

Supporting Information

Hydrocarbon Chain Growth and Hydrogenation on V(100): A Density Functional Theory Study

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1. The AIMD simulations.

In AIMD simulations of CH_x adsorbed on V(100), an energy cutoff of 300 eV was used and the spin polarization was not considered. The AIMD simulations were performed more than 20 ps at three temperatures of 300, 500 and 800 K with a time step of 2 fs.¹ The smaller time step of 1 fs was also tested and gave similar results. The length of the simulation time in the present work may be not enough for strict statistical significance, but should be sufficient to capture the essential feature of the dominant processes.

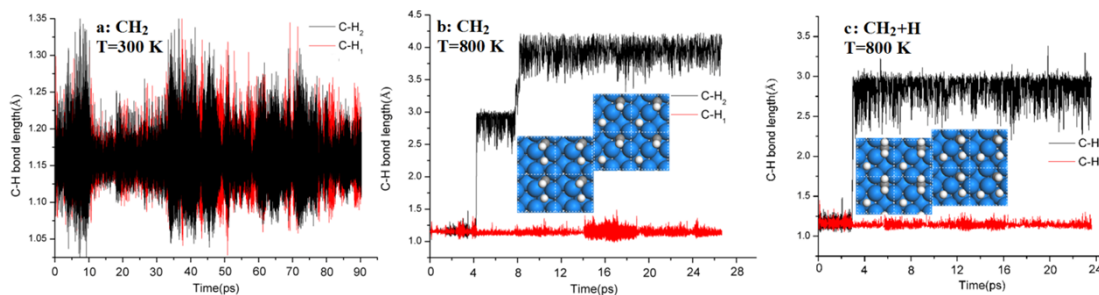


Fig. S1 The C–H bond length (shortest one on the surface) as a function of simulation time during AIMD simulations of $\text{CH}_2/\text{V}(100)$.

2. The vibrational entropy

The vibrational entropy term at the harmonic approximation² for molecules on $\text{V}(100)$ is obtained as follows:

$$S_{\text{vib}} = k_B \sum_{i=1}^s \left[\ln \left(\frac{1}{1 - \exp\left(\frac{-h\nu_i}{k_B T}\right)} \right) + \frac{-h\nu_i}{kT} \times \frac{\exp\left(\frac{-h\nu_i}{k_B T}\right)}{1 - \exp\left(\frac{-h\nu_i}{k_B T}\right)} \right]$$

3. Microkinetic model

We applied the microkinetic modeling technique³⁻⁵ to examine the hydrocarbon chain growth and hydrogenation on $\text{V}(100)$. Elementary steps included in the microkinetic model are summarized in Table 2 (see the main manuscript). Step **1 and 2** were assumed to be in equilibrium and the equilibrium constant K was estimated according to $K = \exp[-(\Delta E_{\text{ads}} - T\Delta S)/k_B T]$, in which ΔE_{ads} is the minus adsorption energy of CO and H_2 on $\text{V}(100)$, while ΔS is the entropy change of them induced by adsorption. The other steps were described by the forward and/or reward rate. On the basis of our result, the dissociation of CH at high H coverage was inhibited and the dissociation of CH_2 is not observed at low temperature, the reverse of reaction 4 was neglected and the reverse of reaction 5 was neglected at low temperature (300-500 K).

Rate constants for steps **3–16** were predicted using transition state theory (TST)⁶, e.g., rate constant for step N can be described as follows

$$k_N = A \exp(-E_{a,N} / k_B T)$$

where $E_{a,N}$ is the activation barriers for the step N, T is temperature and A is the prefactor, respectively. The equilibrium constant K_N can be described as follows

$$K_N = \exp(-\Delta H_N / k_B T)$$

where ΔH_N is the reaction energy for the step N. The coverage of CO and H are $\theta_{CO} = p_{CO} K_1 \theta_*$ and $\theta_H = (p_{H_2} K_2)^{1/2} \theta_*$, respectively. Other surface species including C, CH, CH₂ and CH₃ can be described according to the steady-state approximation as summarized below, where the production and consumption rates of each species are assumed to be equal:

$$1. \frac{d\theta_C}{dt} = r_{3f} - r_{4f} = k_{3f} \theta_{CO} \theta_* - k_{4f} \theta_C \theta_H = 0 \quad (3)$$

$$2. \frac{d\theta_{CH}}{dt} = r_{4f} - r_{5f} = k_{4f} \theta_C \theta_H - k_{5f} \theta_{CH} \theta_H = 0 \quad (4)$$

$$3. \frac{d\theta_{CH_2}}{dt} = r_{5f} - r_{6f} + r_{6r} = k_{5f} \theta_{CH} \theta_H - k_{6f} \theta_{CH_2} \theta_H + k_{6r} \theta_{CH_3} \theta_* = 0 \quad (5)$$

$$4. \frac{d\theta_{CH_3}}{dt} = r_{6f} - r_{6r} + r_{7f} = k_{6f} \theta_{CH_2} \theta_H - k_{6r} \theta_{CH_3} \theta_* + k_{7f} \theta_{CH_3} \theta_H = 0 \quad (6)$$

From eq. 1 – 6, we can obtain surface coverages of C, CH, CH₂ and CH₃ as the function of θ_* .

From the definition of the equilibrium constant K_N , we can obtain the coverage of C₂H_y. For example:

$$K_8 = \frac{\theta_{CC}\theta_*}{\theta_C\theta_C}$$

So $\theta_{CC} = K_8\theta_C\theta_C/\theta_*$

Table S1. The coverage of species on V(100) at considered experimental condition ($P_{CO} = 4$ atm, $P_{H_2} = 8$ atm and T = 300-800 K).

species	Coverage/ θ_*			
	300 K	500 K	800 K	800 K(including step 5r)
CO	2.40E+45	3.57E+22	2.50E+09	2.50E+09
H	2.88E+08	3.17E+03	3.71E+00	3.71E+00
CH ₃	4.58E+48	1.25E+26	1.70E+13	1.70E+13
CH ₂	1.51E+63	2.41E+36	1.90E+21	1.90E+21
CH	6.55E+46	9.75E+24	3.46E+12	4.69E+24
C	2.03E+45	1.21E+24	9.39E+11	9.39E+11
CC	2.30E+63	1.04E+37	7.10E+21	7.10E+21
CCH	1.97E+79	3.76E+46	6.70E+27	9.08E+39
CCH ₂	3.41E+102	1.24E+62	1.39E+39	1.39E+39
CCH ₃	2.75E+102	2.90E+60	3.20E+36	3.20E+36
CHCH	1.30E+77	1.85E+45	1.02E+27	1.87E+51
CH ₂ CH	1.58E+102	7.80E+61	1.04E+39	1.41E+51
CH ₃ CH	1.74E+97	2.20E+57	3.59E+34	4.87E+46
CH ₂ CH ₂	1.41E+106	6.89E+65	1.27E+43	1.27E+43
CH ₂ CH ₃	3.67E+107	1.30E+65	1.07E+41	1.07E+41

Table S2. The forward rate of C-C coupling steps at considered experimental condition ($P_{CO} = 4$ atm, $P_{H_2} = 8$ atm and T = 300-800 K).

species	$r_f(s^{-1})/\theta_*^2$			
	300 K	500 K	800 K	800 K(including step 5r)
CC	2.14E+58	9.92E+33	9.21E+19	2.10E+20
CCH	1.76E+71	5.56E+41	6.41E+24	9.21E+19
CCH ₂	2.79E+88	4.37E+53	7.25E+33	8.70E+36
CCH ₃	2.28E+89	4.10E+52	3.98E+31	7.25E+33
CHCH	1.23E+73	7.11E+42	3.15E+25	3.98E+31
CH ₂ CH	8.88E+88	8.76E+53	1.12E+34	5.80E+49
CH ₃ CH	1.02E+87	1.60E+51	5.24E+30	1.52E+46
CH ₂ CH ₂	8.05E+93	3.11E+58	3.25E+38	7.10E+42
CH ₂ CH ₃	2.25E+100	6.10E+60	2.12E+38	3.25E+38

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