

Co-decorated Cu Alloy Catalyst for C₂ Oxygenates and Ethanol Formations from Syngas on Cu-based Catalyst: Insight into the Role of Co and Cu, as well as the Improved Selectivity

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1. CH_x(x=1-3) Formation on CoCu(211) Surface

1.1 CH Formation

CHO species adsorbed at the Co-Cu mixed site is the dominant product for CO initial activation on CoCu(211) surface; thus, starting from CHO and CHO+H species, four possible pathways with five reactions (**R6~10**) may be responsible for CH formation. Meanwhile, CHO hydrogenation to CH₂O (**R11**) is also considered.

For **R6**, the direct C–O bond cleavage of CHO adsorbed at the bridge-SE-2 Co-Cu site can form CH and O via a transition state TS6, this elementary reaction requires an activation barrier of 169.2 kJ·mol⁻¹ with the reaction energy of -0.1 kJ·mol⁻¹, and the reaction rate constant is 5.73×10⁻⁶ s⁻¹ (*In the text, only the rate constants of all elementary reactions at the temperature of 500 K is presented, those at other temperatures are listed in Table 3*); in TS6, both CH and O species are adsorb at the hollow-2 and bridge-SE-2 sites, respectively, the C–O distance is elongated to 1.926 Å from 1.257 Å in CHO.

Starting from the initial state, CHO+H(1), the dissociation of CHO with H-assisted (**R7**) leads

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to the formations of CH and OH species via a transition state TS7, this elementary reaction has an activation barrier of $155.7 \text{ kJ}\cdot\text{mol}^{-1}$, it is endothermic by $12.9 \text{ kJ}\cdot\text{mol}^{-1}$, and the reaction rate constant is $8.14\times 10^{-4} \text{ s}^{-1}$; in TS7, CH and OH species are adsorbed at the Co-Cu bridge and bridge-SE-2 sites, respectively, in which the O–H distance is 0.978 \AA . Moreover, CHOH may be responsible for CH formation, thus, CHOH formation is firstly investigated.

For **R8**, CHO is hydrogenated to form CHOH via a transition state TS8, this elementary reaction has an activation barrier of $133.0 \text{ kJ}\cdot\text{mol}^{-1}$, it is endothermic by $55.1 \text{ kJ}\cdot\text{mol}^{-1}$, and the reaction rate constant is 0.36 s^{-1} ; in TS8, the O–H distance is decreased to 1.399 \AA from 3.122 \AA in CHO+H(1). Subsequently, CHOH direct dissociation (**R9**) and its dissociation with H-assisted (**R10**) have the activation barriers of 102.0 and $188.1 \text{ kJ}\cdot\text{mol}^{-1}$ with the corresponding reaction energies of -42.2 and $25.2 \text{ kJ}\cdot\text{mol}^{-1}$, respectively.

For **R11**, starting from CHO+H(2), CHO hydrogenation to CH_2O via a transition state TS11 has an activation barrier of $47.7 \text{ kJ}\cdot\text{mol}^{-1}$, this elementary reaction is slightly endothermic by $3.3 \text{ kJ}\cdot\text{mol}^{-1}$, and the reaction rate constant is $7.14\times 10^8 \text{ s}^{-1}$; in TS11, CHO is adsorbed at the bridge-SE site via both C and O atoms, and H is adsorbed at the atop-SE site with the C–H distance of 1.136 \AA .

1.2 CH_2 Formation

Five possible pathways with six reactions (**R12~17**) may form CH_2 . Our results show that for **R12** ($\text{CHO}+\text{H}\rightarrow\text{CH}_2+\text{O}$), CHO prefers to be hydrogenated to CH_2O , then, CH_2O dissociates into CH_2 and O. Meanwhile, CH_2O hydrogenation to CH_3O (**R18**) has been also considered.

For **R13**, the direct C–O bond cleavage of CH_2O can form CH_2 and O via a transition state TS13, this elementary reaction is endothermic by $9.7 \text{ kJ}\cdot\text{mol}^{-1}$ with an activation barrier of $126.7 \text{ kJ}\cdot\text{mol}^{-1}$, and the reaction rate constant is 0.89 s^{-1} ; in TS13, both CH_2 and O species are adsorbed at two adjacent bridge-SE-2 site with the C–O distance of 1.966 \AA .

The dissociation of CH₂O with H-assisted (**R14**) leads to the formation of CH₂ and OH species via a transition state TS14, this elementary reaction has an activation barrier of 96.2 kJ·mol⁻¹, and it is slightly endothermic by 9.5 kJ·mol⁻¹ with the reaction rate constant of 1.88×10³ s⁻¹; in TS14, CH₂O is adsorbed at the atop-SE site, both O and H are adsorbed at the bridge-SE-2 site; the distance between H and O atom is decreased to 0.979 Å from 2.509 Å in CH₂O+H(1).

Similar to CHOH formation, CH₂O hydrogenation to CH₂OH (**R15**) has been firstly investigated. CH₂O can be hydrogenated to form CH₂OH via a transition state TS15 with an activation barrier of 108.3 kJ·mol⁻¹, and this reaction is endothermic by 46.3 kJ·mol⁻¹ with the reaction rate constant of 2.03×10² s⁻¹; in TS15, CH₂O and H species are adsorbed at the atop-SE site, the distance between H and O atom is decreased to 1.283 Å from 2.509 Å in CH₂O+H(1).

For **R16**, CH₂OH direct dissociation into CH₂ and OH via a transition state TS16 has an activation barrier of 51.3 kJ·mol⁻¹, and this elementary reaction is exothermic by 36.8 kJ·mol⁻¹ with the reaction rate constant of 3.17×10⁷ s⁻¹; in TS16, CH₂ and OH species are adsorbed at the atop-SE and bridge-SE-2 sites, respectively, the distance between C and O atom is decreased to 1.844 Å.

CH₂OH dissociation with H-assisted (**R17**) via TS17 needs an activation barrier of 128.8 kJ·mol⁻¹ with the reaction energy of -7.6 kJ·mol⁻¹, and the reaction rate constant is 0.93 s⁻¹; in TS17, CH₂ and H are adsorbed at the bridge-SE-2 site, OH is adsorbed at the atop-SE site, the distance between H and O atom is decreased to 1.538 Å from 2.749 Å in CH₂OH+H.

For **R18**, CH₂O can be hydrogenated to form CH₃O via a transition state TS18 with an activation barrier of 29.2 kJ·mol⁻¹, this elementary reaction is slightly endothermic by 3.4 kJ·mol⁻¹ with the reaction rate constant of 2.92×10¹⁰ s⁻¹; in TS18, CH₂O adsorbs at the bridge-SE-2 site via C and O atom, and H adsorbs at the atop-SE site with the distances between C and H atom of 1.429 Å.

1.3 CH₃ Formation

Similarly, three possible pathways (**R19~21**) are responsible for CH₃ formation. CH₃O hydrogenation to CH₃OH (**R22**) is also considered.

For **R19**, the dissociation of CH₂O with H-assisted leads to the formation of CH₃ and O via a transition state TS19 with an activation barrier of 110.6 kJ·mol⁻¹, and this elementary reaction is exothermic by 12.3 kJ·mol⁻¹ with the reaction rate constant of 6.22 s⁻¹; in TS19, CH₂ and H adsorb at the atop-SE site, O adsorbs at the bridge-SE-2 site, the distance between C and H atom is 1.116 Å.

For **R20**, the direct C–O bond cleavage of CH₃O via a transition state TS20 has an activation barrier of 111.5 kJ·mol⁻¹ with the reaction energy of -15.7 kJ·mol⁻¹, and the reaction rate constant is 4.08×10² s⁻¹; in TS20, CH₃ is adsorbed at the atop-SE site, and O is adsorbed at the bridge-SE-2 site with the C–O distance of 1.878 Å.

For **R21**, the dissociation of CH₃O with H-assisted leads to the formations of CH₃ and OH species via a transition state TS21, this elementary reaction has an activation barrier of 92.8 kJ·mol⁻¹, and it is exothermic by 30.5 kJ·mol⁻¹ with the reaction rate constant of 8.95×10³ s⁻¹; in TS21, CH₃ and H are adsorbed at the atop-SE site, O is adsorbed at the bridge-SE-2 site, and the distance between the C and O is 1.915 Å.

For **R22**, CH₃O hydrogenation to CH₃OH via a transition state TS22 has an activation barrier of 103.5 kJ·mol⁻¹, this elementary reaction is endothermic by 45.1 kJ·mol⁻¹, and the reaction rate constant is 5.01×10² s⁻¹. In TS22, CH₃O is adsorbed at the bridge-SE-2 site via O atom, and H is adsorbed at the atop-SE site with the distances between H and O atom of 1.325 Å.

2. The Formations of C₂ Hydrocarbons and Oxygenates

Starting from the most favorable CH_x monomers, CH₂ and CH₃ species, all possible reactions related to CH₂ and CH₃ species including the dissociation, hydrogenation, coupling and CO/CHO insertion have been examined.

Starting from CH₂ species, CH₂ dissociation into CH and H (**R23**) via a transition state TS23 has an activation barrier and reaction energy of 41.1 and 5.8 kJ·mol⁻¹, respectively, and the reaction rate constant is 1.93×10⁸ s⁻¹; in TS23, CH is adsorbed at the hollow-2 site, and H is adsorbed at the atop-SE Co site with the C–H distance of 1.633 Å.

CH₂ hydrogenation to CH₃ (**R24**) via a transition state TS24 has an activation barrier of 19.0 kJ·mol⁻¹, and it is exothermic by 25.6 kJ·mol⁻¹ with the reaction rate constant of 6.09×10¹⁰ s⁻¹; in TS24, CH₂ is adsorbed at the bridge-SE-2 Co-Cu site, H is adsorbed at the atop-SE Co site; the distance between C and H atom is decreased to 1.705 Å from 2.349 Å in CH₂+H.

For **R25**, CH₂ coupling leads to C₂H₄ via a transition state TS25, this elementary reaction needs an activation barrier of 17.7 kJ·mol⁻¹, and it is strongly exothermic by 104.5 kJ·mol⁻¹ with the reaction rate constant of 1.96×10¹¹ s⁻¹; in TS25, both CH₂ are adsorbed at the bridge-SE-2 Co-Cu sites, the distance between two C atom is decreased to 2.219 Å from 2.716 Å in CH₂+CH₂.

For **R26**, CO insertion into CH₂ can form CH₂CO via a transition state TS26, this elementary reaction is slightly endothermic by 12.1 kJ·mol⁻¹ with an activation barrier of 39.9 kJ·mol⁻¹ and the reaction rate constant of 9.07×10⁸ s⁻¹; in TS26, CH₂ and CO species are adsorbed at the bridge-SE-2 Co-Cu site and atop-SE Co site, respectively, the distance between C₁ and C₂ atoms is decreased to 1.805 Å from 2.474 Å in CH₂+CO.

For **R27**, CHO insertion into CH₂ to CH₂CHO has an activation barrier of 24.7 kJ·mol⁻¹ with the reaction energy of -91.9 kJ·mol⁻¹, and the reaction rate constant is 4.30×10¹⁰ s⁻¹; in TS27, CH₂ and CHO species are adsorbed at the bridge-SE-2 Co-Cu sites with the distance between C₁ and C₂ atoms of 2.025 Å.

Starting from CH₃ species, in **R28**, CH₃ dissociation into CH₂ and H has an activation barrier and reaction energy of 44.6 and 25.6 kJ·mol⁻¹, respectively, and the reaction rate constant is

$5.45 \times 10^7 \text{ s}^{-1}$; TS28 has been presented in the reaction of $\text{CH}_2 + \text{H} \rightarrow \text{CH}_3$ (**R23**).

For **R29**, CH_3 hydrogenation can from CH_4 via a transition state TS29, this elementary reaction is slightly exothermic by $0.2 \text{ kJ}\cdot\text{mol}^{-1}$ with an activation barrier of $87.3 \text{ kJ}\cdot\text{mol}^{-1}$, and the reaction rate constant is $3.23 \times 10^4 \text{ s}^{-1}$; in TS29, CH_3 and H species are adsorbed at the bridge-SE-2 Co-Cu sites; the distance between C and H atom is decreased to 1.477 \AA from 2.425 \AA in the initial state, $\text{CH}_3 + \text{H}$.

For **R30**, CH_3 coupling to C_2H_6 via a transition state TS30 has an activation barrier of $156.2 \text{ kJ}\cdot\text{mol}^{-1}$, and it is exothermic by $39.4 \text{ kJ}\cdot\text{mol}^{-1}$ with the reaction rate constant of $2.41 \times 10^{-2} \text{ s}^{-1}$; in TS30, one CH_3 is adsorbed at the atop-SE site, the other is pre-adsorbed at the bridge-SE-2 site, the distance of two C atoms is decreased to 2.439 \AA .

For **R31**, CO insertion into CH_3 can form CH_3CO via a transition state TS31, this elementary reaction is endothermic by $30.4 \text{ kJ}\cdot\text{mol}^{-1}$ with an activation barrier of $83.1 \text{ kJ}\cdot\text{mol}^{-1}$, and the reaction rate constant is $1.30 \times 10^5 \text{ s}^{-1}$; in TS31, CH_3 adsorbs at the atop-SE Co site, CO adsorbs at the bridge-SE-2 Co-Cu site, the distance between C_1 and C_2 atom is decreased to 1.833 \AA from 2.584 \AA in $\text{CH}_3 + \text{CO}$.

For **R32**, CHO insertion into CH_3 to CH_3CHO has an activation barrier of $41.1 \text{ kJ}\cdot\text{mol}^{-1}$ with the reaction energy of $-66.8 \text{ kJ}\cdot\text{mol}^{-1}$, and the reaction rate constant is $3.56 \times 10^9 \text{ s}^{-1}$; in TS32, CH_3 is adsorbed at the atop-SE Co site, and CHO is adsorbed at the bridge Co-Cu site with the distance between C_1 and C_2 atoms of 1.976 \AA .

3. Ethanol Formation

Since CH_2CO and CH_3CO are the dominant C_2 oxygenates, both can be successively hydrogenated to $\text{C}_2\text{H}_5\text{OH}$.

Starting from CH_2CO , three possible pathways exist. Firstly, CH_2CO hydrogenation to CH_3CO

(**R33**) has an activation barrier of $53.0 \text{ kJ}\cdot\text{mol}^{-1}$ with the reaction energy of $13.6 \text{ kJ}\cdot\text{mol}^{-1}$, and the rate constant is $4.67\times 10^7 \text{ s}^{-1}$; in TS33, CH_2CO and H are adsorbed at two adjacent the bridge-SE-2 Co-Cu sites; the distance between C_2 and H atom is decreased to 1.691 \AA from 2.699 \AA in the initial state, $\text{CH}_2\text{CO}+\text{H}(1)$. Secondly, CH_2CO hydrogenation to CH_2CHO (**R34**) via a transition state TS34, and this elementary reaction needs to overcome an activation barrier of $59.4 \text{ kJ}\cdot\text{mol}^{-1}$ with the reaction energy of $-0.5 \text{ kJ}\cdot\text{mol}^{-1}$, and the rate constant is $3.11\times 10^6 \text{ s}^{-1}$; in TS34, CH_2CO is adsorbed at the bridge-SE-2 Co-Cu site, and H is adsorbed at the atop-SE Co site; the distance between C_1 and H atom is decreased to 1.339 \AA from 2.428 \AA in the initial state, $\text{CH}_2\text{CO}+\text{H}(1)$. Thirdly, CH_2CO hydrogenation to CH_2COH (**R35**) via a transition state TS35, and this elementary reaction needs to overcome an activation barrier of $128.6 \text{ kJ}\cdot\text{mol}^{-1}$ with the reaction energy of $69.1 \text{ kJ}\cdot\text{mol}^{-1}$, and the rate constant is 3.04 s^{-1} ; in TS35, CH_2CO is adsorbed at the atop-SE Co site, and H is adsorbed at the atop-SE Cu site; the distance between O and H atom is decreased to 1.434 \AA from 2.813 \AA in the initial state, $\text{CH}_2\text{CO}+\text{H}(2)$.

Based on the kinetic data, CH_2CO prefers to be hydrogenated to CH_2CHO and CH_3CO , thus, CH_2CHO and CH_3CO further hydrogenation have also been further calculated.

Starting from CH_2CHO , there are two possible pathways for hydrogenation. One is CH_2CHO hydrogenation to CH_3CHO (**R36**) via a transition state TS36, and this elementary reaction needs to overcome an activation barrier of $42.9 \text{ kJ}\cdot\text{mol}^{-1}$ with the reaction energy of $0.1 \text{ kJ}\cdot\text{mol}^{-1}$, and the rate constant is $1.36\times 10^{10} \text{ s}^{-1}$; in TS36, CH_2CHO and H are adsorbed at two adjacent bridge-SE-2 Co-Cu sites; the distance between C_2 and H atom is decreased to 1.571 \AA from 2.393 \AA in the initial state, $\text{CH}_2\text{CHO}+\text{H}(1)$. The other is CH_2CHO hydrogenation to CH_2CHOH (**R37**) via a transition state TS37, which is less favorable than CH_2CHO hydrogenation to CH_3CHO , and this elementary reaction needs to overcome an activation barrier of $94.9 \text{ kJ}\cdot\text{mol}^{-1}$ with the reaction energy of 41.4

$\text{kJ}\cdot\text{mol}^{-1}$, and the rate constant is $1.84\times 10^3 \text{ s}^{-1}$; in TS37, CH_2CHO is adsorbed at the bridge-SE-2 Co-Cu site, and H is adsorbed at atop-SE Co site; the distance between O and H atom is decreased to 1.357 \AA from 2.685 \AA in the initial state, $\text{CH}_2\text{CHO}+\text{H}(2)$.

Starting from CH_3CO , two possible hydrogenation pathways exist. One is CH_3CO hydrogenation to CH_3CHO (**R38**) via a transition state TS38, and this elementary reaction needs to overcome an activation barrier of $57.1 \text{ kJ}\cdot\text{mol}^{-1}$ with the reaction energy of $-14.0 \text{ kJ}\cdot\text{mol}^{-1}$, and the rate constant is $1.16\times 10^8 \text{ s}^{-1}$; in TS38, CH_3CO is adsorbed at the bridge-SE-2 Co-Cu site, and H species is adsorbed at the atop-SE site; the distance between C_1 and H atom is decreased to 1.157 \AA from 2.218 \AA in the initial state, $\text{CH}_3\text{CO}+\text{H}(1)$. The other is CH_3CO hydrogenation to CH_3COH (**R39**) via a transition state TS39, which is less favorable than CH_3CO hydrogenation to CH_3CHO , and this elementary reaction needs to overcome an activation barrier of $123.8 \text{ kJ}\cdot\text{mol}^{-1}$ with the reaction energy of $58.7 \text{ kJ}\cdot\text{mol}^{-1}$, and the rate constant is 6.81 s^{-1} ; in TS39, CH_3CO and H are adsorbed at the atop-SE Co site; the distance between O and H atom is decreased to 1.403 \AA from 3.064 \AA in the initial state, $\text{CH}_3\text{CO}+\text{H}(2)$.

As mentioned above, both CH_2CHO and CH_3CO prefer to be hydrogenated to CH_3CHO . Therefore, CH_3CHO further hydrogenation has also been calculated. CH_3CHO hydrogenation to $\text{CH}_3\text{CH}_2\text{O}$ (**R40**) has an activation barrier of $27.5 \text{ kJ}\cdot\text{mol}^{-1}$ with the reaction energy of $10.4 \text{ kJ}\cdot\text{mol}^{-1}$, and the rate constant is $1.36\times 10^{10} \text{ s}^{-1}$, which is much more favorable both thermodynamically and dynamically than CH_3CHO hydrogenation to CH_3CHOH (**R41**) with the activation barrier and reaction energy of 112.8 and $57.1 \text{ kJ}\cdot\text{mol}^{-1}$, respectively; in TS37, CH_3CHO is adsorbed at the bridge-SE-1 Co-Cu site, and H is adsorbed at the atop-SE Co site; the distance between C_1 and H atom is decreased to 1.469 \AA from 2.692 \AA in the initial state, $\text{CH}_3\text{CHO}+\text{H}(1)$.

Finally, $\text{CH}_3\text{CH}_2\text{O}$ hydrogenation to ethanol (**R42**) via TS42 is endothermic by $48.6 \text{ kJ}\cdot\text{mol}^{-1}$

with an activation barrier of $109.6 \text{ kJ}\cdot\text{mol}^{-1}$, and the rate constant is $5.16\times 10^2 \text{ s}^{-1}$; in TS38, $\text{CH}_3\text{CH}_2\text{O}$ and H are adsorbed at the atop-SE Co sites; the distance between O and H atom is decreased to 1.419 \AA from 2.496 \AA in the initial state.

4. Microkinetic modeling

Microkinetic modeling¹⁻⁴ has been widely employed to investigate the activity and selectivity of the catalyst, for example, Liu *et al.*² have proved that the water dissociation, which is considered as the rate-determining step for water-gas-shift reaction, run faster on Au and Cu nanoparticles than their parent bulk surfaces. Liu and Choi⁴ have investigated the formation of ethanol 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 CoCu(211) surface under the typical experimental conditions ($P_{\text{CO}}=4 \text{ atm}$, $P_{\text{H}_2}=8 \text{ atm}$, and $T=500\sim 600 \text{ K}$). All elementary reactions involved in the optimal formation pathways of CH_3OH , CH_4 and $\text{C}_2\text{H}_5\text{OH}$, as well as the corresponding reaction rates at the temperature of 500, 525, 550, 575 and 600 K used for the microkinetic modeling are summarized in Table S1.

Table S1 All elementary reactions involved in the optimal formation pathways of CH_3OH , CH_4 and $\text{C}_2\text{H}_5\text{OH}$, as well as the corresponding reaction rate constants at the temperature of 500, 525, 550, 575 and 600 K used for the microkinetic modeling.

| Elementary Reactions | Rate constants $k \text{ (s}^{-1}\text{)}$ | | | | | |
|---|--|-------------------|-------------------|-------------------|-------------------|-------------------|
| | 500K | 525K | 550K | 575K | 600K | |
| $\text{CO(g)}+*\leftrightarrow\text{CO}^*$ | | | | | | |
| $\text{H}_2(\text{g})+*\leftrightarrow 2\text{H}^*$ | | | | | | |
| $\text{CO}^*+\text{H}^*\rightarrow\text{CHO}^{**}$ | k_3 | 2.68×10^5 | 8.50×10^5 | 1.45×10^6 | 4.06×10^6 | 5.94×10^6 |

| | | | | | | |
|---|----------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| $\text{CHO}^* + \text{H}^* \rightarrow \text{CH}_2\text{O}^*$ | k_4 | 7.14×10^8 | 1.31×10^9 | 2.27×10^9 | 3.76×10^9 | 5.98×10^9 |
| $\text{CH}_2\text{O}^* + \text{H}^* \rightarrow \text{CH}_2^* + \text{OH}^*$ | k_5 | 1.88×10^3 | 6.11×10^3 | 1.79×10^4 | 4.81×10^4 | 1.19×10^5 |
| $\text{CH}_2\text{O}^* + \text{H}^* \rightarrow \text{CH}_3\text{O}^* + ^*$ | k_6 | 2.92×10^{10} | 4.27×10^{10} | 6.06×10^{10} | 8.34×10^{10} | 1.12×10^{11} |
| $\text{CH}_3\text{O}^* + \text{H}^* \rightarrow \text{CH}_3^* + \text{OH}^*$ | k_7 | 8.95×10^3 | 2.82×10^4 | 8.01×10^4 | 2.08×10^5 | 5.03×10^5 |
| $\text{CH}_3\text{O}^* + \text{H}^* \rightarrow \text{CH}_3\text{OH}(\text{g}) + 2^*$ | k_8 | 5.01×10^2 | 1.75×10^3 | 5.44×10^3 | 1.54×10^4 | 4.00×10^4 |
| $\text{CH}_2^* + \text{H}^* \rightarrow \text{CH}_3^*$ | k_9 | 6.09×10^{10} | 7.90×10^{10} | 1.00×10^{11} | 1.25×10^{11} | 1.53×10^{11} |
| $\text{CH}_2^* + \text{CO}^* \rightarrow \text{CH}_2\text{CO}^* + ^*$ | k_{10} | 9.07×10^8 | 1.49×10^9 | 2.35×10^9 | 3.56×10^9 | 5.22×10^9 |
| $\text{CH}_3^* + \text{H}^* \rightarrow \text{CH}_4(\text{g}) + 2^*$ | k_{11} | 3.23×10^4 | 9.49×10^4 | 2.54×10^5 | 6.24×10^5 | 1.42×10^6 |
| $\text{CH}_3^* + \text{CO}^* \rightarrow \text{CH}_3\text{CO}^* + ^*$ | k_{12} | 1.30×10^5 | 3.55×10^5 | 8.90×10^5 | 2.06×10^6 | 4.46×10^6 |
| $\text{CH}_2\text{CO}^* + \text{H}^* \rightarrow \text{CH}_3\text{CO}^* + ^*$ | k_{13} | 4.67×10^7 | 9.02×10^7 | 1.64×10^8 | 2.85×10^8 | 4.72×10^8 |
| $\text{CH}_2\text{CO}^* + \text{H}^* \rightarrow \text{CH}_2\text{CHO}^* + ^*$ | k_{14} | 3.11×10^6 | 6.38×10^6 | 1.23×10^7 | 2.24×10^7 | 3.89×10^7 |
| $\text{CH}_2\text{CHO}^* + \text{H}^* \rightarrow \text{CH}_3\text{CHO}^* + ^*$ | k_{15} | 1.36×10^{10} | 2.36×10^{10} | 3.91×10^{10} | 6.20×10^{10} | 9.49×10^{10} |
| $\text{CH}_3\text{CO}^* + \text{H}^* \rightarrow \text{CH}_3\text{CHO}^* + ^*$ | k_{16} | 1.16×10^8 | 2.36×10^8 | 4.52×10^8 | 8.19×10^8 | 1.42×10^8 |
| $\text{CH}_3\text{CHO}^* + \text{H}^* \rightarrow \text{CH}_3\text{CH}_2\text{O}^* + ^*$ | k_{17} | 6.43×10^{10} | 9.34×10^{10} | 1.31×10^{11} | 1.80×10^{11} | 2.40×10^{11} |
| $\text{CH}_3\text{CH}_2\text{O}^* + \text{H}^* \rightarrow \text{C}_2\text{H}_5\text{OH}(\text{g}) + 2^*$ | k_{18} | 5.16×10^2 | 1.93×10^3 | 6.43×10^3 | 1.93×10^4 | 5.30×10^4 |
| $\text{OH}^* + \text{H}^* \rightarrow \text{H}_2\text{O}(\text{g}) + 2^*$ | k_{19} | 9.03×10^1 | 3.44×10^2 | 1.16×10^3 | 3.55×10^3 | 9.87×10^3 |

The adsorption reactions of CO and H₂ were assumed in equilibrium. The equilibrium constants were obtained from the below equation:

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

Where E_{ads} refers to the adsorption energy of CO or H₂, and ΔS is the entropy change from the gas phase at the reaction temperature, obtained from NIST Chemistry WebBook.⁵

$$\theta_{\text{CO}} = P_{\text{CO}} K_1 \theta^*$$

$$\theta_{\text{H}} = P_{\text{H}_2}^{1/2} K_2^{1/2} \theta^*$$

For the kinetics of surface reactions, we only consider forward reactions, which is a safe approximation at such high partial pressures of CO and H₂ as it is used in experiment.

The rate constants have been presented in Table 3 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).

$$\begin{aligned} &\theta_{CO} + \theta_H + \theta_{CHO} + \theta_{CH_2O} + \theta_{CH_2} + \theta_{CH_3O} + \theta_{CH_3} + \theta_{CH_2CO} + \theta_{CH_2CHO} + \theta_{CH_3CO} + \theta_{CH_3CHO} \\ &+ \theta_{CH_3CH_2O} + \theta_{OH} + \theta^* = 1 \end{aligned} \quad (1)$$

The surface species including CHO, CH₂O, CH₂, CH₃O, CH₃, CH₂CO, CH₃CO, CH₃CHO, CH₃CH₂O, and OH were described according to the pseudo steady-state approximation,¹ which states that the production rate and consumption rate are equal for all intermediates:

$$1. \text{ CHO: } \frac{d\theta_{CHO}}{dt} = k_3\theta_{CO}\theta_H - k_4\theta_{CHO}\theta_H = 0 \quad (2)$$

$$2. \text{ CH}_2\text{O: } \frac{d\theta_{CH_2O}}{dt} = k_4\theta_{CHO}\theta_H - k_5\theta_{CH_2O}\theta_H - k_6\theta_{CH_2O}\theta_H = 0 \quad (3)$$

$$3. \text{ CH}_2: \frac{d\theta_{CH_2}}{dt} = k_5\theta_{CH_2O}\theta_H - k_9\theta_{CH_2}\theta_H - k_{10}\theta_{CH_2}\theta_{CO} = 0 \quad (4)$$

$$4. \text{ CH}_3\text{O: } \frac{d\theta_{CH_3O}}{dt} = k_6\theta_{CH_2O}\theta_H - k_7\theta_{CH_3O}\theta_H - k_8\theta_{CH_3O}\theta_H = 0 \quad (5)$$

$$5. \text{ CH}_3: \frac{d\theta_{CH_3}}{dt} = k_7\theta_{CH_3O}\theta_H + k_9\theta_{CH_2}\theta_H - k_{11}\theta_{CH_3}\theta_H - k_{12}\theta_{CH_3}\theta_{CO} = 0 \quad (6)$$

$$6. \text{ CH}_2\text{CO: } \frac{d\theta_{CH_2CO}}{dt} = k_{10}\theta_{CH_2}\theta_{CO} - k_{13}\theta_{CH_2CO}\theta_H - k_{14}\theta_{CH_2CO}\theta_H = 0 \quad (7)$$

$$7. \text{ CH}_2\text{CHO: } \frac{d\theta_{CH_2CHO}}{dt} = k_{14}\theta_{CH_2CO}\theta_H - k_{15}\theta_{CH_2CHO}\theta_H = 0 \quad (8)$$

$$8. \text{ CH}_3\text{CO: } \frac{d\theta_{CH_3CO}}{dt} = k_{12}\theta_{CH_3}\theta_{CO} + k_{13}\theta_{CH_2CO}\theta_H - k_{16}\theta_{CH_3CO}\theta_H = 0 \quad (9)$$

$$9. \text{ CH}_3\text{CHO: } \frac{d\theta_{CH_3CHO}}{dt} = k_{15}\theta_{CH_2CHO}\theta_H + k_{16}\theta_{CH_3CO}\theta_H - k_{17}\theta_{CH_3CHO}\theta_H = 0 \quad (10)$$

$$10. \text{ CH}_3\text{CH}_2\text{O: } \frac{d\theta_{CH_3CH_2O}}{dt} = k_{17}\theta_{CH_3CHO}\theta_H - k_{18}\theta_{CH_3CH_2O}\theta_H = 0 \quad (11)$$

$$11. \text{ OH: } \frac{d\theta_{OH}}{dt} = k_5\theta_{CH_2O}\theta_H + k_7\theta_{CH_3O}\theta_H - k_{19}\theta_{OH}\theta_H = 0 \quad (12)$$

By putting all of the coverage expressions (equations (2)~(12)) into equation (1), we can calculate the coverage of surface free sites θ^* . Subsequently, the coverage of all intermediates can be obtained.

The rates for each major product (CH_3OH , CH_4 and $\text{CH}_3\text{CH}_2\text{OH}$) are $r_{\text{CH}_3\text{OH}} = k_8 \theta_{\text{CH}_3\text{O}} \theta_H$; $r_{\text{CH}_4} = k_{11} \theta_{\text{CH}_3} \theta_H$; $r_{\text{CH}_3\text{CH}_2\text{OH}} = k_{18} \theta_{\text{CH}_3\text{CH}_2\text{O}} \theta_H$, respectively.

5. Differential charge density

In order to explain the electronic properties of Cu-Co catalysts, we have investigated the differential charge density of Cu atom over Cu(211) surface, Co atom and its surrounding Cu atoms over CoCu(211) surface. The differential charge density⁶ can be written in equation form as:

$$\Delta\rho = \rho_{\text{full surface}} - \rho_{\text{surface with vacancy}} - \rho_{\text{atom}}$$

Where the $\rho_{\text{full surface}}$ refers to the charge density of Cu atoms of Cu(211) surface and CoCu(211) surface. $\rho_{\text{surface with vacancy}}$ and ρ_{atom} refer to the charge densities of these defective systems and that of the lone Co atom (ρ_{atom}) that is removed, then, it is calculated and compared to the charge densities of the metals without the full surface.

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