Hydrogenation Mechanism of Carbon Dioxide and Carbon Monoxide on the Ru(0001) Surface: A Density Function Theory Study

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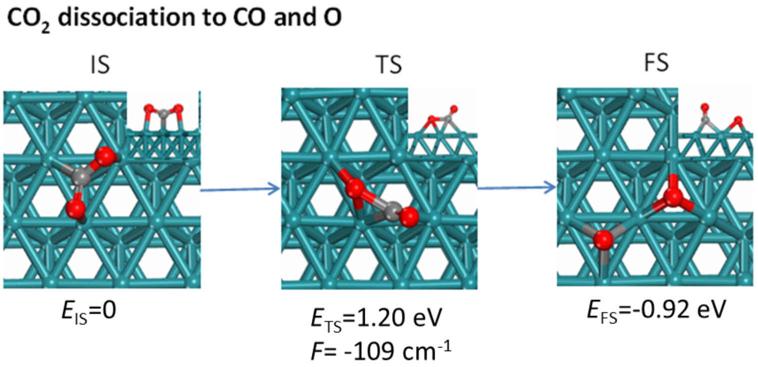


Figure S1 Direct dissociation of CO_2 to CO and O on the Ru(0001) surface (cyan, Ru; red, O; gray, C), denoted with the relative energies of initial state (IS), transition state (TS), final state (FS) of this reaction and the imaginary frequency (*F*) of the TS.

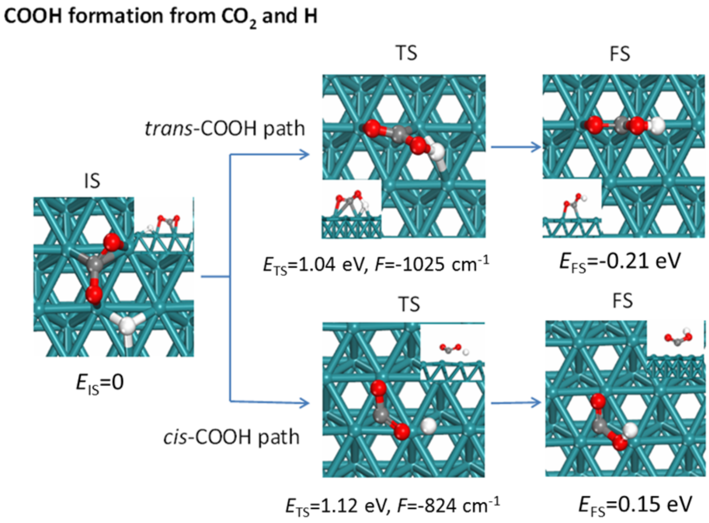


Figure S2 The formation of *trans*- and *cis*-COOH species from CO_2 and H on the Ru(0001) surface (cyan, Ru; red, O; white, H; gray, C), denoted with the relative energies of IS, TS, FS of the two reactions and the imaginary frequencies (*F*) of the TS.

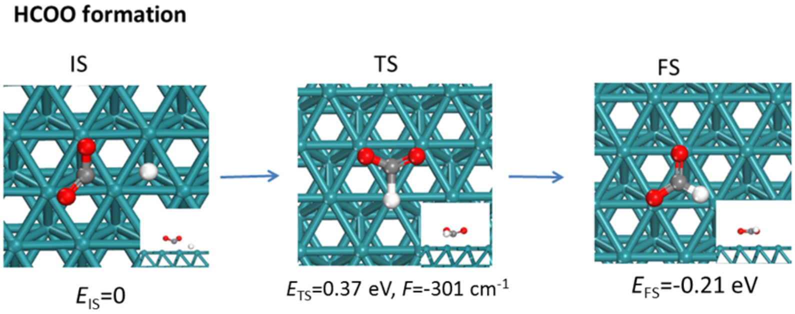


Figure S3 The formation of HCOO from CO_2 and H on the Ru(0001) surface (cyan, Ru; red, O; white, H; gray, C), denoted with the relative energies of IS, TS, FS of this reaction and the imaginary frequency of the TS.

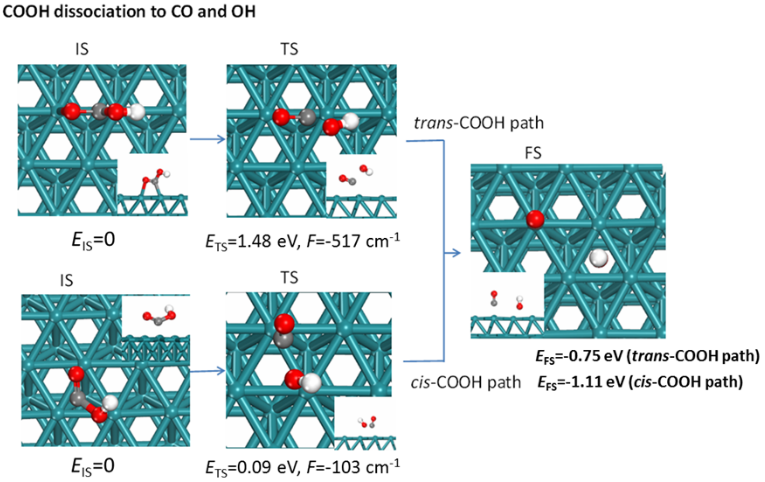


Figure S4 The dissociation of *trans*- and *cis*-COOH to CO and H on the Ru(0001) surface (cyan, Ru; red, O; white, H; gray, C), denoted with the relative energies of IS, TS, FS of the two reactions and the imaginary frequencies of the TS.

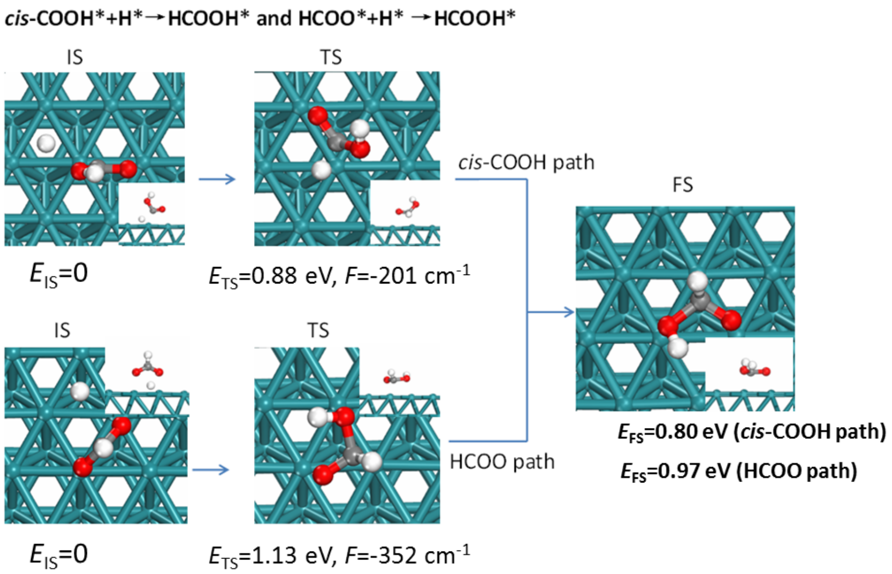


Figure S5 The formation of HCOOH from CO and H on the Ru(0001) surface (cyan, Ru; red, O; white, H; gray, C), denoted with the relative energies of IS, TS, FS of the two reactions and the imaginary frequencies of the TS.

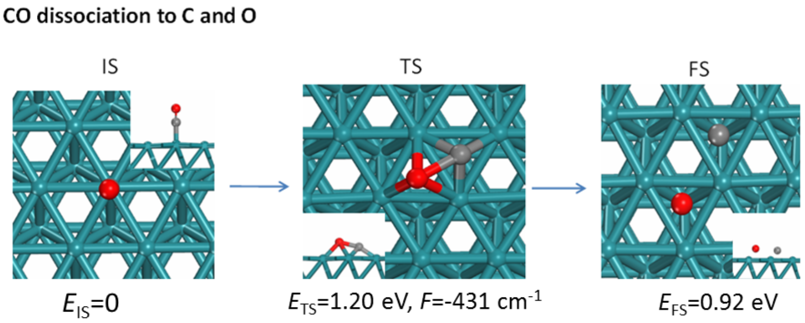


Figure S6 Direct dissociation of CO to C and O on the Ru(0001) surface (cyan, Ru; red, O; gray, C), denoted with the relative energies of IS, TS, FS of this reaction and the imaginary frequency of the TS.

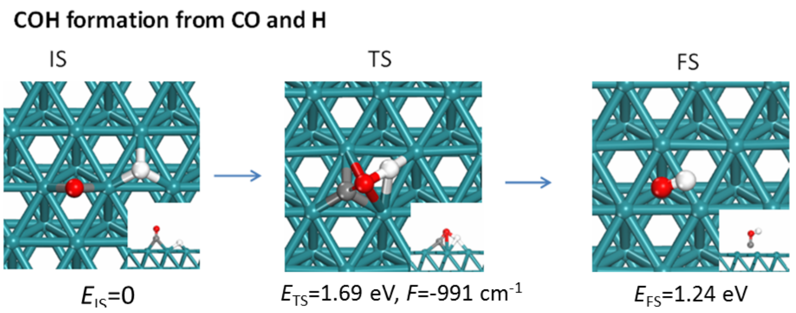


Figure S7 The formation of COH from CO and H on the Ru(0001) surface (cyan, Ru; red, O; white, H; gray, C), denoted with the relative energies of IS, TS, FS of this reaction and the imaginary frequency of the TS.

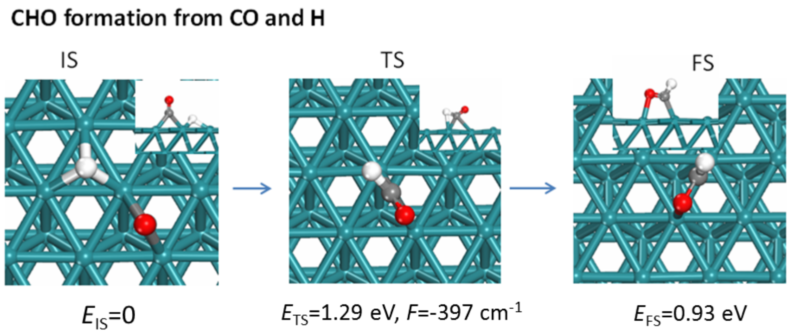


Figure S8 The formation of CHO from CO and H on the Ru(0001) surface (cyan, Ru; red, O; white, H; gray, C), denoted with the relative energies of IS, TS, FS of this reaction and the imaginary frequency of the TS.

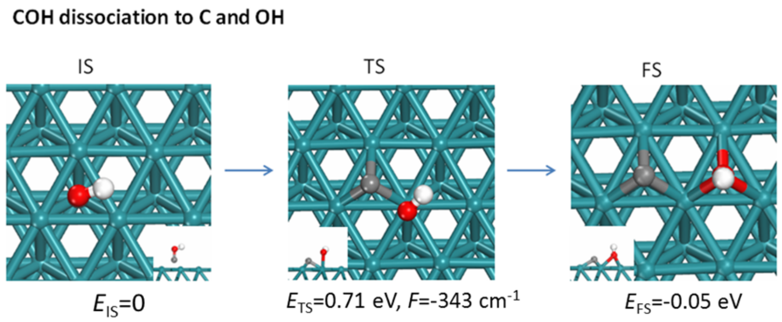


Figure S9 The dissociation of COH to C and OH on the Ru(0001) surface (cyan, Ru; red, O; white, H; gray, C), denoted with the relative energies of IS, TS, FS of this reaction and the imaginary frequency of the TS.

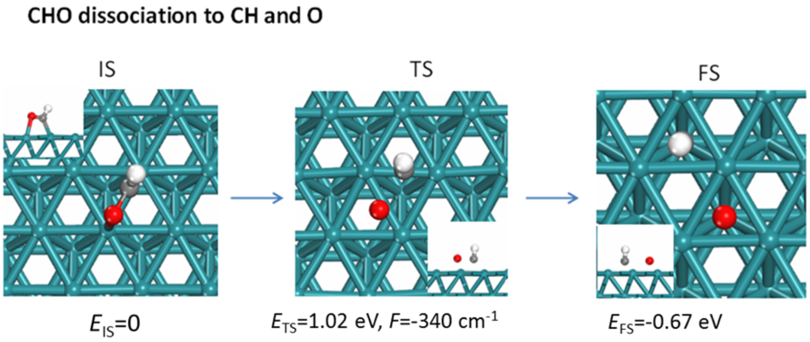


Figure S10 The dissociation of CHO to CH and O on the Ru(0001) surface (cyan, Ru; red, O; white, H; gray, C), denoted with the relative energies of IS, TS, FS of this reaction and the imaginary frequency of the TS.

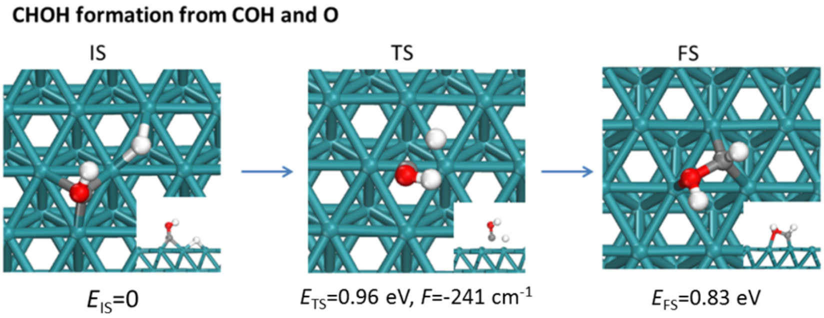


Figure S11 The formation of CHOH from COH and H on the Ru(0001) surface (cyan, Ru; red, O; white, H; gray, C), denoted with the relative energies of IS, TS, FS of this reaction and the imaginary frequency of the TS.

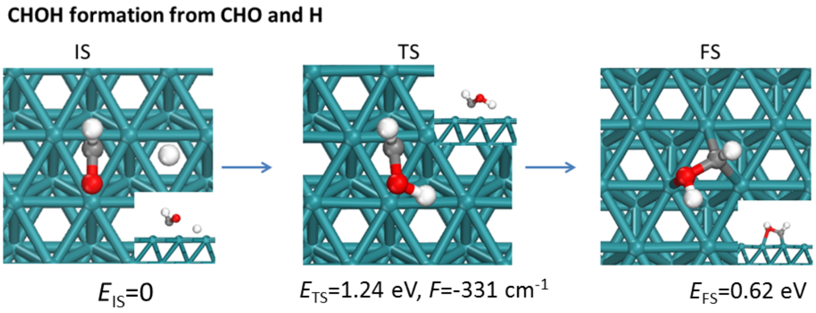


Figure S12 The formation of CHOH from CHO and H on the Ru(0001) surface (cyan, Ru; red, O; white, H; gray, C), denoted with the relative energies of IS, TS, FS of this reaction and the imaginary frequency of the TS.

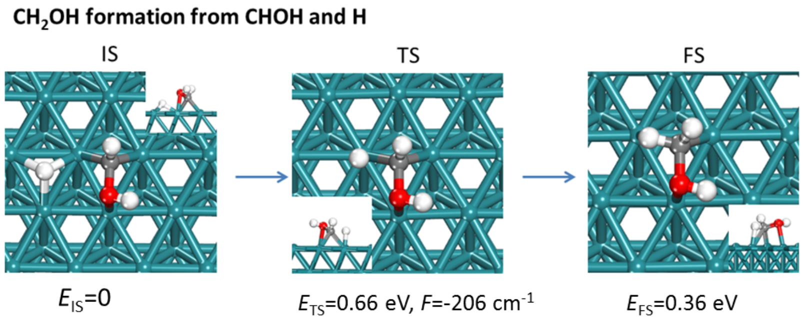


Figure S13 The formation of CH_2OH from CHOH and H on the Ru(0001) surface (cyan, Ru; red, O; white, H; gray, C), denoted with the relative energies of IS, TS, FS of this reaction and the imaginary frequency of the TS.

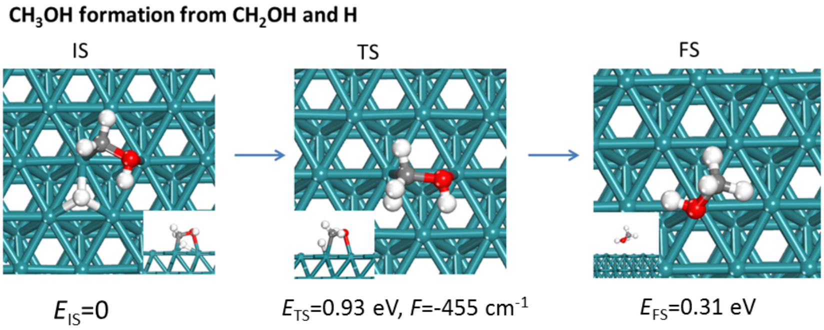
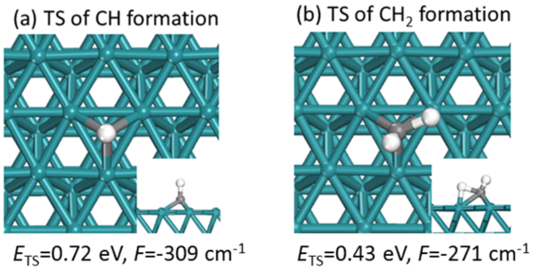
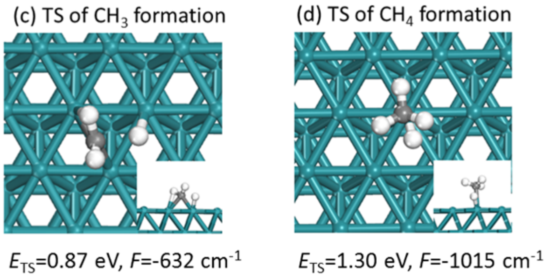


Figure S14 The formation of CH_3OH from CH_2OH and H on the Ru(0001) surface (cyan, Ru; red, O; white, H; gray, C), denoted with the relative energies of IS, TS, FS of this reaction and the imaginary frequency of the TS.


(a) TS of CH formation

(b) TS of CH$_2$ formation


(c) TS of CH$_3$ formation

(d) TS of CH$_4$ formation

Figure S15 The TS of CH (a), CH_2 (b), CH_3 (c), and CH_4 (d) formation (cyan, Ru; red, O; white, H; gray, C), denoted with the relative energies and the imaginary frequency of the TS.

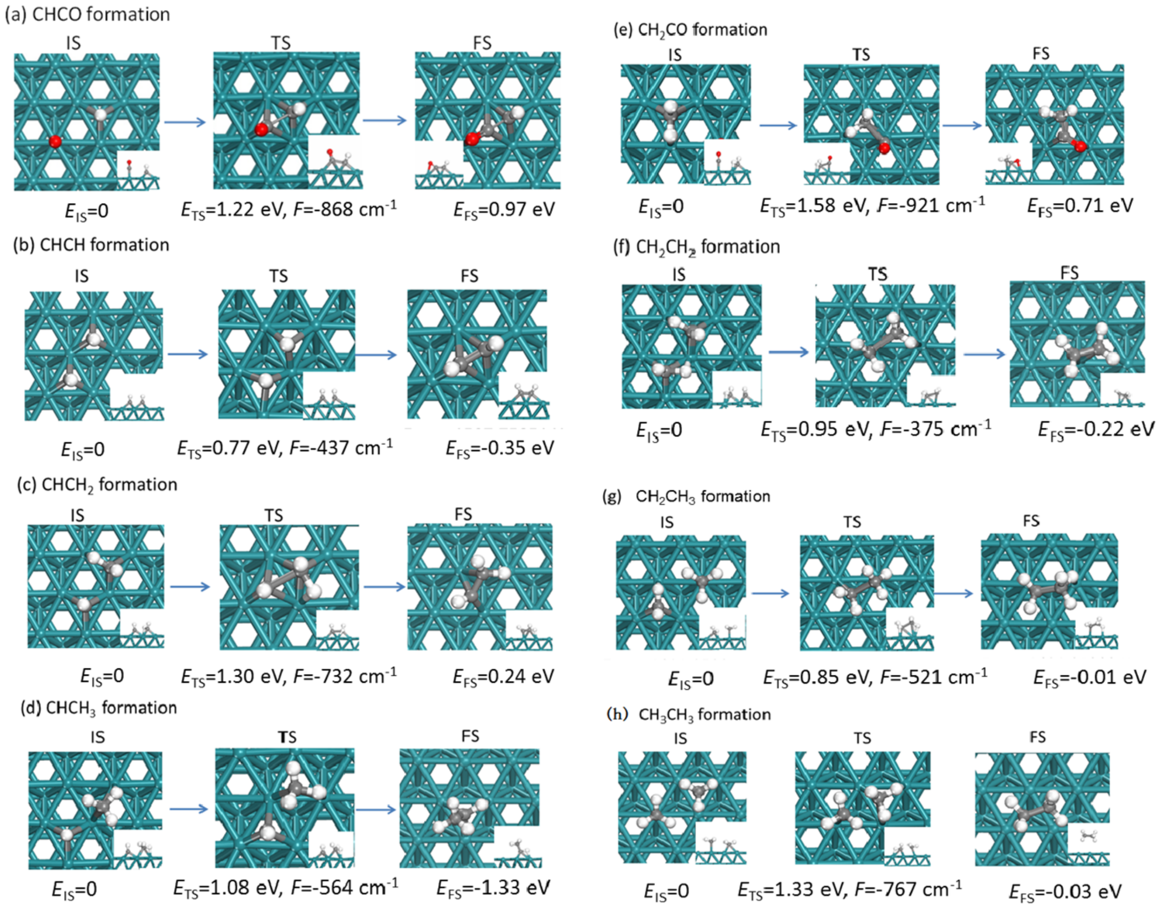


Figure S16 C–C coupling reactions on the Ru(0001) surface (cyan, Ru; red, O; white, H; gray, C), denoted with the relative energies of IS, TS, FS of the eight reactions and the imaginary frequencies of the TS.

The Theory for Kinetic Analysis: According to experimental observations, dissociatively adsorbed H is in equilibrium with H_2 in the gas phase:

$$H_2(g)+2^* \rightleftharpoons 2H^*$$

and

$$K^0 = e^{-\Delta G^0/RT} = \frac{\theta_H^2}{\frac{p_{H_2}}{p^0}\theta_*^2} \tag{1}$$

where K^0 is the standard equilibrium constant; ΔG^0 is the standard difference of Gibbs free energy; p^0 is the standard pressure, and θ_{H} and θ_* are the coverages of adsorbed hydrogen and free surfaces site, respectively.

According to our calculations, the H adsorption energy is about −0.80 e V with respect to H_2 in gas state. Therefore it can be estimated that the standard equilibrium constant K^0 is about 1 when T > 300K. The value of $\theta_{\mathrm{H}}/\theta_*$ can be viewed as a function of the hydrogen partial pressure. Assuming that the methane desorption is irreversible, the formation of methane from C and H can be described as

$$\mathrm{C^*+H^*} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{CH^*+{*}} \quad \text{(i)}$$

$$\mathrm{CH^*+H^*} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{CH_2^*+{*}} \quad \text{(ii)}$$

$$\mathrm{CH_2^*+H^*} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{CH_3^*+{*}} \quad \text{(iii)}$$

$$\mathrm{CH_3^*+H^*} \xrightarrow{k_4} \mathrm{CH_4(g)+{*}} \quad \text{(iv)}$$

At steady state, we can obtain

$$r^{\mathrm{net}} = r_1 - r_{-1} = r_2 - r_{-2} = r_3 - r_{-3} = r_4 \tag{2}$$

$$r_i = k_i \theta_{CH_{i-1}} \theta_{\mathrm{H}} \tag{3}$$

and

$$r_{-i} = k_{-i} \theta_{CH_i} \theta_* \tag{4}$$

where r_i (r_{-i}) is the forward (reverse) reaction rate of each hydrogenation step; r_{net} is the net reaction rate; k_i (k_{-i}) is the forward (reverse) reaction rate constant, and θ_{CH_i} is the coverage of surface species CH_i (i=0, 1, 2, 3). The formation of CH_4 from CH_3 and H (step iv) requires the highest barrier in the sequence hydrogenation of C steps. Combining Eqs. (2)−(4), we can obtain

$$r_{-3} >> r_4 \tag{5}$$

and thus

$$r_{-3} \approx r_3 >> r_{\mathrm{net}} \tag{6}$$

Similarly, we have

$$r_{-2} \approx r_2 >> r_{\mathrm{net}} \tag{7}$$

and

$$r_{-1} \approx r_1 >> r_{\mathrm{net}} \tag{8}$$

Eqs. (6)–(8) suggest that the hydrogenation reactions are in quasi-equilibrium state on the Ru(0001) surface. As a result, the coverages of C, CH, CH_2 and CH_3 on the surface have the following relationship:

$$\frac{\theta_{\mathrm{CH}_i}\theta_*^i}{\theta_{\mathrm{C}}\theta_{\mathrm{H}}^i} = e^{-E_i/(RT)} \tag{9}$$

and therefore,

$$\theta_{\mathrm{CH}_i} = e^{-E_i/(RT)}\theta_{\mathrm{C}}\frac{\theta_{\mathrm{H}}^i}{\theta_*^i} = e^{-E_i/(RT)}\theta_C t^i, i = 1, 2, 3 \tag{10}$$

where θ_* is the coverage of free surface site; t represents $\theta_{\mathrm{H}}/\theta_*$; E_i is the relative stability of CH_i with reference to the C atom and equal to the energy difference between adsorbed CH_i and C. It should be noted that the ratio of H to free surface site coverage, t, is related to the H_2 partial pressure: $t = \sqrt{K^0 p_{\mathrm{H}_2}/p^0}$ (K^0 is the standard equilibrium constant for H_2 dissociation on Ru surface; p^0 is the standard pressure; p_{H_2} is the H_2 partial pressure). If p_{H_2} varies in the range 1−100 atm, the value of t can be estimated between 1 and 10. Assuming that p_{H_2} does not change significantly during the reaction, t can be expected to be a constant.

For the C−C coupling reactions, the reaction rates can be expressed as

$$r_i = k_i\theta_{\mathrm{CH}_x}\theta_{\mathrm{CH}_y} \tag{11}$$

The reaction rates of C–C coupling reactions can be calculated using transition-state theory, which are expressed as

$$r_{\mathrm{CH}_i+\mathrm{CH}_j} = A_1 e^{-(E_{a,i}/RT)} \theta_{\mathrm{CH}_i} \theta_{\mathrm{CH}_j}, \quad i,j = 1-3 \tag{12}$$

and the net reaction rate of the sequence carbon hydrogenation reactions is

$$r_{\mathrm{net}} = r_i - r_{-i} = r_4 = A_2 e^{-(E_{a,3}/RT)} \theta_{\mathrm{CH}_3} \theta_{\mathrm{H}}, \quad i = 1-3 \tag{13}$$

where A_1 and A_2 are the pre-exponential factors (which are usually assumed to be 10^{13} s^{-1});[1] $E_{a,i}$ is the energy barrier; T is the temperature.

References:

(1) J. Chen and Z. P. Liu, *J. Am. Chem. Soc.*, 2007, **130**, 7929.