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Supplementary material

Insight into the Preferable Formation Mechanism of Long-Chain Hydrocarbons in Fischer-Tropsch Synthesis on Hcp Co(10-11) Surface from DFT and Microkinetic Modeling

Hongxia Liu[a] Riguang Zhang[a,*] Lixia Ling[a] Qiang Wang[b] Baojun Wang[a,*] Debao Li[b]

[a] *Key Laboratory of Coal Science and Technology of Ministry of Education and Shanxi Province, Taiyuan University of Technology, Taiyuan 030024, Shanxi, P.R. China*

[b] *State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Science, Taiyuan 030001, Shanxi, PR China*

1. The effect of translational entropy

In the studies by Cortright *et al.*,[1] as for the weakly bound species, CH_4 and CO_2, assuming that both behave as two dimensional gases and maintain the full rotational and vibrational modes of the corresponding gaseous species. The translational, rotational contributions are taken into account for gaseous species and transition states in the reaction. For a gas molecule moving in the three-dimensional (3D) space, the standard molar translational internal energy is

$$U^{\circ}_{\text{trans-3D}} = \frac{3}{2}RT$$

The standard molar translational entropy follows:

$$S^{\circ}{}_{\text{trans}-3\text{D}} = \mathrm{R}\left[\ln\left(\frac{(2\pi \mathrm{m k_B T})^{3/2}}{\mathrm{h}^3}\right) + \ln\left(\frac{\mathrm{V}}{\mathrm{N_g}}\right) + \frac{5}{2}\right]$$

where m is the mass of the molecule and V/Ng is the volume per molecule in the standard state. For a nonlinear molecule, the standard molar rotational internal energy contribution is

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[*] Corresponding author at: No. 79 Yingze West Street, Taiyuan 030024, China. Tel.: +86 351 6018239; Fax: +86 351 6041237 E-*mail address*: zhangriguang@tyut.edu.cn (Riguang Zhang); wangbaojun@tyut.edu.cn; quantumtyut@126.com (Baojun Wang)

$$U_{rot}^{\mathrm{o}} = \frac{3}{2}RT$$

The standard molar rotational entropy contribution is

$$S^{\mathrm{o}}{}_{\mathrm{rot}} = R\left[\ln\left(\frac{8\pi^{2}\sqrt{8\pi^{3}\mathrm{I_{x}I_{y}I_{z}}}\left(\mathrm{k_{B}T}\right)^{3/2}}{\sigma \mathrm{h}^{3}}\right)+\frac{3}{2}\right]$$

where I_x, I_y, and I_z are the three moments of inertia about the principal axes and is the rotational symmetry number.

If it is a linear gaseous molecule, the corresponding standard molar internal energy and entropy contribution are

$$U_{rot}^{\mathrm{o}}\left(linear\right) = RT$$

$$S^{\mathrm{o}}{}_{\mathrm{rot}}\left(\mathrm{linear}\right) = R\left[\ln\left(\frac{8\pi^{2}\left(\mathrm{k_{B}T}\right)}{\sigma \mathrm{h}^{3}}\right)+\frac{3}{2}\right]$$

where I is the moment of inertia of the linear molecule.

As for the tightly bound species including the remaining reactants, transition states, intermediates and products, the translational and rotational modes are replaced by vibrational modes corresponding to frustrated translation and rotation on the surface. Consequently, the internal energy change and entropy of the tightly adsorbed species are given by follows:

$$U_{vib}^{\mathrm{o}} = RT\sum_{i}\frac{hv_{i}/k_{B}T}{e^{hv_{i}/k_{B}T}-1}$$

$$S^{\theta} = R\sum_{\mathrm{i=1}}^{\mathrm{n}}\left[-ln(1-e^{-hvi/k_{\mathrm{B}}\mathrm{T}})+\frac{hvi/k_{\mathrm{B}}\mathrm{T}}{e^{hvi/k_{\mathrm{B}}\mathrm{T}}-1}\right]$$

For the weakly bound species, CH_4, C_2H_6 and C_3H_8, only the entropy of CH_4 in the gas phase at 500 K is obtained from *JANAF book*,[2] which is consistent with the results of NIST Chemistry WebBook.[3] Meanwhile, the tightly bound species, CO, has been also obtained. As shown in Table S1, the *TS* and $T\Delta S$ values of CO and CH_4 species between that obtained by equation (5) and the experiment value obtained from *JANAF* book are compared; the results show that the experimental values are in agreement with the calculated data, especially for the tightly bound CO species. As a result, we think the entropy change obtained by vibrational modes in our present study is reliable.

Table S1 The entropy change comparison between experimental value and formula data of CO and CH_4 species on Co(10-11) surface at 500 K.

	Adsorbed State TS/kJ·mol^{-1}	Gas State/kJ·mol^{-1}		$T\Delta S_{Exp.}$/kJ·mol^{-1}	$T\Delta S_{Cal.}$/kJ·mol^{-1}
		$TS_{Exp.}$	$TS_{Cal.}$		
CO	21.8	106.4	103.0	84.6	81.2
CH_4	74.1	103.5	93.4	29.4	19.3

2. Adsorption of all possible species

The adsorption of all possible species involving in the C–C chain growth from CH_x to C_3H_8 over four adsorption sites of Co(10-11) surface have been examined, and the most stable adsorption configurations are presented in Figure 2, the corresponding adsorption free energies and the key structural parameters are listed in Table 1.

C, H, O, CO C and O atoms prefer to absorb at the 4-fold site; H atom prefers to adsorb at the Fcc site; CO adsorbs via C atom at the 4-fold site with the C–O bond perpendicular to the surface. The adsorption free energies of C, H, O and CO are 797.8, 253.4, 599.9 and 110.1 kJ·mol^{-1}, respectively.

CHO, CH_2O, CH_3O CHO and CH_2O are bound at the 4-fold site with the bridge(C)-bridge (O) configurations; CH_3O absorbs at the Fcc site via O atom. The adsorption free energies of CHO, CH_2O and CH_3O are 205.6, 131.7 and 255.3 kJ·mol^{-1}, respectively.

CHOH, CH_2OH, CH_3OH CHOH prefers to adsorb at the Bridge site via C atom with an adsorption free energy of 154.0 kJ·mol^{-1}; CH_2OH prefers to adsorb at the Bridge site via both C and O atoms, the C–O bond is almost parallel to the surface with an adsorption free energy of 123.6

kJ·mol^{-1}; CH_3OH prefers to adsorb at the top site via O atom with an adsorption free energy of 19.6 kJ·mol^{-1}.

CH, CH_2, CH_3, CH_4 CH adsorbs at the 4-fold site via C atom; CH_2 and CH_3 prefers to adsorb at the Fcc site, the corresponding adsorption free energies of CH, CH_2 and CH_3 are 615.4, 345.9 and 145.9 kJ·mol^{-1}, respectively; CH_4 is weakly bound to the surface with only an adsorption free energy of 9.5 kJ·mol^{-1}.

C_2H_2, CH_2CH, CH_3CH, C_2H_4, CH_3CH_2, C_2H_6 C_2H_2 prefers to adsorb at the 4-fold site via α-C atoms with the adsorption free energy of 209.0 kJ·mol^{-1}; CH_2CH prefers to the Fcc via α-C with the adsorption free energy of 242.7 kJ·mol^{-1}; CH_3CH adsorbs at the Fcc site via α-C atom with the adsorption free energy of 330.2 kJ·mol^{-1}; C_2H_4 adsorbs at the Top via α-C and the bridge site β-C with the adsorption free energy of 53.1 kJ·mol^{-1}; the adsorption configurations of CH_3CH_2 and C_2H_6 are similar to CH_3 and CH_4, respectively, the corresponding adsorption free energies are 131.6 and 1.8 kJ·mol^{-1}, respectively.

C_2, CCO, CHCO, CH_2CO, CH_3CO C_2 and CCO is stably adsorbed via the 4-fold site via β-C with the adsorption free energy of 684.1 and 484.3 kJ·mol^{-1}.CHCO is stably adsorbed via the Fcc(α-C) and Hcp(β-C) configuration with the adsorption free energy of 293.5 kJ·mol^{-1}. CH_2CO is stably adsorbed via the 4-fold configuration with the adsorption free energy of 117.1 kJ·mol^{-1}. CH_3CO is stably adsorbed via the 4-fold configuration an adsorption free energy of 199.0 kJ·mol^{-1}.

CHCHO, CH_2CHO, CH_3CHO, CH_3CH_2O The adsorption of CH_xCHO follow a similar trend with CH_xCO. CHCHO prefers to the bridge(β-C)-bridge(O) configuration with the adsorption free energy of 420.9 kJ·mol^{-1}. With the increasing of H atom, both CH_2CHO and CH_3CHO are adsorbed at the 4-fold site via the bridge(α-C) configurations, respectively, the corresponding adsorption free energies of CH_2CHO and CH_3CHO are 203.6 and 54.6 kJ·mol^{-1}, respectively. CH_3CH_2O prefers to adsorbs at the Fcc site via O atoms with the adsorption free energy 259.1 kJ·mol^{-1}, in which the C–O bond is perpendicular to the Fcc site.

$CHCHOH$, CH_2CHOH, CH_3CHOH, C_2H_5OH CHCHOH prefers to the bridge site via α-C and β-C configuration with the adsorption free energy of 246.5 kJ·mol^{-1}; both CH_2CHOH and CH_3CHOH are adsorbed at the bridge sites via the top(α-C)-top(O) configurations, which have the corresponding adsorption free energies of 56.4 and 97.0 kJ·mol^{-1}, respectively. C_2H_5OH prefers to adsorbs at the top site via O atom with an adsorption free energies of 15.1 kJ·mol^{-1}.

CH_3CHCH, CH_3CH_2CH, $CH_3CH_2CH_2$, C_3H_8 CH_3CHCH prefers to Fcc site with the corresponding adsorption free energies of 235.2 kJ·mol^{-1}. The adsorption configurations of CH_3CH_2CH, $CH_3CH_2CH_2$ and C_3H_8 are similar to CH_3CH, CH_3CH_2 and C_2H_6, respectively, the corresponding adsorption free energies are 340.2, 129.9 and -0.5 kJ·mol^{-1}, respectively, we can see that C_3H_8 is weak adsorption.

CH_3CHCHO, CH_3CH_2CHO, $CH_3CH_2CH_2O$ CH_3CHCHO prefers to 4-fold site with the corresponding adsorption free energies of 181.6 kJ·mol^{-1}. The adsorption configurations CH_3CH_2CHO and $CH_3CH_2CH_2O$ are similar to that of CH_3CHO and CH_3CH_2O, respectively, the corresponding adsorption free energies are 64.6 and 251.1 kJ·mol^{-1}, respectively.

$CH_3CHCHOH$, CH_3CH_2CHOH, C_3H_7OH $CH_3CHCHOH$ prefers to Bridge site with the corresponding adsorption free energies of 23.6 kJ·mol^{-1}. The adsorption configurations of CH_3CH_2CHOH and C_3H_7OH are similar to CH_3CHOH and CH_3CH_2OH, respectively, the corresponding adsorption free energies are 93.7 and 15.2 kJ·mol^{-1}, respectively.

3. CO Initial Activation and CH_3OH Formation

In **R1**, CO direct dissociation can form C+O via TS1, the C–O distance increases to 2.88 Å from 1.86 Å in TS1, the activation free energy is 153.7 kJ·mol^{-1} with the reaction rate constant of 0.24×10^{-2} s^{-1}, and the reaction free energy is -28.8 kJ·mol^{-1}.

In **R2**, CO can hydrogenate to form CHO via TS2, the C−H distance decreases to 1.39 Å in TS2 from 2.85 Å in CO+H, the activation free energy is 112.8 kJ·mol^{-1} with the rate constant of 4.66×10^{1} s^{-1}, and the reaction free energy is 84.0 kJ·mol^{-1}.

In **R3** CHO can dissociate into CH+O via TS3, the C−O distance increases to 1.79 Å in TS3, the activation free energy is 96.6 kJ·mol^{-1} with the rate constant of 2.30×10^{3} s^{-1}, and the reaction free energy is -58.4 kJ·mol^{-1}.

In addition, the effect of supercell size, thermal energy and entropy to the standard molar Gibbs free energies on the activation energy and reaction energy of the reactions related to CO activation on Co(10-11) surface is shown in Table S2.

Table S2 The activation energies and reaction energies of the reactions related to CO activation on Co(10-11) surface in our study and Liu's paper (J. Am. Chem. Soc., 2013, 135 16284−16287).

Reaction / **Model and method**	**CO→C+O**	**CO+H→CHO**	**CHO→CH+O**	**CO+H→CH+O**
	(E_a, ΔE)/eV			
***p*(2x2) Ours**	(1.30, -0.90)	(1.19, 0.74)	(0.71, -0.59)	(1.45, 0.15)
***p*(2x2) Liu's**	(1.21, -0.83)	(1.29, 0.85)	(0.59,-0.72)	(1.44, 0.13)
***p*(3x2) Our DFT**	(1.46, -0.42)	(1.11, 0.69)	(0.92, -0.58)	(1.61, 0.11)
***p* (3x2) Our DFT+G**	(1.42, -0.30)	(1.17, 0.87)	(1.00, -0.61)	(1.87, 0.26)

In **R4**, CHO hydrogenation can form CHOH via TS4, in TS4, the O−H distance decreases to 1.50 Å from 3.05 Å in CHO+H, this reaction has an activation free energy of 162.1 kJ·mol^{-1}, it is endothermic by 93.9 kJ·mol^{-1}.

In **R5**, CHO hydrogenation can form CH_2O via TS5, in TS5, the C–H distance is shortened to 1.58 Å from 2.49 Å in CHO+H, this elementary reaction has an activation free energy of 61.3 kJ·mol^{-1}, and it is endothermic by 27.2 kJ·mol^{-1}.

In **R6**, CH_2O can also hydrogenate to form CH_2OH via TS6, in TS6, the C–H distance is shortened to 1.35 Å from 2.73 Å in CH_2O+H, this elementary reaction has an activation free energy of 141.9 kJ·mol^{-1}, and it is endothermic by 92.3 kJ·mol^{-1}.

In **R7**, CH_2O directly dissociates into CH_2+O via TS7, the C–O distance increases to 2.07 Å in TS7 and 3.04 Å in CH_2+O, this elementary reaction has an activation free energy of 89.2 kJ·mol^{-1} with the reaction free energy of -43.2 kJ·mol^{-1}.

In **R8**, CH_2O can be hydrogenated to CH_3O via TS8, in TS8, the C–H distance is shortened to 2.07 Å from 2.52 Å in CH_2O+H, this elementary reaction has the activation free energy and reaction free energy of 78.8 and -4.2 kJ·mol^{-1}, respectively.

In **R9**, for CH_3O direct dissociation, the C–O distance is elongated to 1.93 Å in TS9 and 3.54 Å in CH_3+O, this elementary reaction is exothermic by 59.3 kJ·mol^{-1} with an activation free energy of 130.6 kJ·mol^{-1}.

In **R10**, CH_3O hydrogenation can form CH_3OH via TS10, in TS10, the O−H distance is shortened to 1.33 Å from 2.74 Å in CH_3O+H, this elementary reaction is endothermic by 77.4 with an activation free energy of 149.5 kJ·mol^{-1}.

4. CH_4 Formation

In **R11**, C hydrogenation can form CH via TS11, the C−H distance decreases to 1.48 Å in TS11 from 2.40 Å in C+H, the activation free energy is 77.5 kJ·mol^{-1} with the rate constant of 2.05×10^5 s^{-1}, and the reaction free energy is 32.7 kJ·mol^{-1}.

In **R12**, CH hydrogenation into CH_2 via TS12 has an activation free energy of 116.8 kJ·mol^{-1} with the rate constant of 1.78×10^{1} s^{-1}, it is endothermic by 69.1 kJ·mol^{-1}, in TS12, the C−H distance decreases to 1.11 Å from 2.07 Å in CH+H.

In **R13**, for CH_2 hydrogenation to CH_3 via TS13, the C−H distance is shortened from 2.62 Å to 1.70 Å in TS13, the activation free energy is 56.8 kJ·mol^{-1} with the rate constant of 3.25×10^{7} s^{-1}, and it is endothermic by 2.8 kJ·mol^{-1}.

In **R14**, for CH_3 hydrogenation to CH_4 via TS14, the C−H distance decreases from 2.82 Å to 1.55 Å, it is exothermic by 49.5 kJ·mol^{-1} with the activation free energy of 95.2 kJ·mol^{-1} and the rate constant of 3.19×10^{3} s^{-1}.

5. C_2 Hydrocarbons Formation

5.1 All reactions related to C species

In **R15**, C self-coupling to C_2 via TS15 has an activation free energy of 208.1 kJ·mol^{-1} and the rate constant of 4.03×10^{-9} s^{-1}, it is endothermic by 178.2 kJ·mol^{-1}, in TS15, the C−C distance decreases to 1.35 Å from 2.75 Å in C+C.

In **R16**, C coupling with CO to form CCO via TS16 needs to overcome an activation free energy of 153.0 kJ·mol^{-1} with the reaction free energy of 28.4 kJ·mol^{-1}, the reaction rate constant is 0.29×10^{-2} s^{-1}, in TS16, the C−C distance deceases to 1.88 Å from 2.88 Å in C+CO.

In **R17**, C coupling with CHO to form CCHO has been considered; however, our results show that this path does not exist.

5.2 All reactions related to CH species

In **R18**, CH self-coupling to C_2H_2 via TS18 needs to overcome an activation free energy of 106.9 kJ·mol^{-1} with the reaction free energy of 44.1 kJ·mol^{-1}, the reaction rate constant is 1.09×10^{2} s^{-}

^{1}, in TS18, the C−C distance deceases to 1.79 Å from 2.73 Å in CH+CH.

In **R19**, CO insertion into CH to CHCO via TS19 is endothermic by 91.2 kJ·mol^{-1} with an activation free energy of 143.6 kJ·mol^{-1} and the rate constant of 0.03×10^{0} s^{-1}, in TS19, the C−C distance is shortened to 1.80 Å from 2.81 Å in CH+CO.

In **R20**, CHO insertion into CH to CHCHO via TS20 has an activation free energy and reaction free energy of 97.7 and 18.1 kJ·mol^{-1}, respectively; the reaction rate constant is 1.76×10^{3} s^{-1}, in TS20, the C−C distance is shortened to 1.85 Å from 2.81 Å in CH+CHO.

5.3 All reactions related to CH_2 species

In **R21**, CH_2 coupling with CH to form CH_2CH via TS21 needs to overcome an activation free energy of 122.4 kJ·mol^{-1} with the reaction free energy of 46.4 kJ·mol^{-1}, the reaction rate constant is 4.57×10^{0} s^{-1}, in TS21, the C−C distance deceases to 1.94 Å from 3.49 Å in CH_2+CH.

In **R22**, CH_2 self-coupling to C_2H_4 via TS22 needs to overcome an activation free energy of 51.0 kJ·mol^{-1} with the reaction free energy of -32.8 kJ·mol^{-1}, the reaction rate constant is 1.34×10^{8} s^{-1}, in TS22, the C−C distance deceases to 2.03 Å from 2.74 Å in CH_2+CH_2.

In **R23**, CO insertion into CH_2 to CH_2CO via TS23 is endothermic by 37.8 kJ·mol^{-1} with an activation free energy of 106.4 kJ·mol^{-1} and a reaction rate constant of 2.17×10^{2} s^{-1}, in TS23, the C−C distance is shortened to 1.95 Å from 2.88 Å in CH_2+CO.

In **R24**, CHO insertion into CH_2 to CH_2CHO via TS24 has an activation free energy and reaction free energy of 61.4 and -22.2 kJ·mol^{-1}, respectively, and the reaction rate constant is 1.10×10^{7} s^{-1}, in TS24, the C−C distance is shortened to 1.98 Å from 2.66 Å in CH_2+CHO.

5.4 All reactions related to CH_3 species

In **R25**, CH_3 coupling with CH to form CH_3CH via TS25 needs to overcome an activation free energy of 124.5 kJ·mol^{-1} with the reaction free energy of 66.0 kJ·mol^{-1}, the reaction rate constant is

2.77×10^{0} s^{-1}, in TS22, the C−C distance deceases to 1.51 Å from 3.52 Å in CH_3+CH.

In **R26**, CH_3 coupling with CH_2 to CH_3CH_2 via TS26 has an activation free energy of 83.4 kJ·mol^{-1} with the reaction free energy of -9.8 kJ·mol^{-1}, the reaction rate constant is 2.52×10^{4} s^{-1}, in TS26, the C−C distance deceases to 2.09 Å from2.92 Å in CH_3+CH_2.

In **R27**, CH_3 self-coupling to form C_2H_6 via TS27 needs to overcome an activation free energy of 241.3 kJ·mol^{-1} with the reaction free energy of -13.9 kJ·mol^{-1}, the reaction rate constant is 1.73×10^{-12} s^{-1}, in TS27, the C−C distance deceases to 2.85 Å from 3.85 Å in CH_3+CH_3.

In **R28**, CO insertion into CH_3 to CH_3CO via TS28 is endothermic by 42.8 kJ·mol^{-1} with an activation free energy of 147.7 kJ·mol^{-1} and the reaction rate constant of 0.01×10^{0} s^{-1}, in TS28, the C−C distance is shortened to 1.96 Å from 3.13 Å in CH_3+CO.

In **R29**, CHO insertion into CH_3 to CH_3CHO via TS29 has an activation free energy and reaction free energy of 100.9 and -1.1 kJ·mol^{-1}, respectively. The reaction rate constant is 8.12×10^{2} s^{-1}. In TS29, the C−C distance is shortened to 1.99 Å from 2.85 Å in CH_3+CHO.

5.5 All reactions related to C_2H_2 and C_2H_4 species

Starting with C_2H_2 species, in **R31**, CH_2CH can be formed by hydrogenation with an activation free barrier of 68.0 kJ·mol^{-1} and the reaction free energy of 19.6 kJ·mol^{-1}. Then, CH_2CH is further hydrogenated, and the possible products are C_2H_4 and CH_3CH in **R32** and **R33**, respectively, the corresponding activation free barriers are 84.5 and 68.1 kJ·mol^{-1} with the reaction free energies of -33.9 and -27.4 kJ·mol^{-1}, respectively, indicating that CH_3CH is easy to be formed. Finally, C_2H_6 is formed by CH_3CH successive hydrogenations at the α-C site.

Starting with C_2H_4 species, in **R34**, C_2H_4 hydrogenation to CH_3CH_2 is endothermic by 11.7 kJ·mol^{-1}, which has an activation free barrier of 48.9 kJ·mol^{-1}. In **R35**, CH_3CH hydrogenation to CH_3CH_2 has an activation free barrier of 59.7 kJ·mol^{-1}, and it is endothermic by 18.2 kJ·mol^{-1}. In

R36, CH_3CH_2 hydrogenation to C_2H_6 has an activation free barrier of 86.3 kJ·mol^{-1}, and it is exothermic by 16.1 kJ·mol^{-1}.

5.6 All reactions related to CH_xCHO(x=1~3) species

CHCHO related reactions Starting from CHCHO, in **R30**, the C–O bond cleavage of CHCHO can form C_2H_2 via TS30, this reaction has the activation free energy and reaction free energy of 121.5 and -24.3 kJ·mol^{-1}, respectively; the reaction rate constant is 5.75×10^{0} s^{-1}. CHCHO hydrogenation can form CHCHOH, CH_2CHO and $CHCH_2O$, respectively; however, our results show that $CHCH_2O$ intermediate cannot exist.

In **R37**, CHCHO hydrogenation to CHCHOH via TS37 has an activation free energy of 109.1 kJ·mol^{-1} with the reaction rate constant of 1.12×10^{2} s^{-1}, the reaction free energy is 0.7 kJ·mol^{-1}.

In **R38** CHCHO hydrogenation to CH_2CHO via TS38 has the activation free energy and reaction free energy of 50.0 and 28.8 kJ·mol^{-1}, respectively, the reaction rate constant is 1.69×10^{8} s^{-1}.

Therefore, CHCHO hydrogenation to CH_2CHO is kinetically favorable than CHCHOH formation and its direct dissociation into CHCH+O.

CH_2CHO related reactions Once CH_2CHO is formed. In **R39** the C–O bond cleavage of CH_2CHO can form CH_2CH via TS39, this reaction has the activation free energy and reaction free energy of 109.5 and -30.9 kJ·mol^{-1}, respectively, the reaction rate constant is 1.01×10^{2} s^{-1}. CH_2CHO hydrogenation can form CH_2CHOH, CH_3CHO and CH_2CH_2O, respectively; however, our results show that CH_2CH_2O intermediate cannot exists.

In **R40**, CH_2CHO hydrogenation to CH_2CHOH via TS40 has an activation free energy of 127.1 kJ·mol^{-1} with the reaction rate constant of 1.47×10^{0} s^{-1} and the reaction free energy of 82.8 kJ·mol^{-1}.

In **R41**, CH_2CHO hydrogenation to CH_3CHO via TS41 has a lower activation free energy of 33.1 kJ·mol^{-1} with reaction rate constant of 9.81×10^{9} s^{-1} and the reaction free energy of 8.4 kJ·mol^{-1}.

Thus, CH_3CHO formation is more favorable than either CH_2CHOH formation or its direct dissociation into CH_2CH and O. Thus, CH_3CHO dissociation and hydrogenation will be examined.

CH_3CHO related reactions Starting from CH_3CHO, in **R42** the C–O bond cleavage of CH_3CHO can form CH_3CH via TS42 has the activation free energy and reaction free energy of 53.9 and -55.8 $kJ \cdot mol^{-1}$, respectively, the reaction rate constant is 6.64×10^{7} s^{-1}.

In **R43**, CH_3CHO hydrogenation to CH_3CHOH via TS43 has an activation free energy of 150.7 $kJ \cdot mol^{-1}$ with reaction rate constant of 0.50×10^{-2} s^{-1} and reaction free energy of 107.0 $kJ \cdot mol^{-1}$.

In **R44**, CH_3CHO hydrogenation to CH_3CH_2O via TS44 has an activation free energy of 83.4 $kJ \cdot mol^{-1}$ with the reaction rate constant of 5.44×10^{4} s^{-1} and the reaction free energy of 3.4 $kJ \cdot mol^{-1}$. Again, the formations of CH_3CH and CH_3CH_2O are more favorable than CH_3CHOH formation. Meanwhile, as mentioned above, CH_3CH successive hydrogenation to form C_2H_6 is considered.

5.7 All reactions related to CH_3CH_2O species

CH_3CH_2O related reactions

In **R45**, the C–O bond cleavage of CH_3CH_2O can form CH_3CH_2 via TS45, this reaction has the activation free energy and reaction free energy of 113.5 and 1.1 $kJ \cdot mol^{-1}$, respectively, the reaction rate constant is 3.94×10^{1} s^{-1}.

In **R46**, CH_3CH_2O hydrogenation to C_2H_5OH via TS46 has an activation free energy of 146.5 $kJ \cdot mol^{-1}$ with the reaction rate constant of 0.14×10^{-1} s^{-1} and the reaction free energy of 74.4 $kJ \cdot mol^{-1}$.

It is worth mentioning that the reverse activation free energy of CH_3CHO hydrogenation to CH_3CH_2O is 80.0 $kJ \cdot mol^{-1}$, which is much lower than the activation free energies of **R45** and **R46**, indicating that CH_3CH_2O prefers to be dissociated into CH_3CHO.

6. C_3 Hydrocarbons Formation

6.1 All reactions related to CH_3CH species

In **R35**, CH_3CH hydrogenation to CH_3CH_2 via TS35 has been mentioned above.

In **R47**, CH_3CH couples with CH via TS47, in TS47, the C−C distance decreases to 2.01 Å from 3.46 Å, it is endothermic by 56.1 kJ·mol^{-1} with the activation free energy of 160.9 kJ·mol^{-1}, the reaction rate constant is 0.04×10^{-2} s^{-1}.

In **R48**, CHO insertion into CH_3CH via TS48 has an activation free energy of 60.3 kJ·mol^{-1} and the reaction rate constant of 1.42×10^{7} s^{-1}, and it is exothermic by 35.8 kJ·mol^{-1}, in TS48, the C−C distance decreases from 2.81 Å to 2.02 Å.

6.2 All reactions related to CH_3CH_2 species

In **R36** CH_3CH_2 hydrogenation to C_2H_6 via TS36 has been mentioned above.

In **R49**, CH_3CH_2 coupling with CH via TS49 is endothermic by 26.1 kJ·mol^{-1} with the activation free energy of 145.8 kJ·mol^{-1}, the reaction rate constant is 0.4×10^{0} s^{-1}, in TS49, the C−C distance decreases to 2.32 Å from 3.20 Å,

In **R50**, CHO insertion into CH_3CH_2 via TS50 has an activation free energy of 102.7 kJ·mol^{-1} and a reaction rate constant of 5.30×10^{2} s^{-1}, and it is exothermic by 18.7 kJ·mol^{-1}, in TS50, the C−C distance decreases from 2.06 Å to 3.29 Å.

In **R51**, CH_3CH_2 coupling with CH_2 via TS51 is exothermic by 33.2 kJ·mol^{-1} with the activation free energy of 54.6 kJ·mol^{-1}, the reaction rate constant is 5.47×10^{7} s^{-1}, in TS51, the C−C distance decreases to 2.21 Å from 2.83 Å.

6.3 All reactions related to CH_3CH_xCHO species

CH_3CHCHO related reactions Starting form CH_3CHCHO, in **R52**, its dissociation into

CH_3CHCH has an activation free energy of 125.6 kJ·mol^{-1}, and it is exothermic by 46.5 kJ·mol^{-1}, the reaction rate constant is 2.10×10^{0} s^{-1}.

For CH_3CHCHO hydrogenation to $CH_3CHCHOH$, in **R53**, the activation free energy is 138.6 kJ·mol^{-1}, the reaction rate constant is 0.56×10^{0} s^{-1}, it is endothermic by 106.0 kJ·mol^{-1}. For its hydrogenation to CH_3CH_2CHO, in **R54**, this reaction has an activation free energy of 31.7 kJ·mol^{-1} with the reaction rate constant of 6.65×10^{10} s^{-1}, and it is endothermic by 8.2 kJ·mol^{-1}. Thus, CH_3CH_2CHO formation by CH_3CHCHO hydrogenation is kinetically favorable than $CH_3CHCHOH$ formation and direct dissociation into CH_3CHCH and O.

CH_3CH_2CHO related reactions Once CH_3CH_2CHO is formed, in **R55**, its dissociation into CH_3CH_2CH has an activation energy of 64.6 kJ·mol^{-1}, and it is exothermic by 57.5 kJ·mol^{-1}, the rate constant is 5.04×10^{7} s^{-1}.

For CH_3CH_2CHO hydrogenation to CH_3CH_2CHOH, in **R56**, the activation free energy is 144.6 kJ·mol^{-1}, the reaction rate constant is 6.99×10^{0} s^{-1}, it is endothermic by 109.8 kJ·mol^{-1}. For its hydrogenation to $CH_3CH_2CH_2O$, in **R57**, this reaction has an activation free energy of 128.6 kJ·mol^{-1} with the reaction rate constant of 6.28×10^{0} s^{-1}, and it is exothermic by 4.9 kJ·mol^{-1}. Thus, CH_3CH_2CHO dissociation into CH_3CH_2CH is more favorable than its hydrogenation to CH_3CH_2CHOH and $CH_3CH_2CH_2O$.

6.4 All reactions related to $CH_3CH_2CH_2O$ species

Starting form $CH_3CH_2CH_2O$, in **R58**, its C–O bond cleavage to form $CH_3CH_2CH_2$ has an activation free energy of 120.5 kJ·mol^{-1} with the reaction rate constant of 3.29×10^{0} s^{-1}, and it is exothermic by 17.6 kJ·mol^{-1}. In **R59**, its hydrogenation to C_3H_7OH (propanol) has an activation free energy of 159.6 kJ·mol^{-1} with the reaction rate constant of 0.50×10^{-3} s^{-1}, and it is endothermic by 89.2 kJ·mol^{-1}. The similar activation free energies of above two reactions indicate that the formations of $CH_3CH_2CH_2$ and $CH_3CH_2CH_2OH$ (propanol) are competitive kinetically.

It is worth mentioning that the reverse activation free energy of CH_3CH_2CHO hydrogenation to $CH_3CH_2CH_2O$ is 133.5 kJ·mol^{-1}, which is much lower than the activation free energies of **R59**, indicating that $CH_3CH_2CH_2O$ prefers to be dissociated into CH_3CH_2CHO species. In **R60**, CH_3CH_2CH hydrogenation to $CH_3CH_2CH_2$ has an activation free barrier of 74.7 kJ·mol^{-1}, and it is endothermic by 15.2 kJ·mol^{-1}. In **R61**, $CH_3CH_2CH_2$ hydrogenation to C_3H_8 has an activation free barrier of 47.3 kJ·mol^{-1}, and it is endothermic by 14.8 kJ·mol^{-1}.

7. Microkinetic modeling

In this study, microkinetic modeling is implemented to probe into the catalytic activity and selectivity of major products in syngas conversion on Co(10-11) surface under the typical experimental conditions (P_{CO}=5 atm, $P_{\mathrm{H_2}}$=10 atm, and T=500 K).

The adsorption reactions of CO and H_2 are assumed to be in equilibrium, the equilibrium constants were defined as follow:[4,5]

$$K = \exp\left[-\left(\Delta E_{ads} - T\Delta S\right)/k_B T\right]$$

Where E_{ads} refers to the adsorption energy of CO or H_2, k_{B} is the Boltzmann constant, T is the reaction temperature and ΔS is the entropy change from the gas phase at the reaction temperature, obtained from NIST Chemistry WebBook.[3]

The rate constants have been presented in Table 2 in the main text. The site balance of intermediate species included in the reaction mechanism can be written in terms of coverage (θ_X: X=surface species).[4,5]

$$\begin{aligned}&\theta_{CO}+\theta_{C}+\theta_{H}+\theta_{CHO}+\theta_{CH_2O}+\theta_{CH_3O}+\theta_{CH}+\theta_{CH_2}+\theta_{CH_3}+\theta_{CHCHO}+\theta_{CH_2CHO}+\theta_{CH_3CHO}+\theta_{CH_3CH_2O}+\theta_{C_2H_4}\\&+\theta_{CH_3CH}+\theta_{CH_3CH_2}+\theta_{CH_3CHCHO}+\theta_{CH_3CH_2CHO}+\theta_{CH_3CH_2CH_2O}+\theta_{CH_3CH_2CH}+\theta_{CH_3CH_2CH_2}+\theta_{*}=1 \qquad [1]\end{aligned}$$

The coverage of CO and H are $\theta_{CO} = P_{CO}K_1\theta_*$ and $\theta_H = P_{H_2}^{1/2}K_2^{1/2}\theta_*$. C, CHO, CH_2O, CH_3O,

CH, CH_2, CH_3, $CHCHO$, CH_2CHO, CH_3CHO, CH_3CH_2O, C_2H_2, CH_2CH, C_2H_4, CH_3CH, CH_3CH_2 CH_3CHCHO, CH_3CH_2CHO, $CH_3CH_2CH_2O$, CH_3CH_2CH and $CH_3CH_2CH_2$ are described according to the pseudo steady-state approximation,[6] in which the production rate and consumption rate are equal for all intermediates:

$$\text{C: } \frac{d\theta_C}{dt} = k_1\theta_{CO}\theta_* - k_{11}\theta_C\theta_H = 0 \tag{1}$$

$$\theta_C = \frac{k_1\theta_{CO}\theta_*}{k_{11}\theta_H}$$

$$\text{CHO: } \frac{d\theta_{CHO}}{dt} = k_2\theta_{CO}\theta_H - k_3\theta_{CHO}\theta_* - k_5\theta_{CHO}\theta_H - k_{20}\theta_{CH}\theta_{CHO} - k_{48}\theta_{CH_3CH}\theta_{CHO} = 0 \tag{2}$$

$$\theta_{CHO} = \frac{k_2\theta_{CO}\theta_H}{k_3\theta_* + k_5\theta_H + k_{20}\theta_{CH} + k_{48}\theta_{CH_3CH}}$$

$$\text{CH}_2\text{O: } \frac{d\theta_{CH_2O}}{dt} = k_5\theta_{CHO}\theta_H - k_8\theta_{CH_2O}\theta_H = 0 \tag{3}$$

$$\theta_{CH_2O} = \frac{k_5\theta_{CHO}}{k_8}$$

$$\text{CH}_3\text{O: } \frac{d\theta_{CH_3O}}{dt} = k_8\theta_{CH_2O}\theta_H - k_{10}\theta_{CH_3O}\theta_H = 0 \tag{4}$$

$$\theta_{CH_3O} = \frac{k_8\theta_{CH_2O}}{k_{10}}$$

$$\text{CH: } \frac{d\theta_{CH}}{dt} = k_3\theta_{CHO}\theta_* + k_{11}\theta_C\theta_H - k_{12}\theta_{CH}\theta_H - k_{18}\theta_{CH}{}^2 - k_{20}\theta_{CH}\theta_{CHO} = 0 \tag{5}$$

$$\theta_{CH} = \frac{-(k_{20}\theta_{CHO} + k_{12}\theta_H \ + \sqrt{(k_{20}\theta_{CHO} + k_{12}\theta_H)^2 + 4k_{18}k_3\theta_{CHO}\theta_*}}{2k_{18}}$$

$$\text{CH}_2\text{: } \frac{d\theta_{CH_2}}{dt} = k_{12}\theta_{CH}\theta_H - k_{13}\theta_{CH_2}\theta_H - k_{22}\theta_{CH_2}{}^2 - k_{51}\theta_{CH_3CH_2}\theta_{CH_2} = 0 \tag{6}$$

$$\theta_{CH_2} = \frac{-(k_{13}\theta_H + k_{51}\theta_{CH_3CH_2} \ + \sqrt{(k_{13}\theta_H + k_{51}\theta_{CH_3CH_2})^2 + 4k_{22}k_{12}\theta_{CH}\theta_H}}{2k_{22}}$$

CH$_3$: $\frac{d\theta_{CH_3}}{dt} = k_{13}\theta_{CH_2}\theta_H - k_{14}\theta_{CH_3}\theta_H = 0$ (7)

$$\theta_{CH_3} = \frac{k_{13}\theta_{CH_2}}{k_{14}}$$

CHCHO: $\frac{d\theta_{CHCHO}}{dt} = k_{20}\theta_{CH}\theta_{CHO} - k_{38}\theta_{CHCHO}\theta_H = 0$ (8)

$$\theta_{CHCHO} = \frac{k_{20}\theta_{CH}\theta_{CHO}}{k_{38}\theta_H}$$

CH$_2$CHO: $\frac{d\theta_{CH_2CHO}}{dt} = k_{38}\theta_{CHCHO}\theta_H - k_{41}\theta_{CH_2CHO}\theta_H = 0$ (9)

$$\theta_{CH_2CHO} = \frac{k_{41}\theta_{CHCHO}}{k_{38}}$$

CH$_3$CHO: $\frac{d\theta_{CH_3CHO}}{dt} = k_{41}\theta_{CH_2CHO}\theta_H - k_{42}\theta_{CH_3CHO}\theta_* - k_{44}\theta_{CH_3CHO}\theta_H = 0$ (10)

$$\theta_{CH_3CHO} = \frac{k_{41}\theta_{CH_2CHO}P_{H_2}^{1/2}K_2^{1/2}}{k_{42} + k_{44}P_{H_2}^{1/2}K_2^{1/2}}$$

CH$_3$CH$_2$O: $\frac{d\theta_{CH_3CH_2O}}{dt} = k_{44}\theta_{CH_3CHO}\theta_H - k_{46}\theta_{CH_3CH_2O}\theta_H = 0$ (11)

$$\theta_{CH_3CH_2O} = \frac{k_{44}\theta_{CH_3CHO}}{k_{46}}$$

C$_2$H$_2$: $\frac{d\theta_{C_2H_2}}{dt} = k_{18}\theta_{CH}{}^2 - k_{31}\theta_{C_2H_2}\theta_H = 0$ (12)

$$\theta_{C_2H_2} = \frac{k_{18}\theta_{CH}{}^2}{k_{31}\theta_H}$$

CH$_2$CH: $\frac{d\theta_{CH_2CH}}{dt} = k_{31}\theta_{C_2H_2}\theta_H - k_{32}\theta_{CH_2CH}\theta_H = 0$ (13)

$$\theta_{CH_2CH} = \frac{k_{31}\theta_{C_2H_2}}{k_{32}}$$

CH$_3$CH: $\frac{d\theta_{CH_3CH}}{dt} = k_{32}\theta_{CH_2CH}\theta_H + k_{42}\theta_{CH_3CHO}\theta_* - k_{35}\theta_{CH_3CH}\theta_H - k_{48}\theta_{CH_3CH}\theta_{CHO} = 0$ (14)

$$\theta_{CH_3CH} = \frac{k_{32}\theta_{CH_2CH}\theta_H + k_{42}\theta_{CH_3CHO}\theta_*}{k_{35}\theta_H + k_{48}\theta_{CHO}}$$

C_2H_4: $\frac{d\theta_{C_2H_4}}{dt} = k_{22}\theta_{CH_2}{}^2 - k_{34}\theta_{C_2H_4}\theta_H = 0$ (15)

$$\theta_{C_2H_4} = \frac{k_{22}\theta_{CH_2}{}^2}{k_{34}\theta_H}$$

CH_3CH_2: $\frac{d\theta_{CH_3CH_2}}{dt} = k_{34}\theta_{C_2H_4}\theta_H + k_{35}\theta_{CH_3CH}\theta_H - k_{36}\theta_{CH_3CH_2}\theta_H - k_{51}\theta_{CH_3CH_2}\theta_{CH_2} = 0$ (16)

$$\theta_{CH_3CH_2} = \frac{k_{34}\theta_{C_2H_4}\theta_H + k_{35}\theta_{CH_3CH}\theta_H}{k_{36}\theta_H + k_{51}\theta_{CH_2}}$$

CH_3CHCHO: $\frac{d\theta_{CH_3CHCHO}}{dt} = k_{48}\theta_{CH_3CH}\theta_{CHO} - k_{54}\theta_{CH_3CHCHO}\theta_H = 0$ (17)

$$\theta_{CH_3CHCHO} = \frac{k_{48}\theta_{CH_3CH}\theta_{CHO}}{k_{54}\theta_H}$$

CH_3CH_2CHO: $\frac{d\theta_{CH_3CH_2CHO}}{dt} = k_{54}\theta_{CH_3CHCHO}\theta_H - k_{55}\theta_{CH_3CH_2CHO}\theta_H - k_{57}\theta_{CH_3CH_2CH_2O}\theta_* = 0$ (18)

$$\theta_{CH_3CH_2CHO} = \frac{k_{54}\theta_{CH_3CHCHO}P_{H_2}^{1/2}K_2^{1/2}}{k_{57} + k_{55}P_{H_2}^{1/2}K_2^{1/2}}$$

$CH_3CH_2CH_2O$: $\frac{d\theta_{CH_3CH_2CH_2O}}{dt} = k_{57}\theta_{CH_3CH_2CHO}\theta_H - k_{59}\theta_{CH_3CH_2CH_2O}\theta_H = 0$ (19)

$$\theta_{CH_3CH_2CH_2O} = \frac{k_{57}\theta_{CH_3CH_2CHO}}{k_{59}}$$

CH_3CH_2CH: $\frac{d\theta_{CH_3CH_2CH}}{dt} = k_{55}\theta_{CH_3CH_2CHO}\theta_* - k_{60}\theta_{CH_3CH_2CH}\theta_H = 0$ (20)

$$\theta_{CH_3CH_2CH} = \frac{k_{55}\theta_{CH_3CH_2CHO}}{k_{60}P_{H_2}^{1/2}K_2^{1/2}}$$

$CH_3CH_2CH_2$: $\frac{d\theta_{CH_3CH_2CH_2}}{dt} = k_{51}\theta_{CH_3CH_2}\theta_{CH_2} + k_{60}\theta_{CH_3CH_2CH}\theta_H - k_{61}\theta_{CH_3CH_2CH_2}\theta_H = 0$ (21)

$$\theta_{CH_3CH_2CH_2} = \frac{k_{51}\theta_{CH_3CH_2}\theta_{CH_2} + k_{60}\theta_{CH_3CH_2CH}\theta_H}{k_{61}\theta_H}$$

By putting all of the coverage expressions (equations (1)—(21)) into equation [1], we can calculate the coverage of surface free sites θ_*. Subsequently, the coverage of all intermediates can be obtained. In fact, in our calculation process of the coverage of all intermediates, R48 reaction is not included in equation (2). If R48 reaction is considered, equation [1] is an unknown equation. The results are very hard to gain.

The rates for each major product (CH_3OH, CH_4, C_2H_5OH, C_2H_6, C_3H_7OH, and C_3H_8) are $r_{CH_3OH} = k_{10}\theta_{CH_3O}\theta_H$; $r_{CH_4} = k_{14}\theta_{CH_3}\theta_H$; $r_{C_2H_5OH} = k_{46}\theta_{CH_3CH_2O}\theta_H$; $r_{C_2H_6} = k_{36}\theta_{CH_3CH_2}\theta_H$; $r_{C_3H_7OH} = k_{59}\theta_{CH_3CH_2CH_2O}\theta_H$; $r_{C_3H_8} = k_{61}\theta_{CH_3CH_2CH_2}\theta_H$.

Here, the relative selectivity is defined by the relative rate for each product, where i is the $r_i / (r_{\mathrm{CH_3OH}} + r_{\mathrm{CH_4}} + r_{\mathrm{C_2H_5OH}} + r_{\mathrm{C_2H_6}} + r_{\mathrm{C_3H_7OH}} + r_{\mathrm{C_3H_8}})$ species of the products.

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