Supporting Information

Formations of C_2 Oxygenates and Ethanol from Syngas on Fe-decorated Cu-based Catalyst: Insight into the Role of Promoter Fe

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1. Adsorptions of all possible species

The adsorption energy with the zero-point-corrected (E_{ads}) is calculated by the equations (1) and (2):[1,2]

$$E_{\text{ads}} = (E_{\text{species}} + E_{\text{slab}} - E_{\text{slab/species}}) + \Delta ZPE_{\text{ads}} \qquad (1)$$

$$\Delta ZPE_{\text{ads}} = \left(\sum_{i=1}^{\text{Vibrations}} \frac{h\nu_i}{2}\right)_{\text{gas}} - \left(\sum_{i=1}^{\text{Vibrations}} \frac{h\nu_i}{2}\right)_{\text{adsorbed}} \qquad (2)$$

Where E_{slab}, E_{species} and $E_{\text{species/slab}}$ represent the total energies of the slab surface, adsorbate species in gas phase, and the slab surface together with the adsorbed species in the equilibrium state,

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respectively. ΔZPE_{ads} refers to the zero-point vibrational energy (ZPE) correction. h and v_i represent the Planck's constant and vibrational frequency, respectively. The adsorption energy and key geometrical parameters of reaction intermediates involved in ethanol formation from syngas on FeCu(211) surface are listed in Table 1 in the main text. The corresponding most stable adsorption configurations are presented in Figure 2.

1.1 C, O, CO, H, OH, H_2O, CH_x(x=1-3), C_2H_4, CH_4, C_2H_6

CO and H as the abundant reactants can be widely adsorbed on FeCu(211) surface, the results show that CO prefers to be adsorbed at Fe site *via* C atom with an adsorption energy of 234.7 kJ·mol^{-1}. H binds at the atop-Fe site with an adsorption energy of 261.3 kJ·mol^{-1}.

CH and CH_2 prefer to adsorb at F_{I-1} and B_{I-1} sites with the corresponding adsorption energies of 633.0 and 435.8 kJ·mol^{-1}, respectively. CH_3 is adsorbed at Fe atom *via* C atom with an adsorption energy of 245.1 kJ·mol^{-1}. C and O are adsorbed at F_{I-1} site with an adsorption energy of 694.6 and 627.7 kJ·mol^{-1}, respectively. OH adsorbs at B_{I-1} site with an adsorption energy of 397.2 kJ·mol^{-1}.

CH_4, C_2H_4 and C_2H_6 are adsorbed at atop-Fe site with the adsorption energies of 32.0, 165.2 and 51.6 kJ mol^{-1}, respectively.

1.2 CH_xOH(x=0-3), CH_xO(x=1-3)

COH adsorbs at F_{I-1} and atop-Fe sites *via* C atom with an adsorption energy of 434.5 kJ·mol^{-1}. CH_xOH(x=1-3) are adsorbed at the atop-Fe with the corresponding adsorption energies of 347.7, 256.1, and 100.9 kJ·mol^{-1}, respectively.

CHO and CH_2O prefer to sit at the atop-Fe *via* both C and O, which have the adsorption energies of 301.0 and 201.3 kJ·mol^{-1}, respectively. CH_3O is adsorbed at the atop-Fe *via* O atom with an adsorption energy of 339.9 kJ·mol^{-1}.

1.3 CH_xCO, CH_xCOH, CH_xCHO(x=2, 3), CH_3CHOH, CH_3CH_2O, C_2H_5OH

CH_xCO, CH_xCHO(x=2, 3) prefer to locate at the $B_{I\text{-}1}$ site *via* C and O atoms, the corresponding adsorption energies are 197.6, 302.1, 308.2, and 170.6 kJ·mol^{-1}, respectively. CH_xCOH (x=2, 3) are adsorbed at the atop-Fe site *via* C atom, and the adsorption energies are 330.5 and 326.2 kJ·mol^{-1}, respectively. CH_3CHOH is adsorbed at the atop-Fe site *via* both C_1 and O atoms with the adsorption energies of 242.2 kJ·mol^{-1}. CH_3CH_2O and C_2H_5OH are adsorbed *via* O atom at the atop-Fe site with the corresponding adsorption energies of 338.5 and 100.6 kJ·mol^{-1}, respectively.

2. The calculations of the activation barrier, reaction energy, and rate constant

The activation barrier with the zero-point vibrational energy (*ZPE*) correction is calculated according to the equations (3) and (4):[1]

$$E_{\mathrm{a}} = (E_{\mathrm{TS}} - E_{\mathrm{R}}) + \Delta ZPE_{\mathrm{barrier}} \qquad (3)$$

Where E_{R} and E_{TS} refer to total energies of the reactant and transition state, respectively, and $\Delta ZPE_{\mathrm{barrier}}$ represents the zero-point vibrational energy (*ZPE*) correction for the activation barrier, which is calculated by the equation (4):

$$\Delta ZPE_{\mathrm{barrier}} = \left(\sum_{i=1}^{Vibrations} \frac{hv_i}{2} \right)_{\mathrm{TS}} - \left(\sum_{i=1}^{Vibrations} \frac{hv_i}{2} \right)_{\mathrm{R}} \qquad (4)$$

The first term includes the vibrational frequencies of the species in the TS, in which the imaginary frequency has not been considered, and the second term includes the vibrational frequencies of the adsorbed reactants.

The reaction energy with the zero-point vibrational energy (*ZPE*) correction is calculated by the equations (5) and (6):

$$\Delta E = (E_{\mathrm{P}} - E_{\mathrm{R}}) + \Delta ZPE_{\mathrm{energy}} \qquad (5)$$

$$\Delta ZPE_{\mathrm{energy}} = \left(\sum_{i=1}^{Vibrations} \frac{hv_i}{2} \right)_{\mathrm{P}} - \left(\sum_{i=1}^{Vibrations} \frac{hv_i}{2} \right)_{\mathrm{R}} \qquad (6)$$

The ΔZPE energy refers to the zero-point vibrational energy (ZPE) correction for the reaction energy, which is determined by the vibrational frequencies of the reactants and products. As a result, a negative (positive) value indicates an exothermic (endothermic), respectively.

The rate constant (k) was calculated by the equation (7):

$$k=\frac{k_{\mathrm{B}}T}{h}\frac{q_{\mathrm{TS}}}{q_{\mathrm{R}}}\exp\left(-\frac{E_{\mathrm{a}}}{k_{\mathrm{B}}T}\right) \tag{7}$$

Where k_{B} is the Boltzmann constant, T is the absolute temperature; E_{a} is the activation barrier with the zero-point vibrational energy (ZPE) correction. The partition function (q) is calculated by the equation (8):

$$q=\frac{1}{\prod_{i=1}^{Vibrations} 1-\exp\left(-\frac{h\nu_i}{k_{\mathrm{B}}T}\right)} \tag{8}$$

Table S1 The rate constant *k* (*s*$^{-1}$) for elementary reactions involved in ethanol formation from syngas at different temperature on FeCu(211) surface.

	Elementary Reactions	**Rate Constant *k* (*s*$^{-1}$)**				
		500 K	525 K	550 K	575 K	600 K
R1	$CO \rightarrow C+O$	8.22×10^{-14}	1.56×10^{-12}	2.31×10^{-11}	2.71×10^{-10}	2.59×10^{-9}
R2	$CO+H \rightarrow COH$	8.57×10^{-6}	6.45×10^{-5}	4.05×10^{-4}	2.17×10^{-3}	1.01×10^{-2}
R3	$CO+H \rightarrow CHO$	1.42×10^{4}	4.87×10^{4}	1.50×10^{5}	4.18×10^{5}	1.07×10^{6}
R4	$CHO \rightarrow CH+O$	8.35×10^{3}	2.35×10^{4}	6.05×10^{4}	1.44×10^{5}	3.19×10^{5}
R5	$CHO+H \rightarrow CHOH$	1.20×10^{-1}	6.00×10^{-1}	2.60	9.96	3.42×10^{1}
R6	$CHOH \rightarrow CH+OH$	6.05×10^{7}	1.05×10^{8}	1.73×10^{8}	2.75×10^{8}	4.22×10^{8}
R7	$CHO+H \rightarrow CH_2O$	2.14×10^{12}	2.61×10^{12}	3.13×10^{12}	3.71×10^{12}	4.34×10^{12}
R8	$CH_2O \rightarrow CH_2+O$	2.25×10^{5}	5.92×10^{5}	1.43×10^{6}	3.22×10^{6}	6.80×10^{6}
R9	$CH_2O+H \rightarrow CH_2OH$	2.96×10^{7}	5.96×10^{7}	1.13×10^{8}	2.03×10^{8}	3.49×10^{8}
R10	$CH_2OH \rightarrow CH_2+OH$	1.67×10^{9}	2.79×10^{9}	4.49×10^{9}	6.94×10^{9}	1.04×10^{10}
R11	$CH_2O+H \rightarrow CH_3O$	3.75×10^{7}	7.92×10^{7}	1.57×10^{8}	2.93×10^{8}	5.21×10^{8}
R12	$CH_3O \rightarrow CH_3+O$	8.05	3.59×10^{1}	1.41×10^{2}	4.91×10^{2}	1.55×10^{3}
R13	$CH_3O+H \rightarrow CH_3OH$	2.01×10^{3}	7.19×10^{3}	2.29×10^{4}	6.61×10^{4}	1.75×10^{5}
R14	$CH_2OH+H \rightarrow CH_3OH$	6.84×10^{3}	1.99×10^{4}	5.24×10^{4}	1.27×10^{5}	2.88×10^{5}
R15	$CH_2 \rightarrow CH+H$	1.00×10^{5}	2.42×10^{5}	5.41×10^{5}	1.13×10^{6}	2.23×10^{6}
R16	$CH_2+H \rightarrow CH_3$	8.01×10^{8}	1.41×10^{9}	2.33×10^{9}	3.70×10^{9}	5.66×10^{9}
R17	$CH_2+CH_2 \rightarrow C_2H_4$	1.91×10^{7}	4.14×10^{7}	8.39×10^{7}	1.60×10^{8}	2.90×10^{8}
R18	$CH_2+CO \rightarrow CH_2CO$	4.80×10^{8}	7.91×10^{8}	1.25×10^{9}	1.89×10^{9}	2.78×10^{9}
R19	$CH_2+CHO \rightarrow CH_2CHO$	1.40×10^{8}	2.57×10^{8}	4.47×10^{8}	7.44×10^{8}	1.19×10^{9}
R20	$CH_3 \rightarrow CH_2+H$	8.92×10^{5}	2.01×10^{6}	4.22×10^{6}	8.34×10^{6}	1.56×10^{7}
R21	$CH_3+H \rightarrow CH_4$	1.73×10^{4}	4.70×10^{4}	1.67×10^{5}	2.68×10^{5}	5.77×10^{5}
R22	$CH_3+CH_3 \rightarrow C_2H_6$	6.09×10^{-4}	3.77×10^{-3}	1.98×10^{-2}	9.03×10^{-2}	3.60×10^{-1}
R23	$CH_3+CO \rightarrow CH_3CO$	3.36×10^{5}	8.43×10^{5}	1.95×10^{6}	4.18×10^{6}	8.45×10^{6}
R24	$CH_3+CHO \rightarrow CH_3CHO$	8.95×10^{5}	2.24×10^{6}	5.17×10^{6}	1.11×10^{7}	2.24×10^{7}
R25	$CH_2CO+H \rightarrow CH_3CO$	3.98×10^{12}	4.83×10^{12}	5.78×10^{12}	6.82×10^{12}	7.94×10^{12}
R26	$CH_2CO+H \rightarrow CH_2CHO$	1.24×10^{5}	3.46×10^{5}	8.77×10^{5}	2.05×10^{6}	4.48×10^{6}
R27	$CH_2CO+H \rightarrow CH_2COH$	3.64×10^{5}	9.44×10^{5}	2.25×10^{6}	4.99×10^{6}	1.04×10^{7}
R28	$CH_3CO+H \rightarrow CH_3CHO$	7.43×10^{5}	2.11×10^{6}	5.45×10^{6}	1.30×10^{7}	2.89×10^{7}
R29	$CH_3CO+H \rightarrow CH_3COH$	1.33×10^{4}	4.28×10^{4}	1.24×10^{5}	3.29×10^{5}	8.06×10^{5}
R30	$CH_3CHO+H \rightarrow CH_3CH_2O$	1.20×10^{11}	1.62×10^{11}	2.13×10^{11}	2.73×10^{11}	3.43×10^{11}
R31	$CH_3CHO+H \rightarrow CH_3CHOH$	4.56×10^{6}	9.46×10^{6}	1.84×10^{7}	3.39×10^{7}	5.92×10^{7}
R32	$CH_3CH_2O+H \rightarrow C_2H_5OH$	2.40×10^{1}	9.28×10^{2}	3.19×10^{2}	9.84×10^{2}	2.77×10^{3}

3. Microkinetic Modeling

Microkinetic modeling[3-6] has been widely employed to investigate the activity and selectivity of the catalyst, for example, Liu *et al.*[4] have proved that the water dissociation, as the rate-determining step for water-gas-shift reaction, is faster on Au and Cu nanoparticles than their parent bulk surfaces. Liu and Choi[6] have investigated ethanol formation from syngas on Rh(111) surface, suggesting that the productivity and selectivity for ethanol are only controlled by CH_4 formation and the C−C bond formation *via* CO insertion into CH_3.

As a result, in this study, microkinetic modeling is implemented to probe into the catalytic activity and selectivity of major products in syngas conversion on FeCu(211) surface under the typical experimental conditions (P_{CO}=4 atm, $P_{\mathrm{H_2}}$=8 atm, and T=500~600 K). All elementary reactions involved in the optimal formation pathways of CH_3OH, CH_4 and C_2H_5OH, as well as the corresponding reaction rates at 500, 525, 550, 575 and 600 K are summarized in Table S2 for the calculations of microkinetic modeling.

The adsorption reaction of CO and H_2 is assumed in equilibrium. The equilibrium constants were calculated by the equation (9):

$$K = \exp\left[-\left(\Delta E_{\mathrm{ads}} - T\Delta S\right)/RT\right] \qquad (9)$$

Where E_{ads} refers to the adsorption energy of CO or H_2, and ΔS is the entropy change from the gas phase at the reaction temperature, obtained from NIST Chemistry WebBook.[7]

$$\theta_{CO} = P_{CO} K_1 \theta^* \qquad (10)$$

$$\theta_H = P_{H_2}^{1/2} K_2^{1/2} \theta^* \qquad (11)$$

For the kinetics of surface reactions, we only consider forward reactions, which is a safe approximation at such high partial pressures of CO and H_2 as it is used in experiment.

Table S2 All elementary reactions involved in the optimal formation pathways of CH_3OH, CH_4 and C_2H_5OH, as well as the corresponding reaction rate constants at 500, 525, 550, 575 and 600 K.

Elementary Reactions		**Rate constant *k* (s^{-1})**				
		500K	525K	550K	575K	600K
$CO(g)+{*}\leftrightarrow CO{*}$						
$H_2(g)+2{*}\leftrightarrow 2H{*}$						
$CO{*}+H{*}\rightarrow CHO{*}+{*}$	k_3	1.42×10^4	4.87×10^4	1.50×10^5	4.18×10^5	1.07×10^6
$CHO{*}+H{*}\rightarrow CH_2O{*}$	k_4	2.14×10^{12}	2.61×10^{12}	3.13×10^{12}	3.71×10^{12}	4.34×10^{12}
$CH_2O{*}+{*}\rightarrow CH_2{*}+O{*}$	k_5	2.25×10^5	5.92×10^5	1.43×10^6	3.22×10^6	6.80×10^6
$CH_2O{*}+H{*}\rightarrow CH_2OH{*}+{*}$	k_6	2.96×10^7	5.96×10^7	1.13×10^8	2.03×10^8	3.49×10^8
$CH_2OH{*}+{*}\rightarrow CH_2{*}+OH{*}$	k_7	1.67×10^9	2.79×10^9	4.49×10^9	6.94×10^9	1.04×10^{10}
$CH_2O{*}+H{*}\rightarrow CH_3O{*}+{*}$	k_8	3.75×10^7	7.92×10^7	1.57×10^8	2.93×10^8	5.21×10^8
$CH_3O{*}+H{*}\rightarrow CH_3OH(g)+2{*}$	k_9	2.01×10^3	7.19×10^3	2.29×10^4	6.61×10^4	1.75×10^5
$CH_2{*}+CO{*}\rightarrow CH_2CO{*}+{*}$	k_{10}	4.80×10^8	7.91×10^8	1.25×10^9	1.89×10^9	2.78×10^9
$CH_2{*}+H{*}\rightarrow CH_3{*}+{*}$	k_{11}	8.1×10^8	1.41×10^9	2.33×10^9	3.70×10^9	5.66×10^9
$CH_3{*}+CO{*}\rightarrow CH_3CO{*}+{*}$	k_{12}	3.36×10^5	8.43×10^5	1.95×10^6	4.18×10^6	8.45×10^6
$CH_3{*}+H{*}\rightarrow CH_4(g)+2{*}$	k_{13}	1.73×10^4	4.70×10^4	1.67×10^5	2.68×10^5	5.77×10^5
$CH_2CO{*}+H{*}\rightarrow CH_3CO{*}+{*}$	k_{14}	3.98×10^{12}	4.83×10^{12}	5.78×10^{12}	6.82×10^{12}	7.94×10^{12}
$CH_3CO{*}+H{*}\rightarrow CH_3CHO{*}+{*}$	k_{15}	7.43×10^5	2.11×10^6	5.45×10^6	1.30×10^7	2.89×10^7
$CH_3CHO{*}+H{*}\rightarrow CH_3CH_2O{*}+{*}$	k_{16}	1.20×10^{11}	1.62×10^{11}	2.13×10^{11}	2.73×10^{11}	3.43×10^{11}
$CH_3CH_2O{*}+H{*}\rightarrow C_2H_5OH(g)+2{*}$	k_{17}	2.40×10^1	9.28×10^2	3.19×10^2	9.84×10^2	2.77×10^3
$O{*}+H{*}\rightarrow OH{*}+{*}$	k_{18}	1.81×10^4	5.19×10^4	1.35×10^5	3.25×10^5	7.28×10^6
$OH{*}+H{*}\rightarrow H_2O(g)+2{*}$	k_{19}	1.39×10^7	2.63×10^7	4.71×10^7	8.03×10^7	1.31×10^8

The site balance of intermediate species included in the reaction mechanism can be written in terms of coverage (θ_X: X=surface species).

$$\begin{aligned}&\theta_{CO}+\theta_H+\theta_{CHO}+\theta_{CH_2O}+\theta_{CH_2OH}+\theta_{CH_2}+\theta_{CH_3O}+\theta_{CH_3}+\theta_{CH_2CO}+\theta_{CH_3CO}+\theta_{CH_3CHO}\\&+\theta_{CH_3CH_2O}+\theta_O+\theta_{OH}+\theta^*=1\end{aligned}\tag{12}$$

CO: $$\theta_{CO}=P_{CO}K_1\theta^*\tag{13}$$

H: $$\theta_H=P_{H_2}^{1/2}K_2^{1/2}\theta^*\tag{14}$$

CHO: $$\frac{d\theta_{CHO}}{dt}=k_3\theta_{CO}\theta_H-k_4\theta_{CHO}\theta_H=0\tag{15}$$

CH$_2$O: $\frac{d\theta_{CH_2O}}{dt} = k_4\theta_{CHO}\theta_H - k_5\theta_{CH_2O}\theta^* - k_6\theta_{CH_2O}\theta_H - k_8\theta_{CH_2O}\theta_H = 0$ (16)

CH$_2$OH: $\frac{d\theta_{CH_2OH}}{dt} = k_6\theta_{CH_2O}\theta_H - k_7\theta_{CH_2OH}\theta^* = 0$ (17)

CH$_2$: $\frac{d\theta_{CH_2}}{dt} = k_5\theta_{CH_2O}\theta^* - k_7\theta_{CH_2OH}\theta^* - k_{10}\theta_{CH_2}\theta_{CO} - k_{11}\theta_{CH_2}\theta_H = 0$ (18)

CH$_3$O: $\frac{d\theta_{CH_3O}}{dt} = k_8\theta_{CH_2O}\theta_H - k_9\theta_{CH_3O}\theta_H = 0$ (19)

CH$_3$: $\frac{d\theta_{CH_3}}{dt} = k_{11}\theta_{CH_2}\theta_H - k_{12}\theta_{CH_3}\theta_{CO} - k_{13}\theta_{CH_3}\theta_H = 0$ (20)

CH$_2$CO: $\frac{d\theta_{CH_2CO}}{dt} = k_{10}\theta_{CH_2}\theta_{CO} - k_{14}\theta_{CH_2CO}\theta_H = 0$ (21)

CH$_3$CO: $\frac{d\theta_{CH_3CO}}{dt} = k_{12}\theta_{CH_3}\theta_{CO} + k_{14}\theta_{CH_2CO}\theta_H - k_{15}\theta_{CH_3CO}\theta_H = 0$ (22)

CH$_3$CHO: $\frac{d\theta_{CH_3CHO}}{dt} = k_{15}\theta_{CH_3CO}\theta_H - k_{16}\theta_{CH_3CHO}\theta_H = 0$ (23)

CH$_3$CH$_2$O: $\frac{d\theta_{CH_3CH_2O}}{dt} = k_{16}\theta_{CH_3CHO}\theta_H - k_{17}\theta_{CH_3CH_2O}\theta_H = 0$ (24)

O: $\frac{d\theta_{OH}}{dt} = k_5\theta_{CH_2O}\theta^* - k_{18}\theta_O\theta_H = 0$ (25)

OH: $\frac{d\theta_{OH}}{dt} = k_7\theta_{CH_2OH}\theta^* + k_{18}\theta_O\theta_H - k_{19}\theta_{OH}\theta_H = 0$ (26)

By putting all of the coverage expressions (equations (13)~(26)) into the equation (12), the coverage of surface free sites θ^* can be calculated. Subsequently, the coverage of all intermediates can be obtained. And the rates of each major product (CH$_3$OH, CH$_4$ and CH$_3$CH$_2$OH) are $r_{CH_3OH} = k_9\theta_{CH_3O}\theta_H$, $r_{\mathrm{CH_4}} = k_{13}\theta_{\mathrm{CH_3}}\theta_{\mathrm{H}}$, $r_{CH_3CH_2OH} = k_{17}\theta_{CH_3CH_2O}\theta_H$, respectively. Here, the relative selectivity is defined by the relative rate for each product, $r/(r_{\mathrm{CH_3OH}} + r_{\mathrm{CH_4}} + r_{\mathrm{C_2H_5OH}})$, where *i* is the species of the products.

4. Differential Charge Density

In order to explain the electronic property of FeCu bimetallic catalyst, the differential charge densities of Fe atom in the FeCu(211) surface have been examined. The differential charge density can be written according to the following equation:[8]

$$\Delta\rho = \rho_{\mathrm{FeCu(211)\ surface}} - \rho_{\mathrm{Cu(211)surface}} - \rho_{\mathrm{Fe\ atom}}$$

Where the $\rho_{\mathrm{FeCu(211)\ surface}}$, $\rho_{\mathrm{Cu(211)\ surface}}$ and $\rho_{\mathrm{Fe\ atom}}$ refer to the charge density for the metal of FeCu(211) surface, Cu(211) surface and Fe atom, respectively.

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