Supporting information

Promotional effect of in-situ generated hydroxyl on olefin selectivity of Co-catalyzed Fischer-Tropsch synthesis

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Figure S1. The degree of rate control of the transition states (i.e., C_3H_6 -H and C_3H_7 -H) in the two hydrogenation steps. Microkinetic analysis was performed by using the CatMAP module¹. The reaction temperatures considered are from 325K to 425 K and gas pressure is from 1 bar to 2 bar. The experimental gas ratio is used. The different color represents the degree of rate control.

SI1 The equation derivation for turnover frequency of propene hydrogenation

The stepwise hydrogenation pathway is shown as follows.

$C_3H_6^+ * \leftrightarrow C_3H_6^*$	[1]
$H_2 + 2^* \leftrightarrow 2H^*$	[2]
$C_3H_6^* + H^* \leftrightarrow C_3H_7^* + *$	[3]
$C_3H_7^* + H^* \rightarrow C_3H_8 + 2^*$	[4]

Assume steps before the RDS are all in equilibrium.

$$\theta_{C_3H_6} = K_{C_3H_6} P_{C_3H_6} \theta_*$$

$$\theta_H = \sqrt{K_{H_2} P_{H_2}} \theta_*$$

$$\theta_{C_3H_7} = \frac{K_{hy1} \theta_{C_3H_6} \theta_H}{\theta_*}$$

The reaction rate based on the proposed RDS can be expressed as follow:

$$TOF = k_{hy2}\theta_{C_{3}H_{7}}\theta_{H} = \frac{k_{hy2}^{f}K_{hy1}\theta_{C_{3}H_{6}}\theta_{H}^{2}}{\theta_{*}} = k_{hy2}K_{hy1}K_{C_{3}H_{6}}K_{H_{2}}P_{C_{3}H_{6}}P_{H_{2}}\theta_{*}^{2}$$
$$TOF = \frac{k_{B}T}{h}exp^{[m]}(-\frac{E_{f,hy2} + E_{f,hy1} - E_{r,hy1} + E_{ads,C3H6} + E_{ads,H2}}{RT})P_{C_{3}H_{6}}P_{H_{2}}\theta_{*}^{2}$$
$$TOF = \frac{k_{B}T}{h}exp^{[m]}(-\frac{E_{eff}}{RT})P_{C_{3}H_{6}}P_{H_{2}}\theta_{*}^{2}$$

Apply site conservation on clean surface.

$$\theta_{c_{3}H_{6}} + \theta_{H} + \theta_{c_{3}H_{7}} + \theta_{*} = 1$$

$$\theta_{*} = \frac{1}{1 + K_{c_{3}H_{6}}P_{c_{3}H_{6}} + \sqrt{K_{H_{2}}P_{H_{2}}} + K_{hy1}K_{c_{3}H_{6}}P_{c_{3}H_{6}}\sqrt{K_{H_{2}}P_{H_{2}}}}$$

Table S1. d band center ε_d of first layer surface atoms before propene adsorption $\varepsilon_{d,b,}$ after propene adsorption ε_d and the difference $\Delta \varepsilon_d$

	ε _{d,b} (eV)	ε _d (eV)	$\Delta \varepsilon_{d}(eV)$
C ₃ H ₆ +H ₂ O	-1.048	-1.100	-0.052
C ₃ H ₆ +OH	-1.177	-1.131	0.046
C ₃ H ₆ +O	-0.929	-1.221	-0.292

Table S2. Bader charge of the cobalt surface for adsorption of H₂O, OH and O

	Surface with H ₂ O	Surface with OH	Surface with O
Before adsorption	0.022	0.022	0.022
After adsorption	0.016	-0.047	-0.009
Difference	-0.005	-0.069	-0.102

Table S3. Bader charge changes of the surface atoms and propene after the adsorption of propene on the clean surface and surfaces with H₂O, OH and O

	∆C1	∆C2	∆C3	Total C	Total C ₃ H ₆	H ₂ O/OH/O	Surface
C ₃ H ₆	0.040	0.022	0.206	0.268	0.290		-0.036
C ₃ H ₆ +H ₂ O	0.052	0.072	0.121	0.245	0.257	0.026	-0.032

C ₃ H ₆ +OH	0.072	0.055	0.158	0.286	0.311	0.560	-0.042
C ₃ C ₆ +O	0.066	0.035	0.162	0.263	0.222	0.954	-0.034



Figure S2. The relationship between adsorption energies of propene on different surfaces and the d band center (left) and the d band center shift (right) of the first layer surface atoms.

SI2 The calculation of free energy

Firstly, the equation to calculate the free energy is defined as shown.

$$G = E + E_{ZPE} + \Delta H^o(0 \rightarrow T) - TS$$

Where G is free energy, E refers to electronic energy determined by DFT, E_{ZPE} is zero point energy. H is enthalpy. S is entropy. T is temperature.

$$E_{ZPE} = \sum_{i=1}^{3N-6(5)} \frac{N_A h v_i}{2}$$

Where N_A and h refers to Avogadro's number and Plank's constant, and v_i and N is the frequency of the normal mode and the number of atoms.

The evaluation of enthalpy (H) and entropy (S) were shown below.

The standard entropies of gas-phase species have three contributions from transitional, rotational and vibrational modes. The detailed equations to calculate the entropy has been reported by Dumesic et.al² and can use the date from the handbook³. The enthalpy of gas phase species can be calculated as follow.

$$\Delta H(T) = H_{tran} + H_{rot} + \Delta H_{vib}$$

$$\Delta H(T) = \frac{5}{2}RT + \frac{3}{2}RT(or RT for linear molecules) + R \sum_{i}^{3N-6} \frac{x_{i}T}{e^{x_{i}} - 1}$$

Where $x_i = \frac{hv_i}{k_B T}$, k_B refers to the Boltzmann constant, v_i is normal-mode vibrational frequency.

As for the adsorbates, the enthalpy (H) is equal to the internal energy (U) with neglecting the PV contributions. It has two solutions according to the intensity of adsorption.

For weakly adsorbed species, we may assume to a first approximation that they behave as twodimensional gases and maintain all rotational and vibrational modes of the corresponding gaseous species. So the standard internal energy and the entropy change of adsorption is calculated according to

$$\Delta U_{trans, 2D}^{o}(0 \rightarrow T) - \Delta U_{trans, 3D}^{o}(0 \rightarrow T) = -\frac{1}{2}RT$$
$$\Delta S = S_{trans, 2D} - S_{trans, 3D} = R \left[ln \left(\frac{\frac{h}{k_B T}}{(2\pi m k_B T)^{1/2}} \left(\frac{SA}{N_{sat}} \right) P^0 \right) - \frac{1}{2} \right]$$

Where SA/N_{sat} refers to the area occupied per adsorbed molecule at the standard state conditions. Generally, the standard state is assumed to be monolayer coverage and SA/N_{sat} is equal to the reciprocal of the surface concentration of sites.

For strongly adsorbed species, the frustrated translational and rotational modes are treated as special cases of vibrational modes. Accordingly, the entropy and the internal energy is evaluated according to the following equations.

$$\Delta U^{0}(0 \to T) = U_{vib} = R \sum_{i}^{3N} \frac{x_{i}T}{e^{x_{i}} - 1}$$

$$S = S_{vib} = R \sum_{i}^{3N} \left(\frac{x_{i}}{e^{x_{i}} - 1} - ln(1 - e^{-x_{i}}) \right)$$

$$\Delta H(T) = H_{tran} + H_{rot} + \Delta H_{vib} = \frac{5}{2}RT + \frac{3}{2}RT + R \sum_{i}^{3N} \frac{x_{i}T}{e^{x_{i}} - 1}$$

Where $x_i = \frac{hc}{k_B T \lambda_i}$, c and k_B refer to speed of light and Boltzmann constant, 1/ λ i is wavenumber corresponding to each vibrational frequency.

	E _{ads,C3H6}		Ε	f,hy1	E _{f.hy2}	
	BEEF- vdW	optPBE- vdW	BEEF- vdW	optPBE- vdW	BEEF- vdW	optPBE- vdW
clean surface	-0.55	-0.98	0.51	0.54	0.67	0.69
ОН	-0.42	-0.86	0.48	0.51	0.68	0.68
20 H	-0.32	-0.76	0.52	0.56	0.66	0.66

Table S4. The adsorption energies and activation energies with BEEF-vdW and optPBE-vdW.

The adsorption energies with BEEF-vdW and optPBE-vdW show the same trend although the absolute value strongly depends on the functional. The strong dependence of adsorption energies on functional has been demonstrated by literature⁴. It is found that BEEF-vdW may underestimate the adsorption energy of ethylene⁵. The small adsorption energies calculated by BEEF-vdW will lead to positive adsorption free energies since the entropy change during adsorption process is large at 400K. Therefore, the adsorption energies calculated by optPBE-vdW are employed in the free energy profile. The trends of free energy profiles are the same for these two functional and the conclusion is consistent with two functional.

References

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