
defined as: $S = \frac{R_{(C_8H_8O)}}{(R_{(C_8H_8O)} + R_{(C_6H_5CH_2CHO)} + R_{(C_6H_5CHCHO)})}$. The partial pressure of styrene

is 5×10^{-6} Pa, which is used to simulate the UHV condition. The simulation results showed that the formation rate of styrene oxide on Ag(111) and Ag(110) is near zero although the selectivity towards the formation of styrene oxide on Ag(111) surface is higher than that on Ag(110) surface. By checking the parameters used in the micro-kinetic model analysis, it was found that the binding energy of styrene plays a key role in controlling the styrene epoxidation process. It should be noted here that the present calculated adsorption energy of styrene on Ag(110) and Ag(111) surface is smaller than the experimental results. The temperature programmed desorption

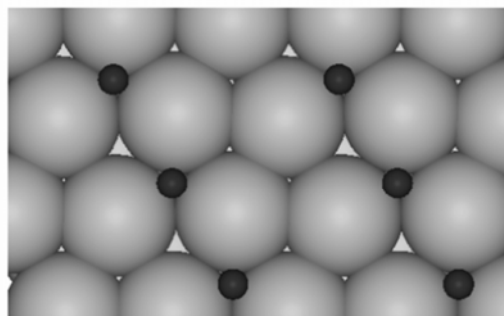
experiment performed by Zhou and Madix ¹ showed that the desorption temperature of styrene is 230 K on Ag(110) and 200 K on Ag(111), and the estimated binding energy is 0.62 eV on Ag(110) and 0.53 eV on Ag(111) if the desorption process is assumed to be first order and the pre-exponential factor is 10^{13} s^{-1} . After the correction of dispersion effect ², the adsorption energy of styrene is quite close to the experimental values. In order to compare with the experimental results directly, we used the experimental binding energy of styrene ¹ (namely, 0.62 eV on Ag(110) and 0.53 eV on Ag(111)) during the micro-kinetic model analysis. Moreover, the ZPE correction is also considered for the activation barriers of different reaction steps (See Table 2). Figure 8 shows the temperature-dependence of relative selectivity for epoxidation process on Ag(111) and Ag(110) surface. The relative selectivity of styrene epoxidation on Ag(111) surface(0.38) is much higher than on Ag(110) surface(0.003), and the reaction rate of styrene oxide formation on Ag(111) is $10^{-5} \text{ site}^{-1} \cdot \text{s}^{-1}$ at the reaction temperature of 280 K. The possible reasons for the lower selectivity on Ag(110) is that *the energy barrier for the styrene epoxidation formation is higher than the formation of phenyl acetaldehyde and combustion intermediate*(Scheme 1 as well as Table 2).

References:

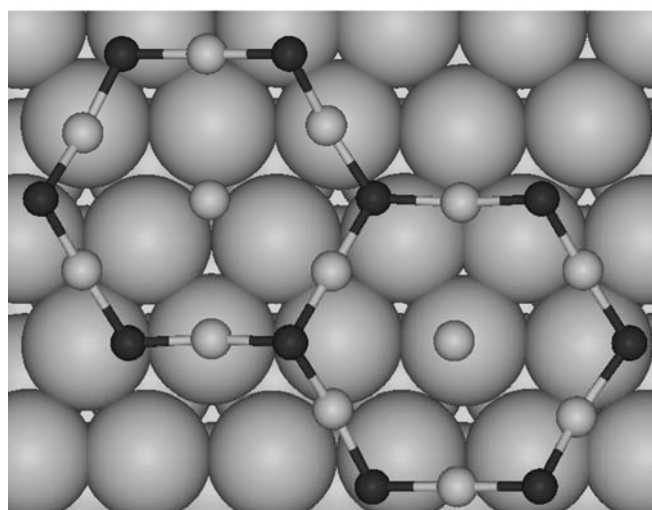
- (1) Zhou, L.; Madix, R. J. *Surf. Sci.* **2009**, *603*, 1751.
- (2) Tonigold, K.; Groß, A. *J. Chem. Phys.* **2010**, *132*, 224701.



110



111



surface oxide Ag_{11}O_6

Fig.S1 The top view of surface models used in our calculation

The light grey and black sphere represent Ag and oxygen atom, respectively.

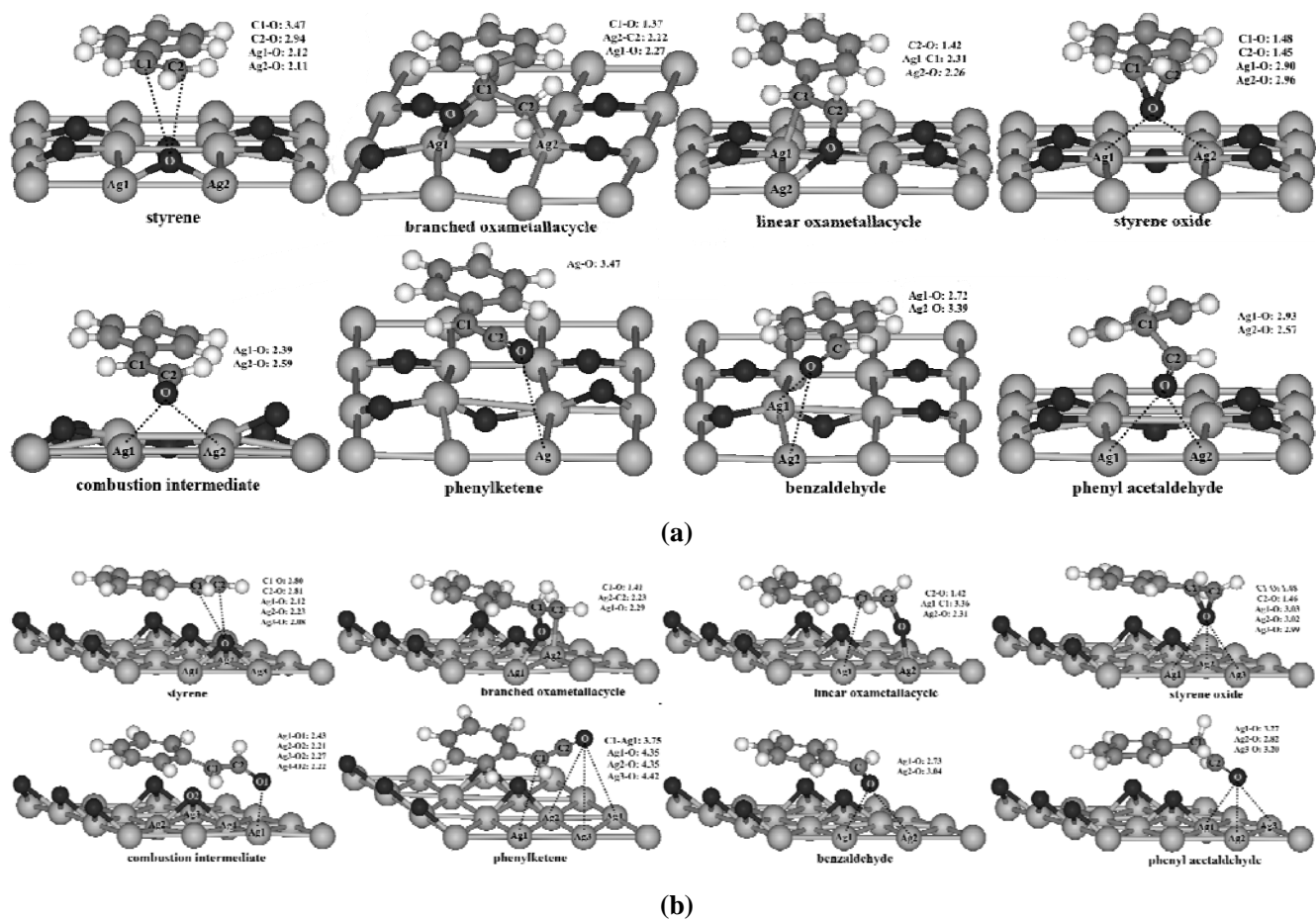


Fig.S2 Adsorption configuration of possible species during styrene epoxidation process on Ag(110) (a) and Ag(111) (b)

The dark grey and white sphere represent carbon and hydrogen atom, respectively.

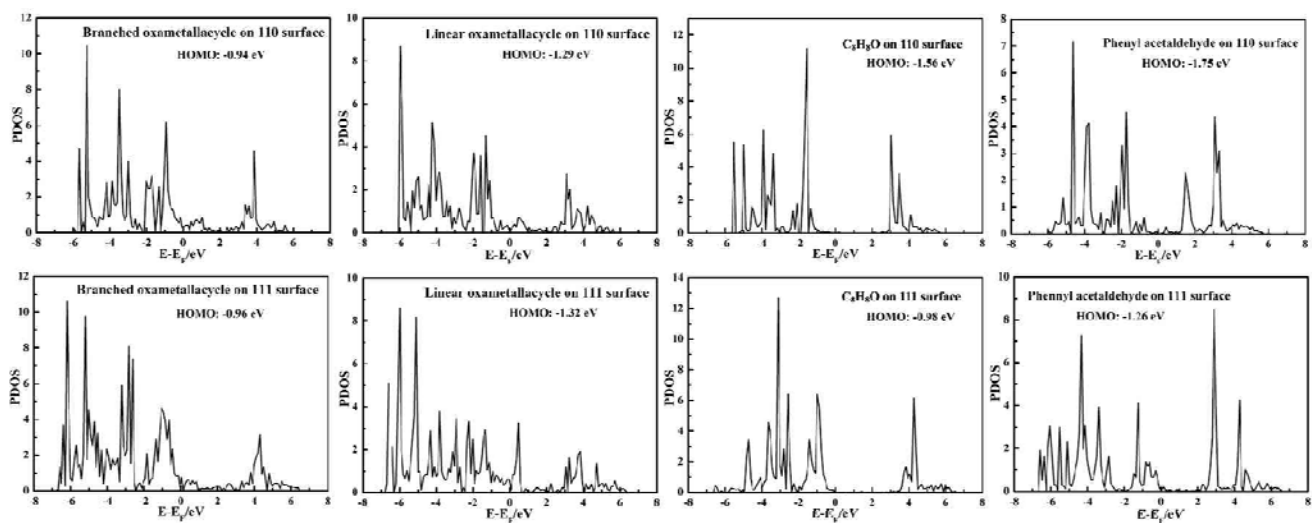


Fig.S3 PDOS onto molecular orbital of different species on different surfaces

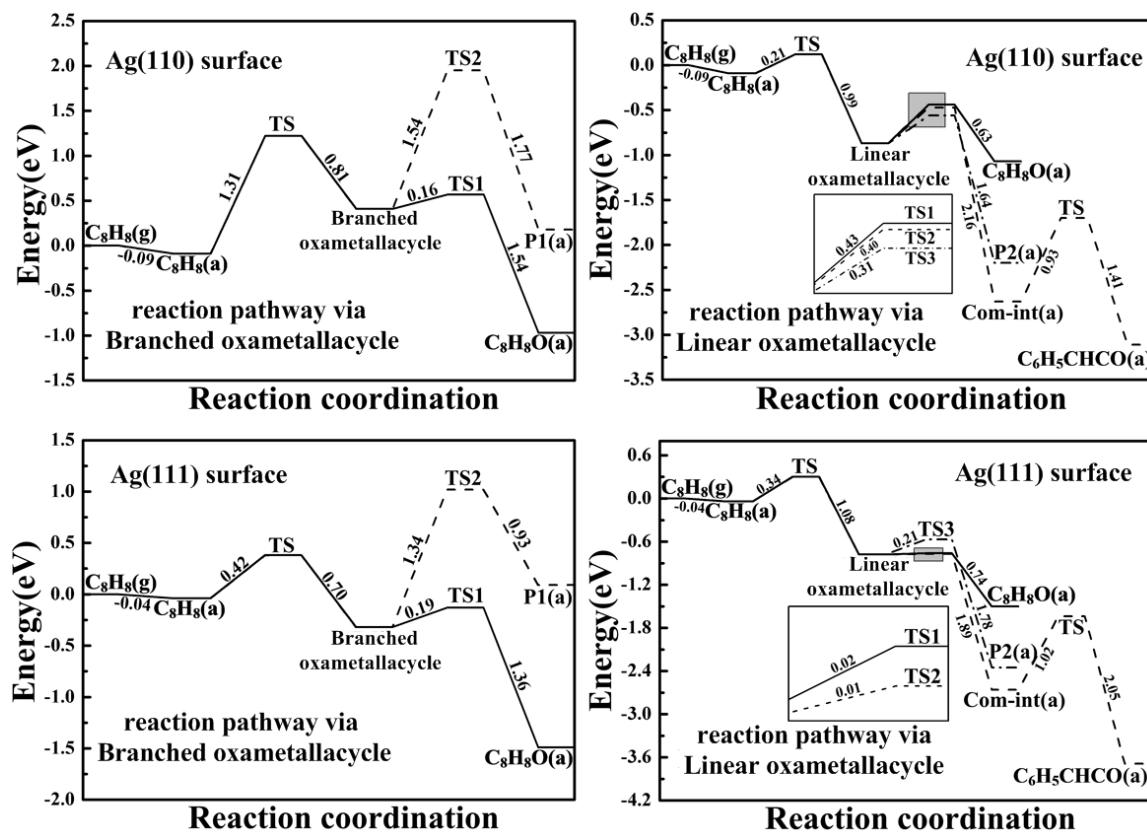
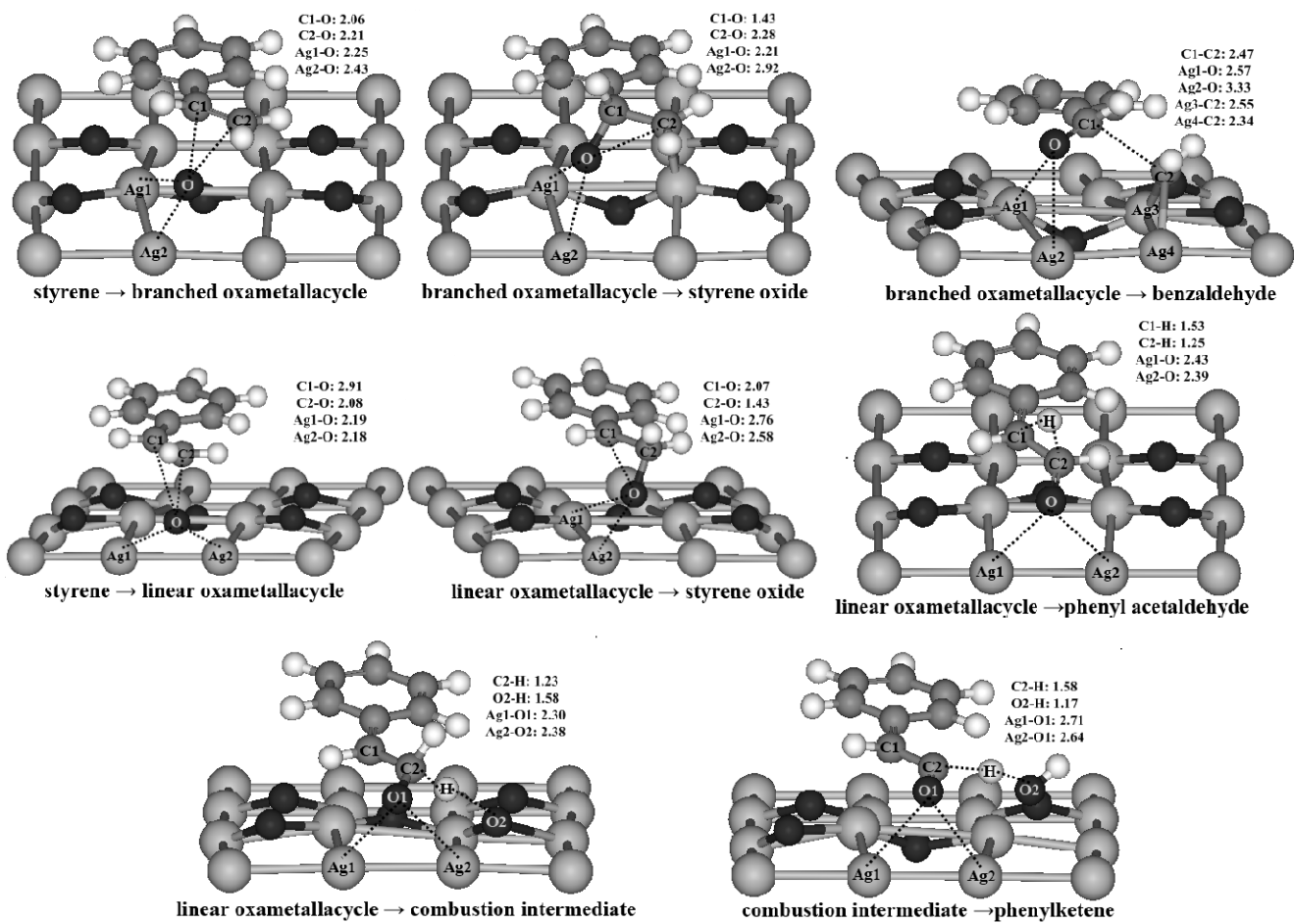
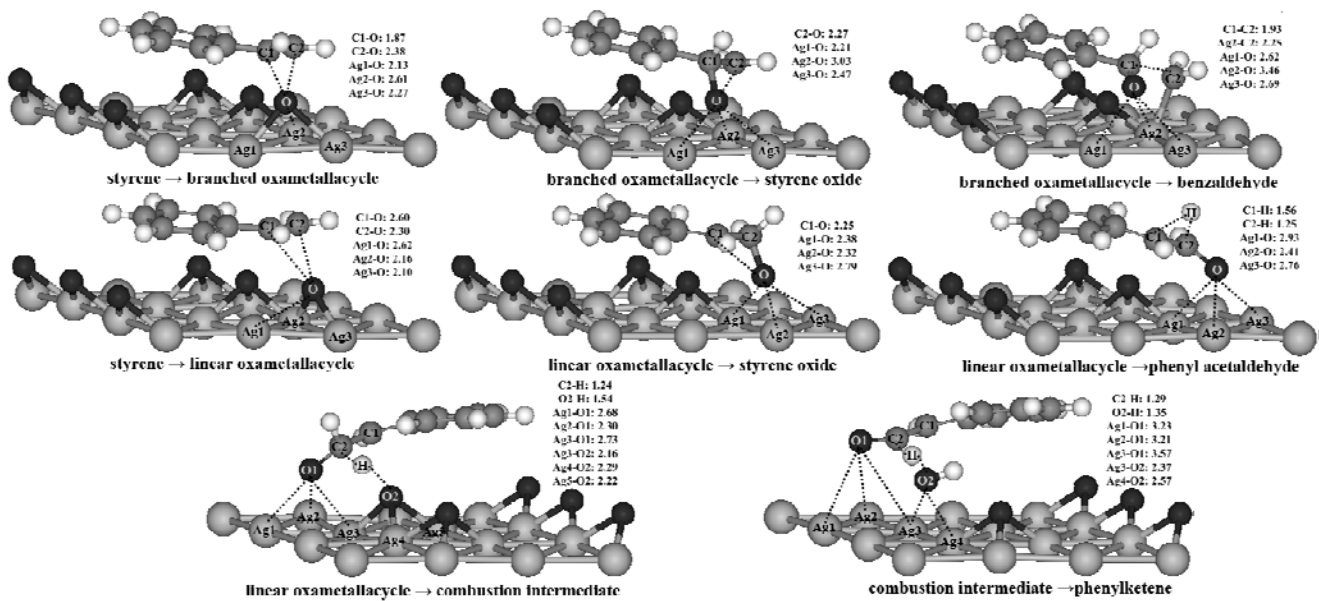


Fig.S4 The reaction coordination of styrene epoxidation on different surfaces via different pathways



(a)



(b)

Fig.S5 The TS configuration of different reaction steps on different surfaces

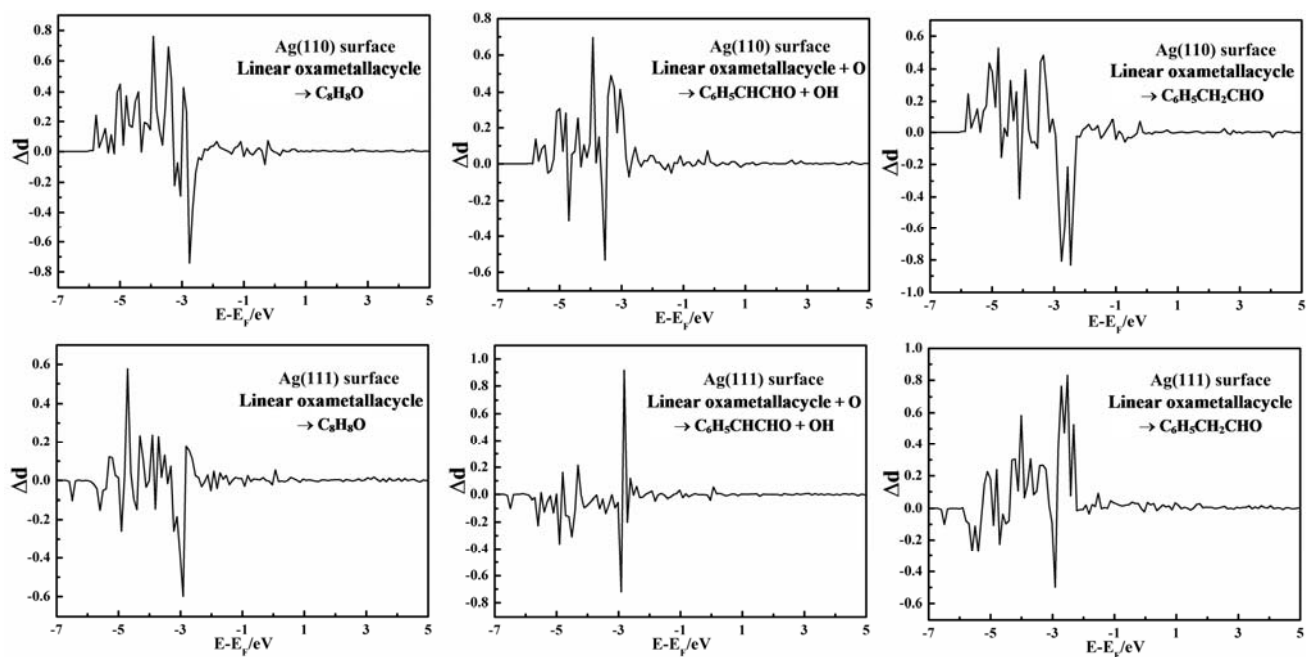


Fig.S6 The normalized density of states onto surface Ag atoms at the TS of different reaction steps

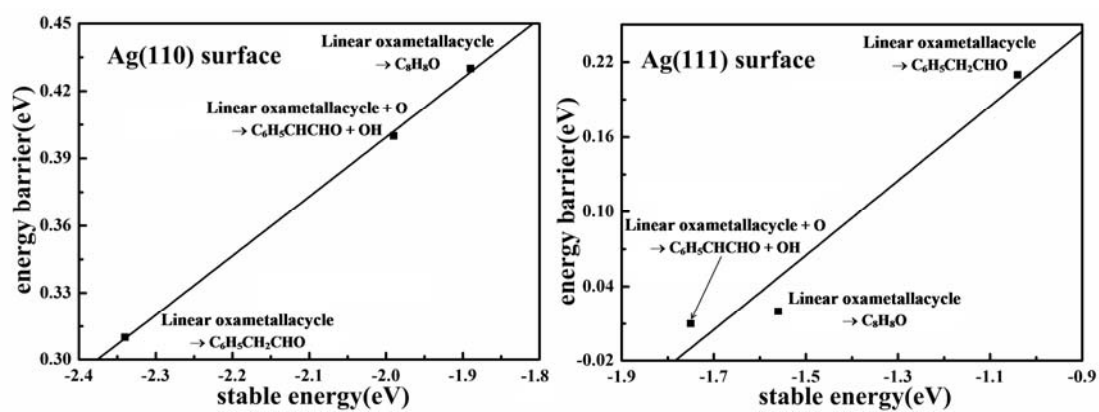


Fig.S7 The relationships between energy barriers and calculated stable energy