

(Electronic Supplementary Information)

**Molecular mechanism of methane dry reforming on  $\text{Co}_3\text{Mo}_3\text{N}$  catalyst with dual sites**

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**FIGURE LIST**

**Fig. S1.** Optimized structures of the intermediates listed in Table 2 on Co(0001). C, O, H, and Co are depicted in brown, red, light pink, and dark blue, respectively.

**Fig. S2.** Optimized structures of the intermediates listed in Table 2 on Mo<sub>2</sub>N(110). C, O, H, Mo, and N are depicted in brown, red, light pink, dark blue, and light blue, respectively.

**Fig. S3.** Optimized transition state structures on Co(0001). Atomic distances (in Å) are labeled and indicated in dashed lines. C, O, H, and Co are depicted in brown, red, white, and dark blue, respectively.

**Fig. S4.** Optimized transition state structures on Mo-terminated Mo<sub>2</sub>N(110). Atomic distances (in Å) are labeled and indicated in dashed lines. C, O, H, Mo, and N are depicted in brown, red, white, pink, and light blue, respectively.

**Fig. S5.** Free energy profiles depicting on Co<sub>3</sub>Mo<sub>3</sub>N(111) (black), Co(0001) (red dashed), and Mo<sub>2</sub>N(110) (blue dotted) emphasizing the CH<sub>4</sub> activation and COH oxidation pathway at 1000 K and 1 bar. Gas phase CO<sub>2</sub> and CH<sub>4</sub> and corresponding clean surfaces were used as the zero energy references. Similarly, gas phase CO and H<sub>2</sub>, following the reaction stoichiometry, are considered as the final products. The kinetically critical C–H activation step and carbon formation are highlighted with grey bars. The inset figure illustrates the accompanying CO<sub>2</sub> dissociation on respective Co<sub>3</sub>Mo<sub>3</sub>N(111) (black), Co(0001) (red dashed), and Mo<sub>2</sub>N(110) (blue dotted) surfaces under the same condition.

**Fig. S6.** Optimized transition states for CH<sub>4</sub> activation on transition metal surfaces. The distances (in Å) of the dissociating C–H bond are labeled and indicated in dashed lines.

**Fig. S7.** Linear scaling relations of the binding energy corresponding to fragments bound in the most stable adsorption site for (a) H versus C/O, (b) CH versus C, (c) CO versus O, (d) OH versus O. The standard deviations, MAE, and MAX are also shown.

**Fig. S8.** BEP relationship for CH<sub>4</sub> C-H bond activation in terms of dissociation energies ( $\Delta E$ ) and energy barriers ( $E_a$ ). The standard deviations, MAE, and MAX are also shown.

## **TABLE LIST**

**Table S1.** Lattice parameters of surface models.

**Table S2.** Binding energies (eV) of H, CH<sub>3</sub> on their preferred binding sites of the close-packed transition metal surfaces; CH<sub>4</sub> dissociation energies ( $\Delta E$ ); and C–H bond activation energy barriers ( $E_a$ ). Literature values are shown in the parentheses.

**Table S3.** Rate constants of the elementary DRM steps on Co<sub>3</sub>Mo<sub>3</sub>N(111), Co(0001), Mo<sub>2</sub>N(110), and Ni(111). The elementary step indices correspond to the mechanism shown in Table 2 of the main text.

**Table S4.** Rate constants and equilibrium constants on Co<sub>3</sub>Mo<sub>3</sub>N(111), Ni(111), Co(0001), and Mn<sub>2</sub>N(110) used in Eqns. (S3, S4, S6, S7).

**Appendix 1.** Derivations of single-site and dual-site microkinetic models for DRM.

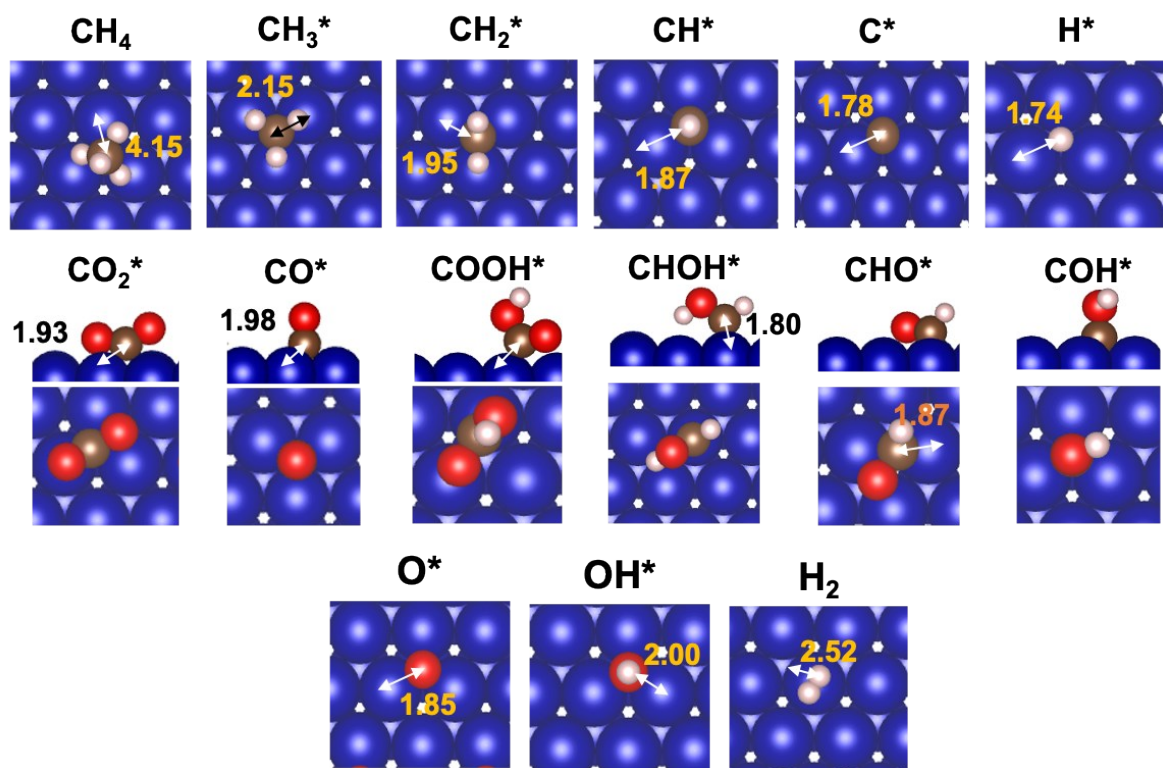


Fig. S1

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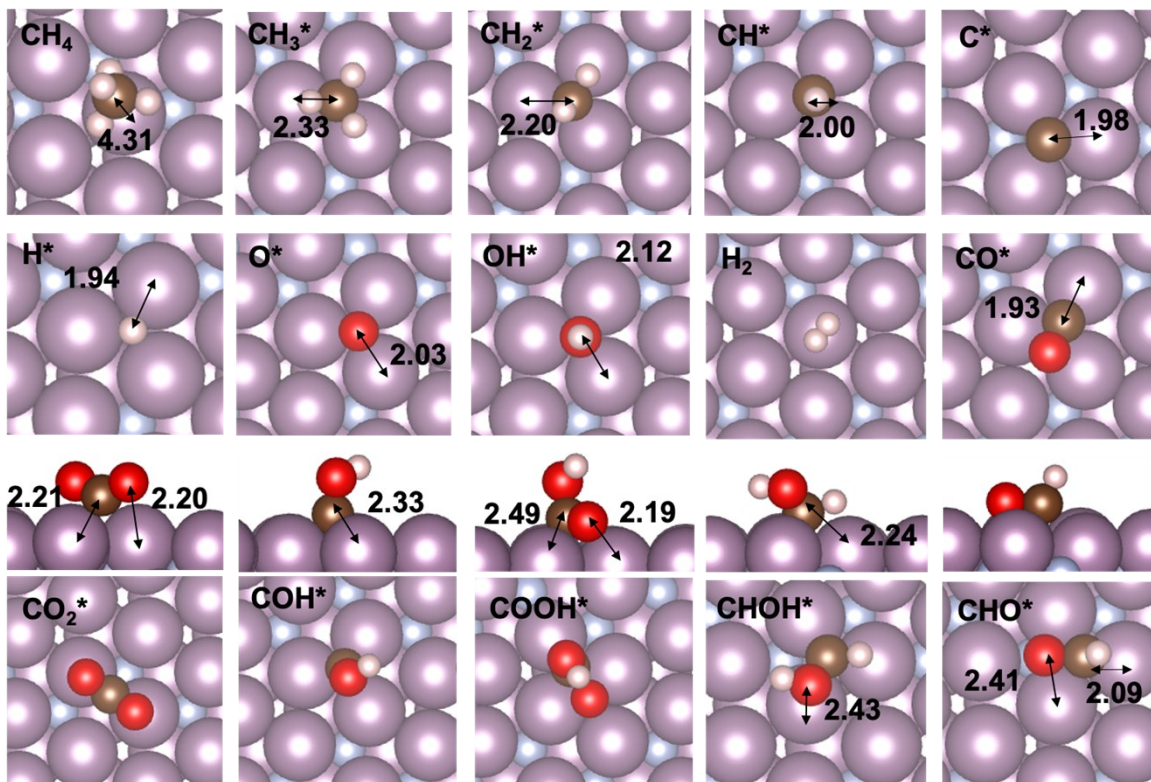


Fig. S2

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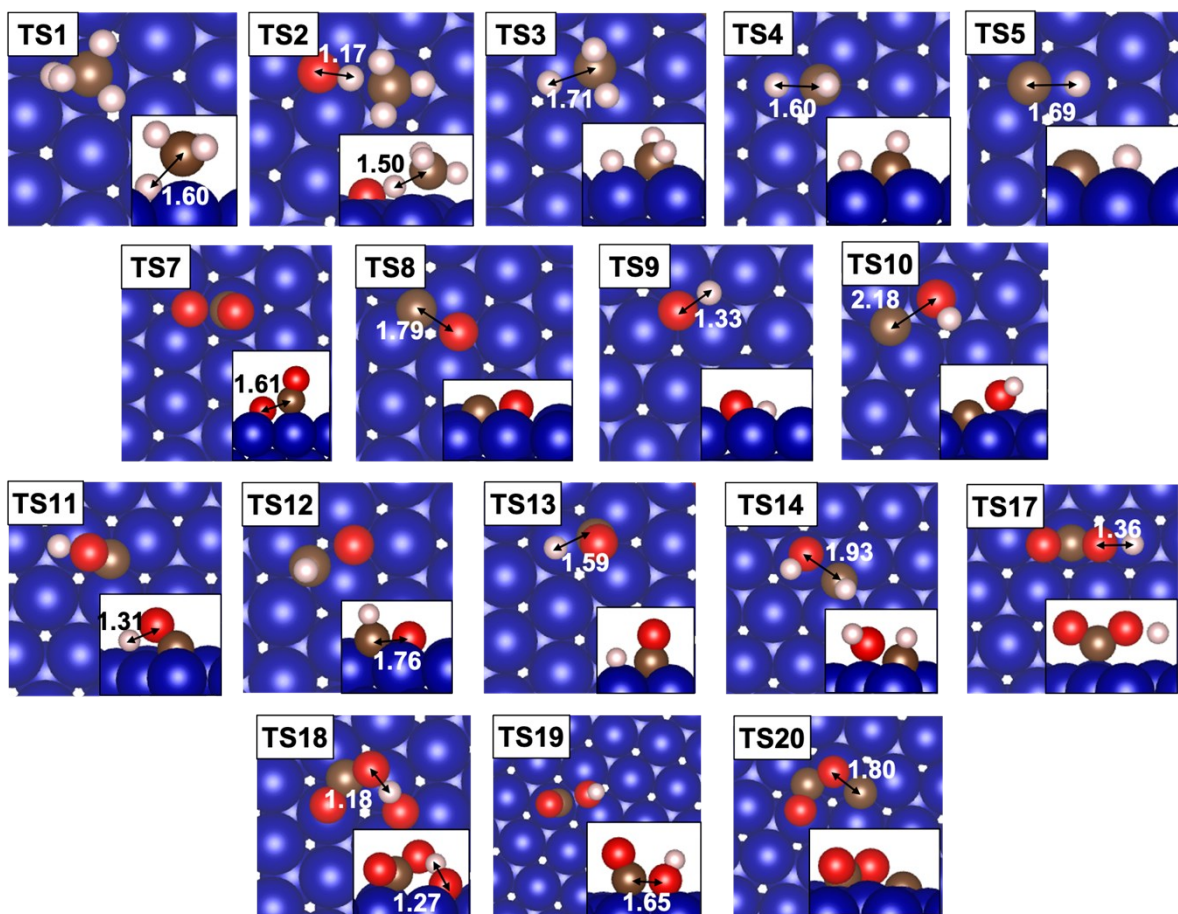


Fig. S3

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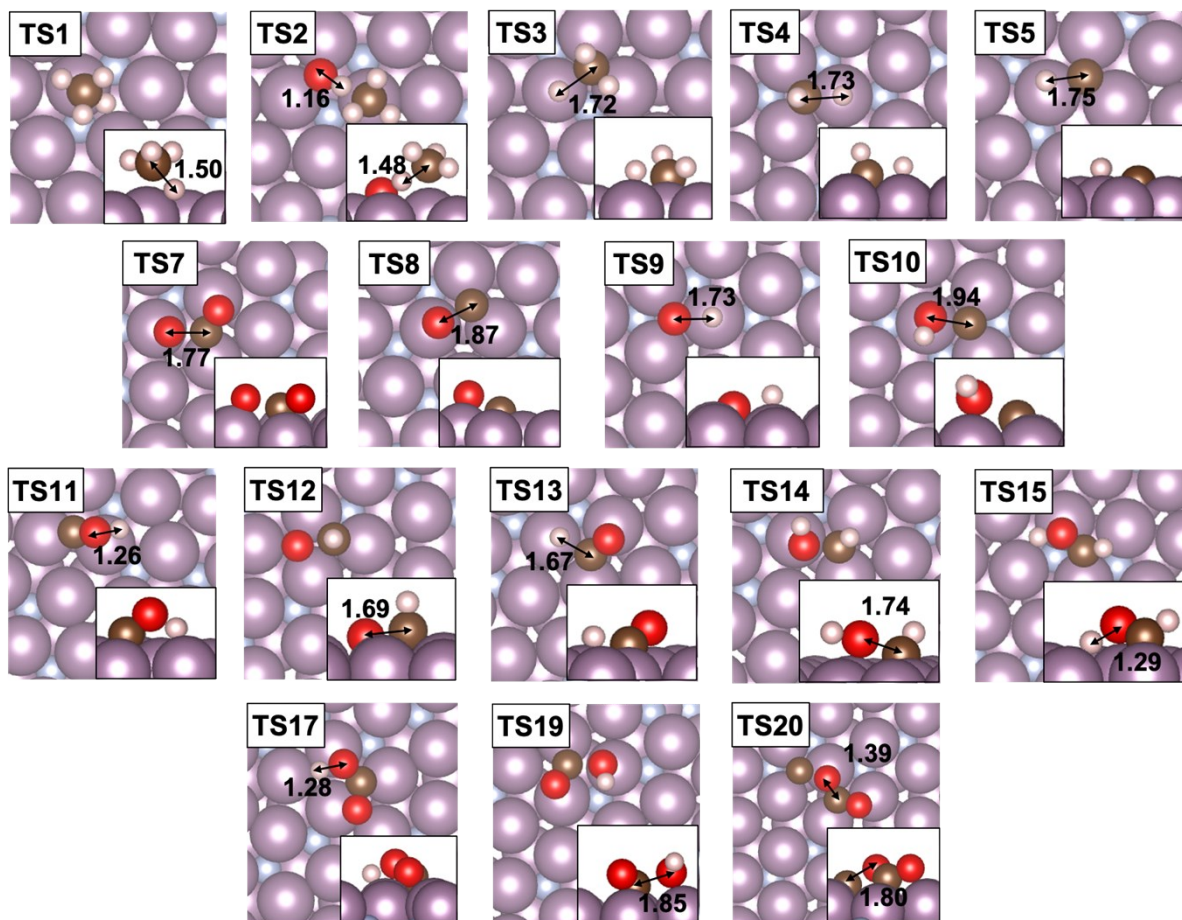


Fig. S4

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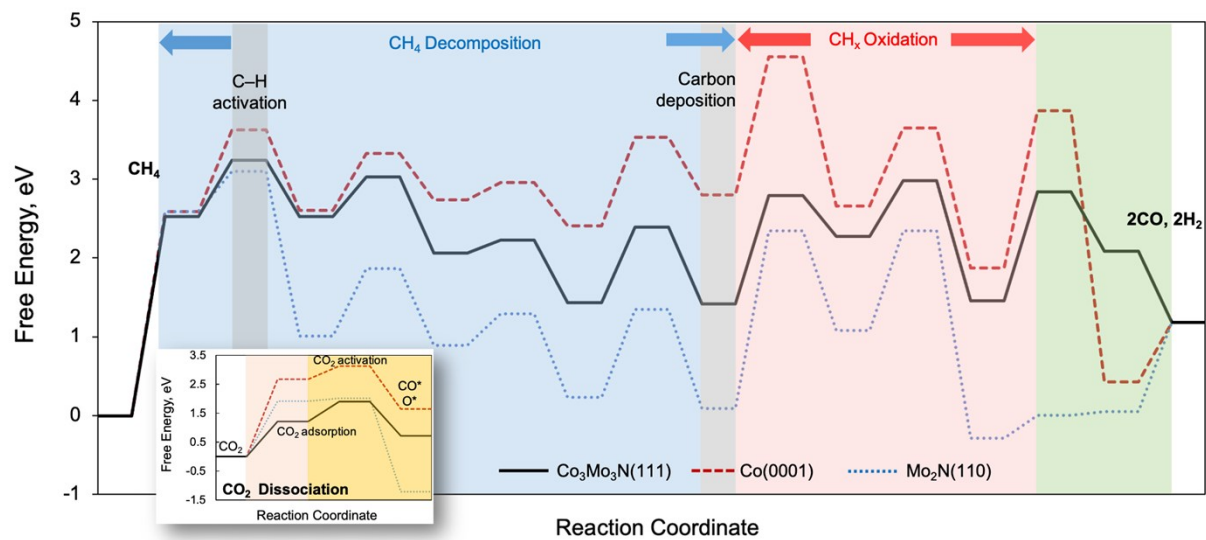


Fig. S5

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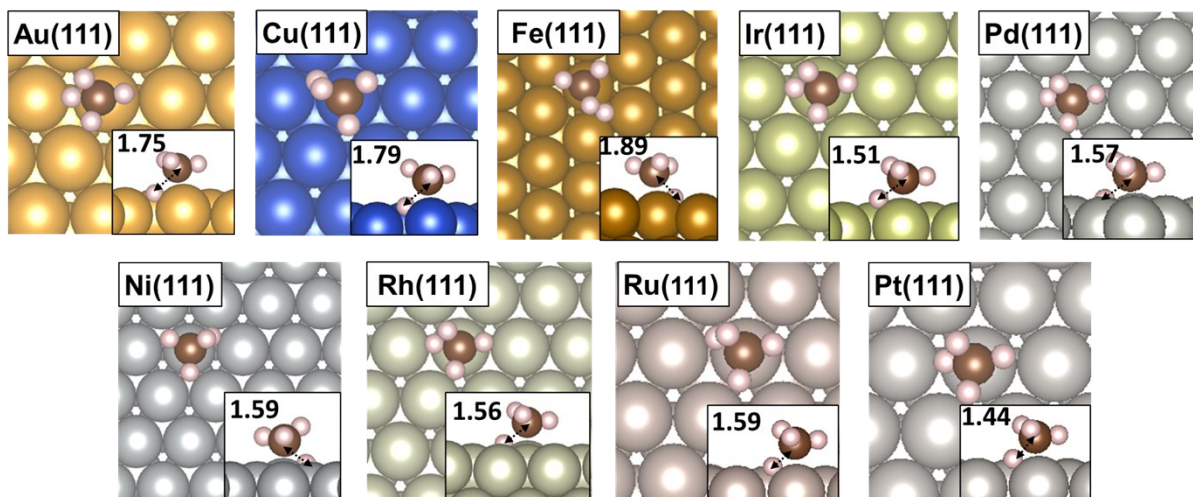
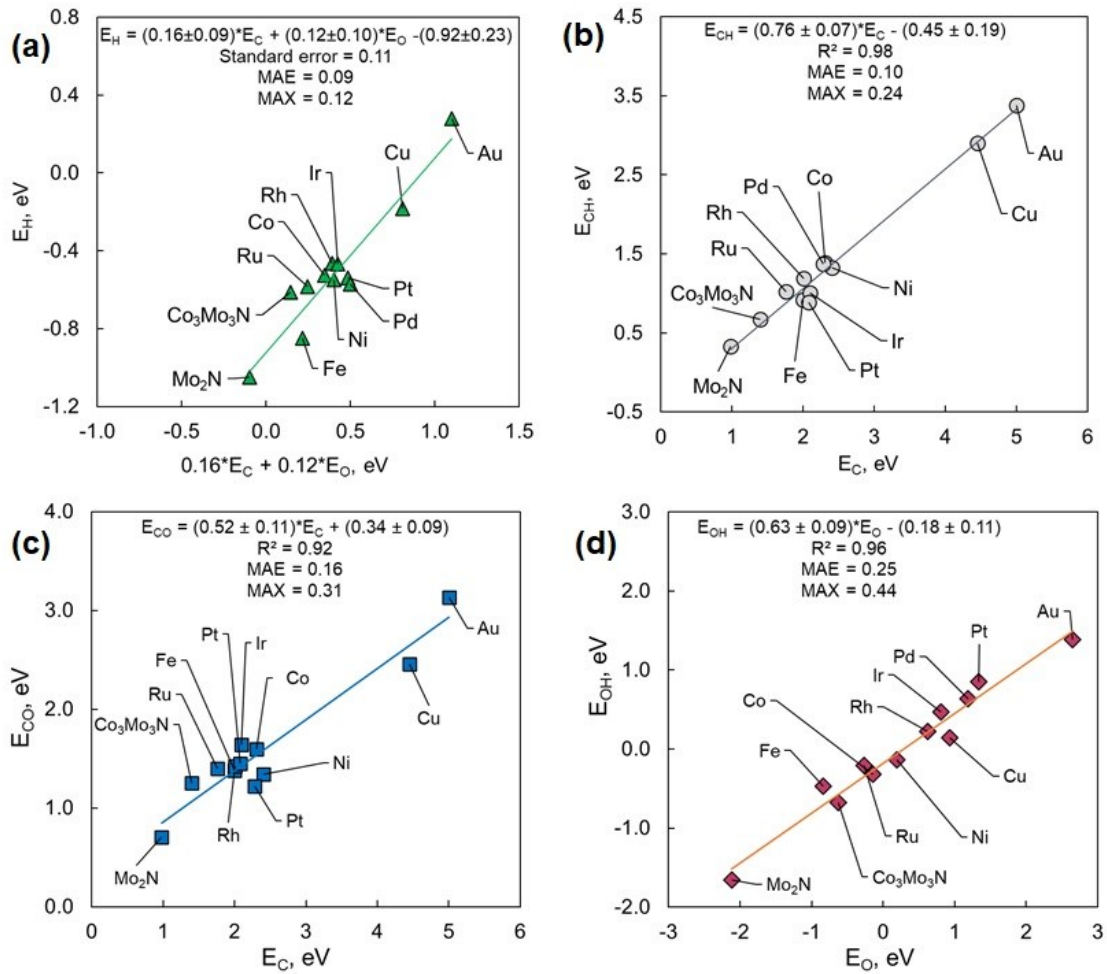


Fig. S6

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**Fig. S7**

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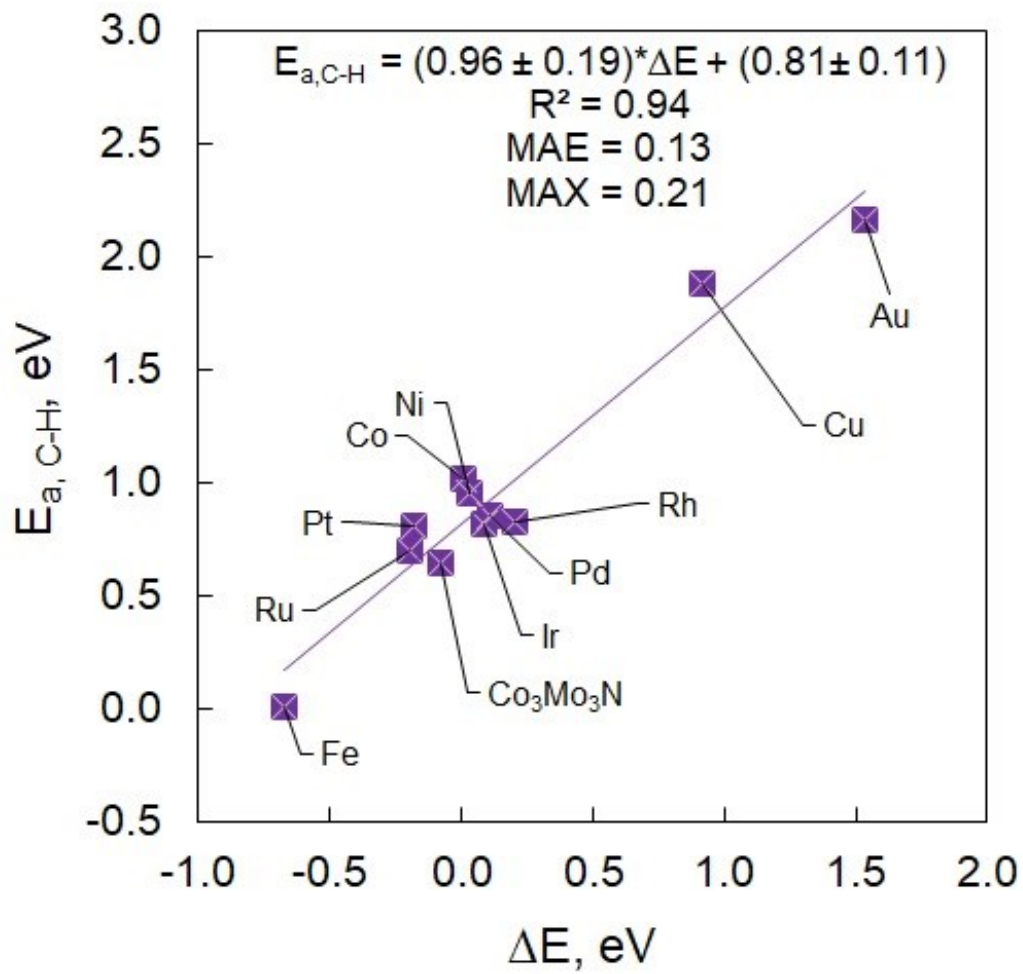


Fig. S8

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**Table S1.** Lattice parameters of surface models.

Surface	Lattice parameter (Å)	Experimental lattice (Å)
Co(0001)	2.476	2.501
Mo <sub>2</sub> N(110)	4.999	5.044
Co <sub>3</sub> Mo <sub>3</sub> N(111)	7.783	7.813
Ni(111)	2.491	2.481
Pt(111)	2.804	2.812
Cu(111)	2.580	2.561
Au(111)	2.949	2.950
Ir(111)	2.714	2.741
Rh(111)	2.705	2.721
Fe(111)	2.440	2.578
Pd(111)	2.751	2.798
Ru(111)	2.711	2.705

**Table S2.** Binding energies (eV) of H and CH<sub>3</sub> and their preferred binding sites on close-packed transition metal surfaces; CH<sub>4</sub> dissociation energies ( $\Delta E$ ); and C–H bond activation energy barriers ( $E_a$ ). The literature values are shown in the parentheses.

Surface	H		CH <sub>3</sub>		CH <sub>4</sub> dissociation	
	Site	BE, eV (BE <sub>lit.</sub> )	Site	BE (eV) (BE <sub>lit.</sub> )	$\Delta E$ , eV	$E_a$ , eV
<b>Ir(111)</b>	top	-2.72 (-2.73 <sup>1</sup> )	fcc	-1.92 (-1.88 <sup>1</sup> )	0.09 (0.06 <sup>2</sup> )	0.82 (0.95 <sup>2</sup> )
<b>Rh(111)</b>	fcc	-2.72 (-2.86 <sup>3</sup> )	fcc	-1.80 (-1.84 <sup>4</sup> , -1.83 <sup>5</sup> )	0.21 (0.12 <sup>6</sup> , 0.09 <sup>3</sup> , 0.05 <sup>2</sup> )	0.83 (0.82 <sup>6</sup> , 0.72 <sup>3</sup> , 1.00 <sup>2</sup> )
<b>Ni(111)</b>	fcc	-2.81 (-2.80 <sup>7</sup> )	top	-1.89 (-1.91 <sup>7</sup> )	0.03 (0.13 <sup>8,9</sup> , 0.01 <sup>7</sup> , 0.15 <sup>10</sup> )	0.95 (1.18 <sup>8,9</sup> , 1.17 <sup>10</sup> , 0.90 <sup>11</sup> , 0.88 <sup>7</sup> )
<b>Cu(111)</b>	fcc	-2.44 (-2.51 <sup>9</sup> )	fcc	-1.37 (-2.03 <sup>12</sup> )	0.92 (1.07 <sup>12</sup> , 1.25 <sup>2</sup> )	1.88 (1.77 <sup>12</sup> , 1.80 <sup>2</sup> )
<b>Fe(111)</b>	hcp	-2.98	fcc	-2.29 (-2.81 <sup>9</sup> )	-0.67 (-0.63 <sup>14</sup> )	0.01
<b>Pt(111)</b>	top	-2.79 (-2.74 <sup>13</sup> )	top	-2.10 (-2.02 <sup>13</sup> )	-0.18 (-0.13 <sup>14</sup> , 0.07 <sup>15</sup> , 0.04 <sup>2</sup> )	0.81 (0.84 <sup>14</sup> , 0.77 <sup>15</sup> , 1.10 <sup>2</sup> )
<b>Au(111)</b>	fcc	-1.98	-	-1.21	1.53 (1.75 <sup>2</sup> )	2.16 (2.25 <sup>2</sup> )
<b>Pd(111)</b>	fcc	-2.82 (-2.68)	top	-1.79 (-1.81 <sup>16</sup> )	0.11 (0.26)	0.85 (0.97)
<b>Ru(111)</b>	fcc	-2.84	fcc	-2.08	-0.20 (-0.23)	0.70 (0.80 <sup>17</sup> )

**Table S3.** Calculated rate constants for the elementary DRM steps on Co<sub>3</sub>Mo<sub>3</sub>N(111), Co(0001), Mo<sub>2</sub>N(110), and Ni(111). The elementary step indices correspond to the mechanism shown in Table 2 of the main text.

Elementary step	Co <sub>3</sub> Mo <sub>3</sub> N(111)		Co(0001)		Mo <sub>2</sub> N(110)		Ni(111)	
	$k_f$	$k_r$	$k_f$	$k_r$	$k_f$	$k_r$	$k_f$	$k_r$
<b>R1</b>	1.85E-01	1.60E+13	7.28E-02	7.44E+11	1.65E+00	6.69E+05	4.01E-02	9.08E+11
<b>R2</b>	2.15E-02	3.40E+13	1.52E-04	9.75E+08	5.44E-07	3.27E+06	-	-
<b>R3</b>	6.62E+10	1.92E+08	3.78E+09	1.78E+10	8.03E+08	1.92E+08	7.46E+09	1.11E+10
<b>R4</b>	2.55E+10	1.39E+07	1.47E+12	2.87E+10	1.72E+11	6.56E+07	2.87E+11	3.00E+09
<b>R5</b>	2.44E+08	3.93E+08	2.85E+07	3.36E+09	1.53E+11	2.87E+10	1.28E+06	7.13E+08
<b>R6</b>	1.49E+01	7.56E+05	2.65E+02	4.79E+13	2.78E+01	2.97E+09	4.01E+02	1.63E+13
<b>R7</b>	5.41E+09	1.39E+07	1.35E+11	3.89E+05	6.15E+11	3.79E+03	1.58E+10	1.69E+05
<b>R8</b>	2.39E+02	2.53E+07	5.99E+03	6.69E+00	1.03E-01	8.26E+04	1.05E+05	2.46E-02
<b>R9</b>	3.33E+06	9.83E+09	5.36E+06	3.49E+08	1.00E+03	6.62E+10	1.77E+07	1.70E+08
<b>R10</b>	1.63E+06	4.11E+10	1.75E+04	3.30E+03	4.00E+01	5.36E+06	2.33E+06	4.72E+03
<b>R11</b>	4.26E+09	2.72E+05	4.42E+08	3.59E+04	5.36E+06	4.85E-01	2.44E+08	2.60E+03
<b>R12</b>	5.77E+04	5.03E+11	1.18E+05	5.41E+09	1.89E+02	2.37E+12	2.14E+05	8.33E+07
<b>R13</b>	1.72E+11	8.33E+07	1.03E+12	2.62E+06	2.35E+09	2.51E+04	2.10E+12	7.07E+05
<b>R14</b>	7.60E+03	8.10E+11	3.07E+05	2.01E+10	1.12E+00	1.94E+11	6.27E+05	3.79E+09
<b>R15</b>	3.24E+10	6.27E+05	-	-	1.53E+11	1.67E+02	4.26E+09	2.53E+07
<b>R16</b>	1.31E+12	2.16E+08	1.03E+12	1.34E+08	-	-	6.15E+12	1.02E+09
<b>R17</b>	7.96E+05	3.39E+12	8.97E+05	2.24E+07	3.09E+08	2.55E+10	7.96E+05	3.39E+12
<b>R18</b>	1.70E+08	2.46E+11	6.56E+07	1.57E+07	-	-	1.70E+08	2.46E+11
<b>R19</b>	1.07E+11	1.90E+05	1.16E+12	9.74E+06	1.31E+12	6.45E+01	1.07E+11	1.90E+05
<b>R20</b>	8.89E+02	1.09E+04	7.60E+03	2.44E-05	8.97E+05	4.43E-05	8.89E+02	1.09E+04
<b>R21</b>	2.72E+03	1.07E-02	1.62E+05	2.82E-01	4.03E+00	2.40E-02	1.68E+04	1.29E-01
<b>R22</b>	2.62E+07	1.82E+01	2.07E+08	2.22E+01	8.15E+02	2.00E+01	1.26E+08	9.84E+00
<b>R23</b>	1.22E+07	1.60E+02	2.40E+09	6.42E+02	5.71E-01	1.93E+02	1.56E+10	3.38E+02

## Appendix 1. Derivation of single-site and dual-site microkinetic models for DRM

All elementary steps are generally described by Eqn. (S1),



where  $AB^\ddagger$  represents the activated transition state. According to Eqn. (S2), the rate constants ( $k$ ) becomes:

$$k = \frac{k_B T}{h} \exp\left(\frac{-E_a}{RT}\right), \quad (\text{S2})$$

where  $k_B$  is the Boltzmann constant,  $h$  is the Planck's constant,  $R$  is the gas constant (i.e., 8.314 J/K mole), and  $T$  is temperature (in K). All  $E_a$  were obtained from DFT CI-NEB and dimer calculations detailed in the main text.

Specifically, the forward and reverse rate constants for the rate-determining  $\text{CH}_4$  dissociative adsorption are expressed by Eqns. (S3-S4):

$$k_f = \frac{k_B T}{h} \frac{q^\ddagger}{q_{\text{CH}_4(g)}} \exp\left(-\frac{E_{af}}{RT}\right), \quad (\text{S3})$$

$$k_r = \frac{k_B T}{h} \frac{q^\ddagger}{q_{\text{CH}_3^*} q_{\text{H}^*}} \exp\left(-\frac{E_{ar}}{RT}\right), \quad (\text{S4})$$

where  $q_{TS}$ ,  $q_{\text{CH}_4}$ ,  $q_{surf}$ ,  $q_{\text{CH}_3^*}$ , and  $q_{\text{H}^*}$  are the partition functions for the transition state (TS), the reactant, and product states with respect to their ground states, respectively. These partition functions were estimated based on the standard statistical mechanical approach at 1 bar and 973.15 K.

$E_{af}$  and  $E_{ar}$ , with zero-point energy (ZPE) corrections included, correspond to the activation energies of the forward and reverse elementary step, respectively.

For molecular adsorption and desorption process (e.g., CO<sub>2</sub> adsorption), as expressed by Eqn. (S5),



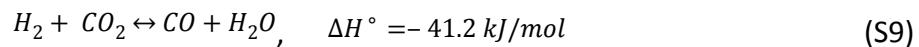
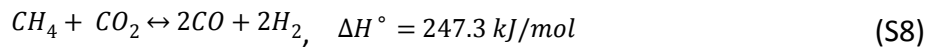
It can be shown that the rate constants for molecular adsorption and desorption can be expressed by Eqns. (S6) and (S7) <sup>18</sup>:

$$k_{adsorption} = \frac{1}{N_0 \sqrt{2\pi} k_B T M_A q_{rA(g)} q_{vA(g)}} q_{A^*} \quad (S6)$$

$$k_{desorption} = e^{-\frac{k_B T}{h}} \exp\left(-\frac{\Delta E}{RT}\right) \quad (S7)$$

where  $N_0$  is the number of surface sites of the exposed surface.  $M_A$  is the molecular mass of the adsorbate (A).  $q_{rA(g)}$  and  $q_{vA(g)}$  are the rotational and vibrational partition functions of the gas-phase adsorbate, respectively.  $\Delta E$  is approximated with the binding energy of the adsorbate.

A *Mathematica* script was developed to obtain the DRM turnover frequencies (TOFs) and surface coverage at  $P = 1$  bar and 973.15 K. The initial feed consists of equimolar CH<sub>4</sub> and CO<sub>2</sub> (i.e.,  $p_{CH_4} = p_{CO_2} = 0.5$  bar) at a molar flow rate of 1 mole/s. The composition for the exiting gas stream consisting of CO, H<sub>2</sub> and H<sub>2</sub>O, and the unreacted CH<sub>4</sub>, CO<sub>2</sub>, was estimated based on the overall equilibrium constant. The relevant reactions consist of the DRM (S8) and the reverse water-gas shift reaction (S9):



The estimated equilibrium constants at 1 bar and 973.15 K are 5.92 and 0.594, respectively. Hence, thermodynamics will favor DRM strongly over the reverse water-gas shift

reaction at high temperatures. The composition of the exiting gas stream were determined with Eqns. (S10) and (S11):

$$K_{DRM}(T) = \frac{\left(\frac{p_{H_2}}{P}\right)^2 \left(\frac{p_{CO}}{P}\right)^2}{\left(\frac{p_{CH_4}}{P}\right) \left(\frac{p_{CO_2}}{P}\right)}, \quad (S10)$$

$$K_{RWGS}(T) = \frac{p_{H_2} * p_{CO_2}}{p_{CO} * p_{H_2O}}, \quad (S11)$$

where the partial pressures are represented by Eqns. (S12-S16) in terms of CH<sub>4</sub> conversion ( $x_{CH_4}$ ) and the extent of reaction of RWGS ( $\xi$ ).

$$p_{CH_4} = \frac{1 - x_{CH_4}}{2 * (1 + x_{CH_4})} P \quad (S12)$$

$$p_{CO_2} = \frac{1 - x_{CH_4} * \xi}{2 * (1 + x_{CH_4})} P \quad (S13)$$

$$p_{CO} = \frac{2 * F_0 * x_{CH_4} + \xi}{2 * F_0 * (1 + x_{CH_4})} P \quad (S14)$$

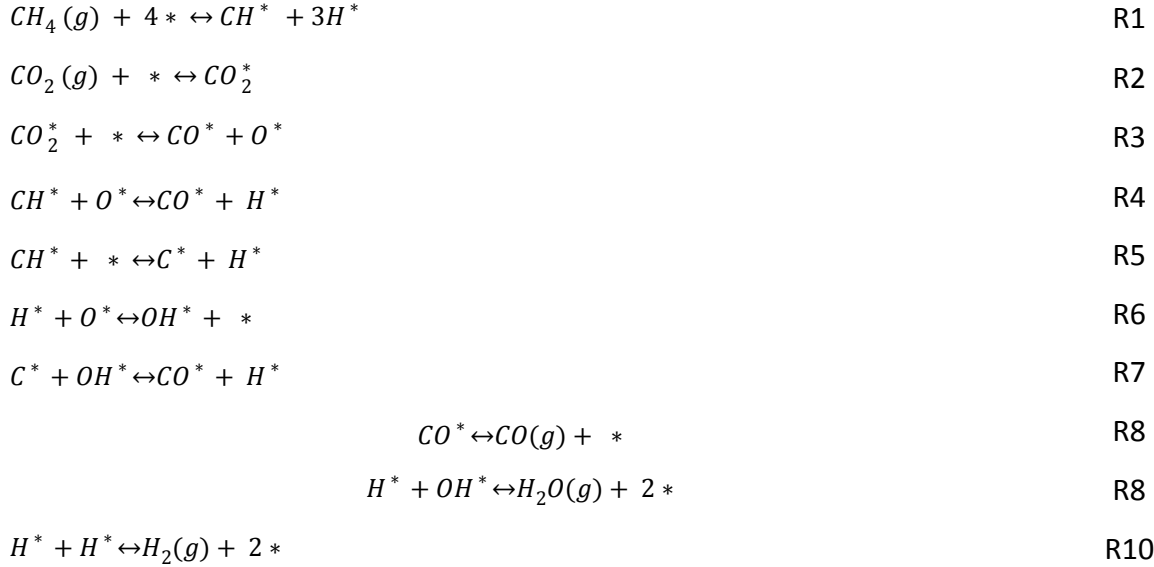
$$p_{CO} = \frac{2 * F_0 * x_{CH_4} - \xi}{2 * F_0 * (1 + x_{CH_4})} P \quad (S15)$$

$$p_{H_2O} = \frac{\xi}{2 * F_0 * (1 + x_{CH_4})} P \quad (S16)$$

As mentioned in the main text, a reduced DRM mechanism was adopted to facilitate microkinetic modeling. The first activation of CH<sub>4</sub> was still treated as the rate-limiting step (RLS) and will be used to determine the rate of DRM. In addition, the CH<sub>4</sub> decomposition sequence was represented as a *lumped* step (forming CH, see R), by neglecting the formation and oxidations of CH<sub>2</sub> and CH<sub>3</sub>. Because the formation of CHOH is significantly slower (see Table S4),



the CHOH intermediate will be omitted. Instead, the oxidation of carbonaceous species (i.e., C and CH) is represented by R4 and R7, to form CO. The oxidants (i.e., O and OH) are generated via R3 and R6, respectively. Hence, there are 10 elementary steps, involving 5 gas phase species (CH<sub>4</sub>, CO<sub>2</sub>, CO, H<sub>2</sub>, and H<sub>2</sub>O) and 8 surface intermediates (\*, C, CH, CO<sub>2</sub>, CO, O, H, and OH) in the reduced DRM model.



The quasi-steady state assumption (QSSA) was applied to each surface species (excluding vacancies) in order to establish a set of differential equations describing each surface species, as in Eqns. (S17-S24):

$$r_1 = k_{1f}P_{CH_4}\theta_*^4 - k_{1r}\theta_{CH}\theta_H^3 \quad (S17)$$

$$\frac{d\theta_{CO_2}}{dt} = k_{2f}P_{CO_2}\theta_* - k_{2r}\theta_{CO_2} \quad (S18)$$

$$\frac{d\theta_O}{dt} = k_{3f}\theta_{CO_2}\theta_* - k_{3r}\theta_{CO}\theta_O \quad (S19)$$

$$\frac{d\theta_{CH}}{dt} = -k_{4f}\theta_{CH}\theta_O + k_{4r}\theta_{CO}\theta_H - k_{5f}\theta_{CH}\theta_* + k_{5r}\theta_C\theta_H \quad (S20)$$

$$\frac{d\theta_{OH}}{dt} = k_{6f}\theta_O\theta_H + k_{6r}\theta_{OH}\theta_* \quad (S21)$$

$$\frac{d\theta_c}{dt} = -k_{7f}\theta_c\theta_{OH} + k_{7r}\theta_{CO}\theta_H \quad (S22)$$

$$\frac{d\theta_{CO}}{dt} = -k_{8f}\theta_{CO} + k_{8r}P_{CO}\theta_* \quad (S23)$$

$$\frac{d\theta_H}{dt} = -k_{9f}\theta_{OH}\theta_H + k_{9r}P_{H_2O}\theta_*^2 - k_{10f}\theta_H^2 + k_{10r}P_{H_2}\theta_*^2 \quad (S24)$$

The rate constants corresponding to the above model are listed in Table S5.

**Table S4.** Rate constants and equilibrium constants on Co<sub>3</sub>Mo<sub>3</sub>N(111), Ni(111), Co(0001), and Mn<sub>2</sub>N(110) used in Eqns. (S3, S4, S6, S7).

Elementary step	Co <sub>3</sub> Mo <sub>3</sub> N(111)			Ni(111)		
	$k_{fi}$	$k_{ri}$	$K_i$	$k_{fi}$	$k_{ri}$	$K_i$
<b>R1</b>	1.85E-01	1.39E+07	1.33E-08	4.00E-02	3.00E+9	3.33E-11
<b>R2</b>	1.48E+01	7.57E+05	1.96E-05	4.01E+02	1.63E+13	2.46E-11
<b>R3</b>	5.41E+09	1.39E+07	3.89E+02	1.58E+10	1.69E+05	9.35E+04
<b>R4</b>	5.77E+04	8.33E+07	6.92E-04	2.14E+05	7.07E+05	3.03E-01
<b>R5</b>	2.44E+08	3.93E+08	6.21E-01	1.28E+06	7.13E+08	1.80E-03
<b>R6</b>	3.33E+06	9.83E+09	3.39E-04	1.77E+07	1.70E+08	1.04E-01
<b>R7</b>	1.63E+06	2.72E+05	5.99E+00	2.33E+06	2.60E+03	8.96E+02
<b>R8</b>	2.72E+03	1.07E-02	2.54E+05	1.68E+04	1.28E-01	1.31E+05
<b>R9</b>	1.22E+07	1.60E+02	7.63E+04	1.56E+10	3.38E+02	4.62E+07
<b>R10</b>	2.62E+07	1.82E+01	1.44E+06	1.25E+08	9.84E+00	1.27E+07
Elementary step	Co(0001)			Mo <sub>2</sub> N(110)		
	$k_{fi}$	$k_{ri}$	$K_i$	$k_{ri}$	$K_i$	
<b>R1</b>	7.28E-02	1.78E+09	4.09E-11	1.65E+00	6.69E+05	2.46E-06
<b>R2</b>	1.00E+00	4.79E+13	2.09E-12	2.78E+01	2.97E+09	9.36E-09
<b>R3</b>	1.35E+11	3.89E+05	3.47E+05	6.15E+12	3.79E-04	1.62E+16
<b>R4</b>	1.18E+05	2.62E+06	4.50E-02	1.89E+02	2.51E+04	7.53E-03
<b>R5</b>	2.85E+07	3.36E+09	8.48E-03	1.53E+11	2.87E+10	5.33E+00
<b>R6</b>	5.36E+06	3.49E+08	1.54E-02	1.00E+03	6.62E+10	1.51E-08
<b>R7</b>	1.75E+04	3.30E+02	5.30E+01	4.00E+01	4.85E-01	8.25E+01
<b>R8</b>	1.62E+05	2.82E-01	5.74E+06	4.03E+00	2.40E-02	1.68E+02
<b>R9</b>	2.40E+09	6.42E+02	3.74E+06	5.70E-01	1.93E+02	2.95E-03
<b>R10</b>	2.07E+08	2.22E+01	9.32E+06	8.15E+02	2.00E+01	4.08E+01

According to QSSA, the surface coverage expressions are represented by Eqns. (S25-S32 in Table S5) for the *single-site* mechanism.

<i>Single-site mechanism</i>	<i>Dual-site mechanism</i>
(S25) $\theta_{CO_2} = K_2 p_{CO_2} \theta_*$	(S43) $\theta_{CO_2} = K_2 p_{CO_2} \theta_{1*}$
(S26) $\theta_O = \frac{K_3 \theta_{CO_2} \theta_*}{\theta_{CO}} = \frac{K_2 K_3 K_8 p_{CO_2} \theta_*}{p_{CO}} \theta_*$	(S44) $\theta_O = \frac{K_3 \theta_{CO_2} \theta_{2*}}{\theta_{CO}} = \frac{K_2 K_3 K_8 p_{CO_2} \theta_{2*}}{p_{CO}} \theta_{2*}$
(S27) $\theta_{CH} = \frac{\frac{k_{4r} p_{CO}}{K_8} + \frac{k_{5r} p_{CO}^2}{K_2 K_3 K_6 K_7 K_8^2 p_{CO_2}}}{\frac{k_{4f} K_2 K_3 K_8 p_{CO_2}}{p_{CO}} + k_{5f}} \times \sqrt{\frac{\frac{k_{9r} p_{H_2O} + k_{10r} p_{H_2}}{K_2 K_3 K_6 K_8 k_{9f} p_{CO_2}} + k_{10f}}{p_{CO}}} \theta_*$	(S45) $\theta_{CH} = \frac{\frac{k_{4r} p_{CO}}{K_8} \theta_{2*} + \frac{k_{5r} p_{CO}^2}{K_2 K_3 K_6 K_7 K_8^2 p_{CO_2}} \theta_{1*}}{\frac{k_{4f} K_2 K_3 K_8 p_{CO_2}}{p_{CO}} + k_{5f}} \sqrt{\frac{\frac{k_{9r} p_{H_2O} + k_{10r} p_{H_2}}{K_2 K_3 K_6 K_8 k_{9f} p_{CO_2}} + k_{10f}}{p_{CO}}} \theta_{2*}$
(S28) $\theta_{OH} = \frac{K_2 K_3 K_6 K_8 p_{CO_2}}{p_{CO}} \times \sqrt{\frac{\frac{k_{9r} p_{H_2O} + k_{10r} p_{H_2}}{K_2 K_3 K_6 K_8 k_{9f} p_{CO_2}} + k_{10f}}{p_{CO}}} \theta_*$	(S46) $\theta_{OH} = \frac{K_2 K_3 K_6 K_8 p_{CO_2}}{p_{CO}} \sqrt{\frac{\frac{k_{9r} p_{H_2O} + k_{10r} p_{H_2}}{K_2 K_3 K_6 K_8 k_{9f} p_{CO_2}} + k_{10f}}{p_{CO}}} \theta_{2*}$
(S29) $\theta_C = \frac{\theta_{CO} \theta_H}{K_7 \theta_{OH}} = \frac{p_{CO}^2}{K_2 K_3 K_6 K_7 K_8^2 p_{CO_2}} \theta_*$	(S47) $\theta_C = \frac{\theta_{CO} \theta_H}{K_7 \theta_{OH}} = \frac{p_{CO}^2}{K_2 K_3 K_6 K_7 K_8^2 p_{CO_2}} \theta_{1*}$
(S30) $\theta_{CO} = \frac{p_{CO}}{K_8} \theta_*$	(S48) $\theta_{CO} = \frac{p_{CO}}{K_8} \theta_{1*}$
(S31) $\theta_H = \sqrt{\frac{\frac{k_{9r} p_{H_2O} + k_{10r} p_{H_2}}{K_2 K_3 K_6 K_8 k_{9f} p_{CO_2}} + k_{10f}}{p_{CO}}} \theta_*$	(S49) $\theta_H = \sqrt{\frac{\frac{k_{9r} p_{H_2O} + k_{10r} p_{H_2}}{K_2 K_3 K_6 K_8 k_{9f} p_{CO_2}} + k_{10f}}{p_{CO}}} \theta_{2*}$

<p>(S32) <math>\theta_* + \theta_C + \theta_{CH} + \theta_{CO} + \theta_{CO_2} + \theta_O + \theta_{OH} + \theta</math></p>	<p>(S50) <math>\theta_{1*} + \theta_C + \theta_{CO} + \theta_{CO_2} = 0.7</math></p> <p>(S51) <math>\theta_{2*} + \theta_O + \theta_{OH} + \theta_H + \theta_{CH} = 0.3</math></p>
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The concentrations of all surface species are related to  $\theta_*$ . Then, the RLS ( $r_1$ ) can be expressed by Eqn. (S33).

$$r_1 = k_{1f} p_{CH_4} \left[ 1 - \frac{\frac{k_{4r} p_{CO}}{K_8} + \frac{k_{5r} p_{CO}^2}{K_2 K_3 K_6 K_7 K_8^2 p_{CO_2}}}{K_1 p_{CH_4} \left( \frac{k_{4f} K_2 K_3 K_8 p_{CO_2}}{p_{CO}} + k_{5f} \right)} \left( \frac{k_{9r} p_{H_2O} + k_{10r} p_{H_2}}{K_2 K_3 K_6 K_8 k_{9f} p_{CO_2}} + k_{10f} \right) \right]^2 \theta_*^4 \quad (S33)$$

From a dimensional analysis, the RLS can be further simplified as Eqn. (S34):

$$r_1 = k_{1f} p_{CH_4} \theta_*^4 \left[ 1 - \frac{p_{CO}^2 p_{H_2}^2}{K_1 K_2 K_3 K_5 K_6 K_7 K_8^2 p_{CH_4} p_{CO_2}} \right] \quad (S34)$$

The *dual-site* mechanism accounts for DRM occurring on two distinct active sites, denoted as  $\theta_{1*}$  and  $\theta_{2*}$ , as established by Eqns. (S35-S42). We assumed that each species occupies their preferred binding sites and the diffusions between different active domains be neglected. The surface coverage for each intermediate are represented by Eqns. (S43-S51) listed in Table S5.

$$r_1 = k_{1f} p_{CH_4} \theta_{1*}^4 - k_{1r} \theta_{CH} \theta_H^3 \quad (S35)$$

$$\frac{d\theta_{CO_2}}{dt} = k_{2f} p_{CO_2} \theta_{2*} - k_{2r} \theta_{CO_2} \quad (S36)$$

$$\frac{d\theta_O}{dt} = k_{3f} \theta_{CO_2} \theta_{1*} - k_{3r} \theta_{CO} \theta_O \quad (S37)$$

$$\frac{d\theta_{CH}}{dt} = -k_{4f} \theta_{CH} \theta_O + k_{4r} \theta_{CO} \theta_H - k_{5f} \theta_{CH} \theta_{1*} + k_{5r} \theta_C \theta_H \quad (S38)$$

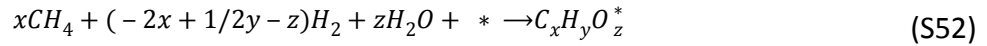
$$\frac{d\theta_{OH}}{dt} = k_{6f} \theta_O \theta_H + k_{6r} \theta_{OH} \theta_{2*} \quad (S39)$$

$$\frac{d\theta_C}{dt} = -k_{7f}\theta_C\theta_{OH} + k_{7r}\theta_{CO}\theta_H \quad (S40)$$

$$\frac{d\theta_{CO}}{dt} = -k_{8f}\theta_{CO} + k_{8r}P_{CO}\theta_{1*} \quad (S41)$$

$$\frac{d\theta_H}{dt} = -k_{9f}\theta_{OH}\theta_H + k_{9r}P_{H_2O}\theta_{2*}^2 - k_{10f}\theta_H^2 + k_{10r}P_{H_2}\theta_{2*}^2 \quad (S42)$$

The heat map contour plot was generated using  $BE_C$  and  $BE_O$ , which are in general ( $C_xH_yO_z^*$ ) defined by Eqns. (S52-S53).



$$E_{C_xH_yO_z^*} = E_{C_xH_yO_z^*}^{vasp} - xE_{CH_4}^{vasp} + (2x - 1/2y + z)E_{H_2}^{vasp} - zE_{H_2O}^{vasp} - E_*^{vasp} \quad (S53)$$

Then, the binding energies of H, CH, CO, and OH were estimated using Eqns. S54-S57. These linear scaling relationships were established and illustrated in Figure S7. Moreover, the C–H bond activation energies were estimated using a BEP relationship based on Eqn. S58 (also see Figure S8).

$$BE_H = 0.16BE_C + 0.12BE_O - 0.92 \quad (S54)$$

$$BE_{CH} = 0.76 BE_C - 0.45 \quad (S55)$$

$$BE_{CO} = 0.52 BE_C + 0.34 \quad (S56)$$

$$BE_{OH} = 0.63 BE_O - 0.18 \quad (S57)$$

$$E_{a,C-H} = 0.96 \Delta E + 0.81 = 0.96 (BE_{CH} + 3BE_H) + 0.81 \quad (S58)$$

## Notes and references

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