Supporting Information

Propagating DFT Uncertainty to Mechanism Determination, Degree of Rate Control and Coverage Analysis: The Kinetics of Dry Reforming of Methane

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1. Species and elementary defined for DRM and optimized structures

1.1 Species defined for DRM

Gas:

CO_2, CO, H_2, CH_4

Intermediates:

C*, CH*, CH_2*, CH_2O*, CH_2OH*, CH_3*, CH_3O*, CH_3OH*, CHO*, CHOH*, CO*, COH*, COOH*, H*, HCOO*, O*, OH*

Transition states:

C-H*, CH_2-H*, CH_2-O*, CH_2O-H*, CH_2-OH*, CH_3-H*, CH_3-O*, CH_3O-H*, CH_3-OH*, CH-H*, CH-O*, CHO-H*, CH-OH*, CHO-O*, C-O*, CO-H*, C-OH*, CO-O*, CO-OH*, COO-H*, H-CH_2O*, H-CH_2OH*, H-CHO*, H-CHOH*, H-CO*, H-COH*, H-COO*, O-H*

1.2 Elementary steps defined in DRM

C*	+	H*	↔	C-H*	+	*	↔	CH*	+	*
C*	+	O*	↔	C-O*	+	*	↔	CO*	+	*
CH*	+	H*	↔	CH-H*	+	*	↔	CH_2*	+	*
CH*	+	O*	↔	CH-O*	+	*	↔	CHO*	+	*
CH*	+	OH*	↔	CH-OH*	+	*	↔	CHOH*	+	*
CH_2*	+	H*	↔	CH_2-H*	+	*	↔	CH_3*	+	*
CH_2O*	+	*	↔	CH_2-O*	+	*	↔	CH_2*	+	O*
CH_2O*	+	*	↔	H-CHO*	+	*	↔	CHO*	+	H*
CH_2O*	+	H*	↔	CH_2O-H*	+	*	↔	CH_2OH*	+	*
CH_2O*	+	H*	↔	H-CH_2O*	+	*	↔	CH_3O*	+	*
CH_2OH*	+	*	↔	CH_2-OH*	+	*	↔	CH_2*	+	OH*
CH_4(g)	+	2*	↔	CH_3-H*	+	*	↔	CH_3*	+	H*
CHO*	+	*	↔	H-CO*	+	*	↔	CO*	+	H*
CHO*	+	O*	↔	CHO-O*	+	*	↔	HCOO*	+	*
CHOH*	+	*	↔	CHO-H*	+	*	↔	CHO*	+	H*
CHOH*	+	*	↔	H-COH*	+	*	↔	COH*	+	H*
CO*	+	OH*	↔	CO-OH*	+	*	↔	COOH*	+	*
CO_2(g)	+	2*	↔	CO-O*	+	*	↔	CO*	+	O*
COH*	+	*	↔	C-OH*	+	*	↔	C*	+	OH*
COH*	+	*	↔	CO-H*	+	*	↔	CO*	+	H*

$$OH^* + * \leftrightarrow O\text{-}H^* + * \leftrightarrow O^* + H^*$$

$$CH_2OH^* + * \leftrightarrow H\text{-}CHOH^* + * \leftrightarrow H^* + CHOH^*$$

$$CH_3^* + OH^* \leftrightarrow CH_3\text{-}OH^* + * \leftrightarrow CH_3OH^* + *$$

$$CH_3OH^* + * \leftrightarrow H\text{-}CH_2OH^* + * \leftrightarrow CH_2OH^* + H^*$$

$$CH_3OH^* + * \leftrightarrow CH_3O\text{-}H^* + * \leftrightarrow CH_3O^* + H^*$$

$$CH_3^* + O^* \leftrightarrow CH_3\text{-}O^* + * \leftrightarrow CH_3O^* + *$$

$$CO_2(g) + H^* \leftrightarrow COO\text{-}H^* \leftrightarrow COOH^*$$

$$CO_2(g) + H^* \leftrightarrow H\text{-}COO^* \leftrightarrow HCOO^*$$

$$CO^* \leftrightarrow CO(g) + *$$

$$2H^* \leftrightarrow H_2(g) + 2^*$$

1.3 Optimized structures of absorbates and transition states on Ni(111)

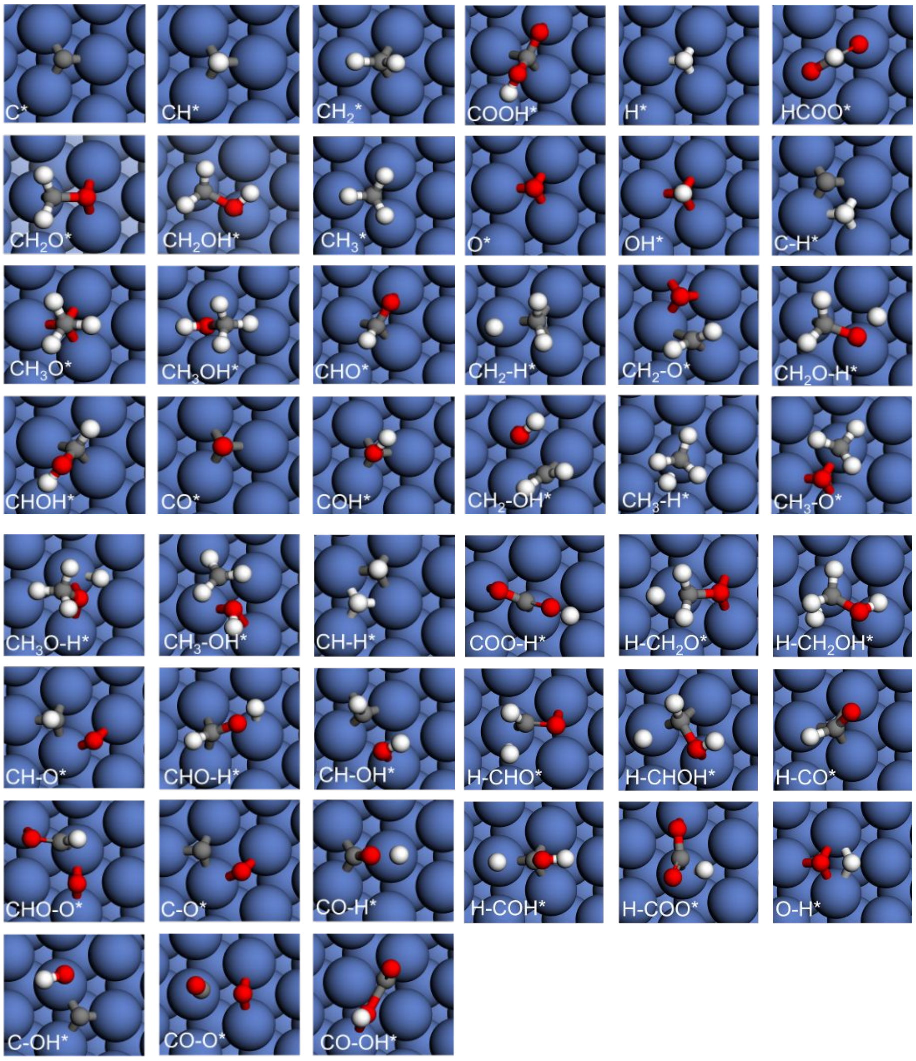


Figure S1. Optimized structures of absorbates and transition states on Ni(111).

1.4 Optimized structures of absorbates and transition states on Pt(111)

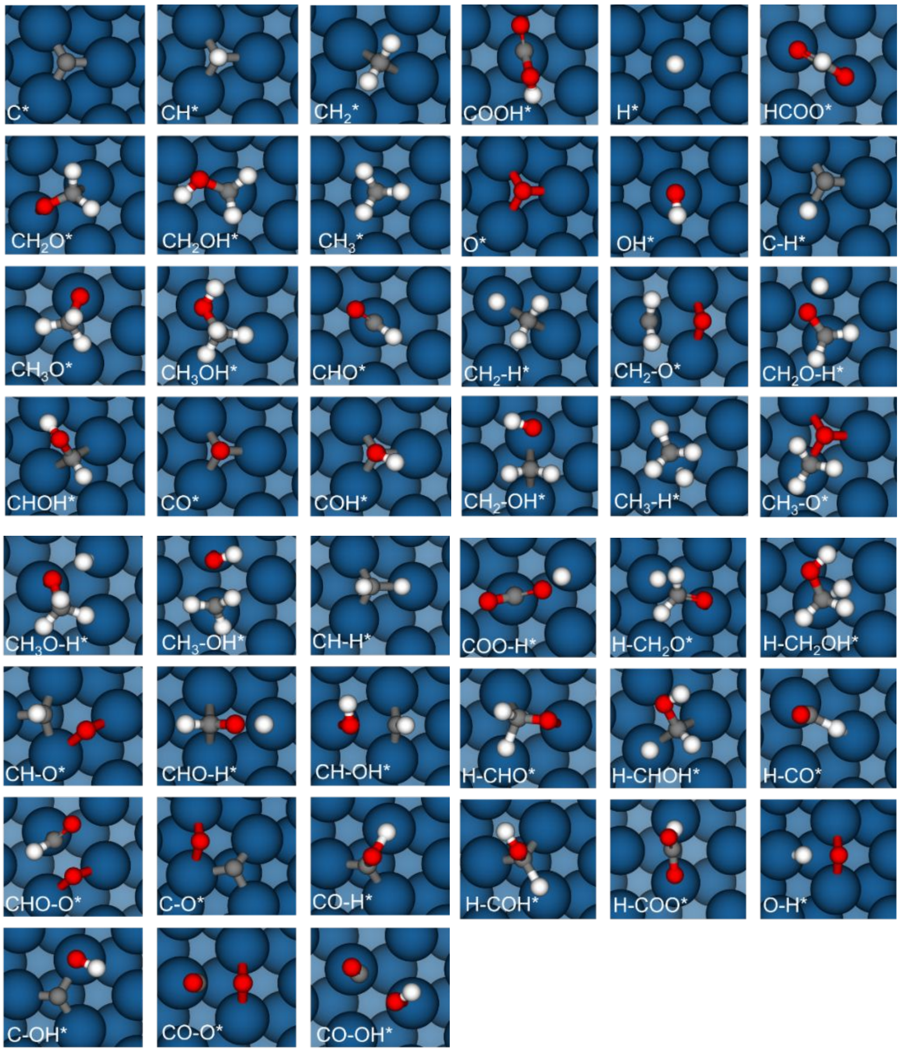


Figure S2. Optimized structures of absorbates and transition states on Pt(111).

2. BEEF-vdW ensembles and error estimation

Bayesian error estimation functional with van der Waals correlations (BEEF-vdW) is a semi-empirical exchange correlation functional developed based on several training data sets including molecular formation energies, molecular reaction energies, chemisorption on solid surfaces, molecular reaction barriers, non-covalent interactions, and solid-state properties. The exchange correlation energy in the BEEF-vdW exchange correlation functional is expressed as the sum of the exchange energy under the generalized gradient approximation (GGA) exchange expanded in Legendre polynomials, the local density approximation (LDA) and the PBE correlation energies, and the non-local correlation energy from vdW-DF2, following the equation below

$$E_{XC} = \sum_{m=0}^{M_x - 1} a_m E_m^{GGA-x} + \alpha_c E^{LDA-c} + (1 - \alpha_c) E^{PBE-c} + E^{nl-c} \quad \text{(S1)}$$

where M_x represents the degree of the polynomial and a_m are expansion coefficients. Practically, the parameters a_m and α_c in the equation are optimized to obtain the best fit with respect to the training data sets mentioned above. The error estimation ensemble of exchange correlation functionals is generated with a probability distribution function of the parameters, i.e. a_m and α_c. Further details can be found from the reference. [1]

The frequency of the transition state of index s with maximum DRC, denoted as F_s, can be written as:

$$F_s = \frac{1}{N_f} \sum_{n=1}^{N_f} \delta\left(s - \underset{s' \in S_a}{\arg\max}\, DRC(n,s')\right) \quad \text{(S2)}$$

where S_a is the indexes of all transition states, $DRC(n,s')$ denotes the DRC of the transition state with index s', calculated using the DFT functional with index n. Arguments of the maxima (arg max) DRC donotes the index of transition state when its DRC is maximum. Similarly, the frequency of intermediates of index c with the maximum coverage, denoted as F_c, can be written as:

$$F_c = \frac{1}{N_f} \sum_{n=1}^{N_f} \delta\left(c - \underset{c' \in C_a}{\arg\max}\, Coverage(n,c')\right) \quad \text{(S3)}$$

where C_a is the indexes of all intermediates, $Coverage(n,c')$ denotes the coverage of the intermediate with index c', calculated using the DFT functional with index n.

3. Details of pruning results

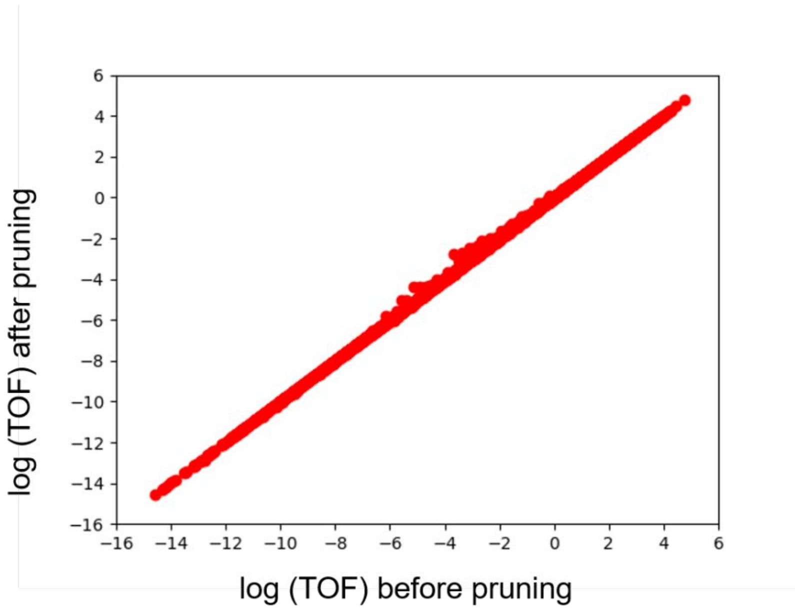


Figure S3. Parity plot between the log(TOF) obtained before and after pruning.

4. DRC distribution

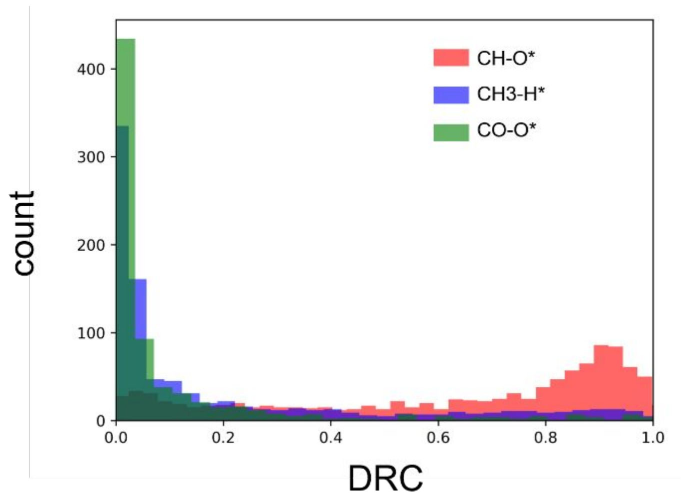
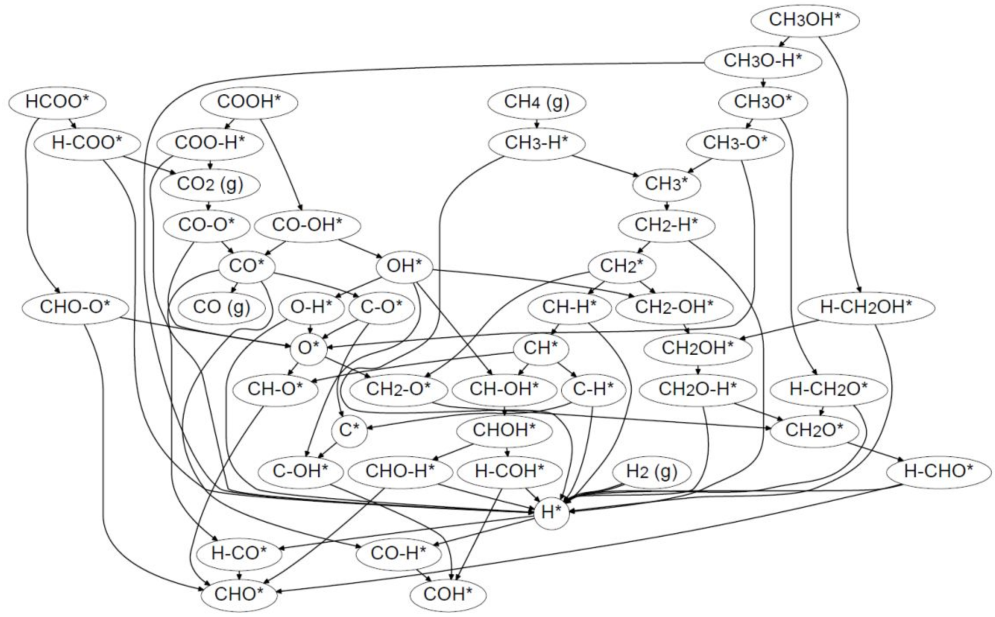
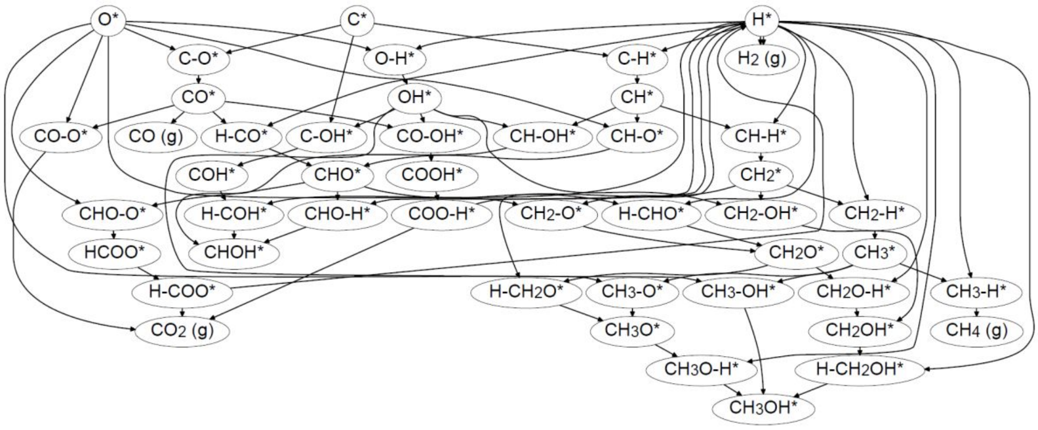


Figure S4. Distribution of 3 highest DRC on Ni(111) at 823 K.

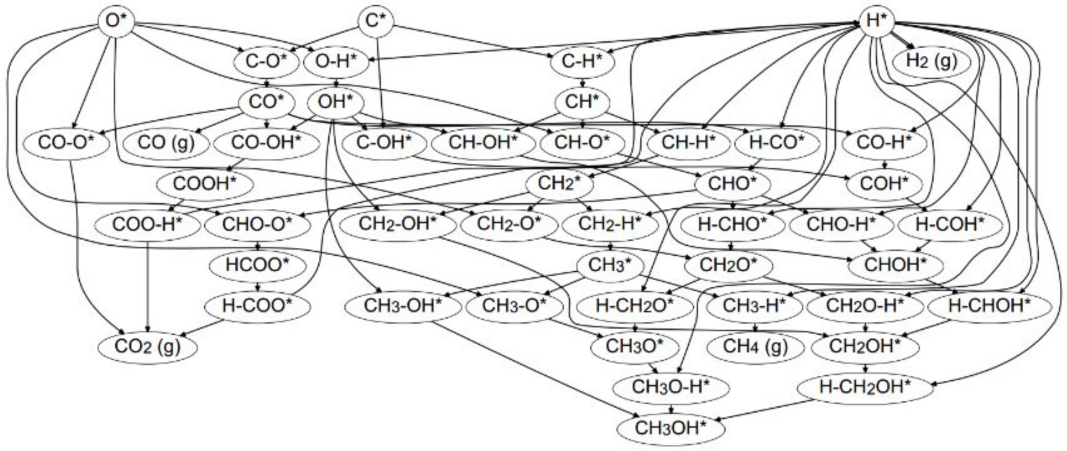
5. Invalid reaction pathways D, E and F on Ni(111) and Pt(111)



Path D



Path E



Path F

Figure S5. Invalid reaction pathways identified with a certain confidence (>9%) on Ni(111) and Pt(111).

6. Occurance requency of species with most negative DRC

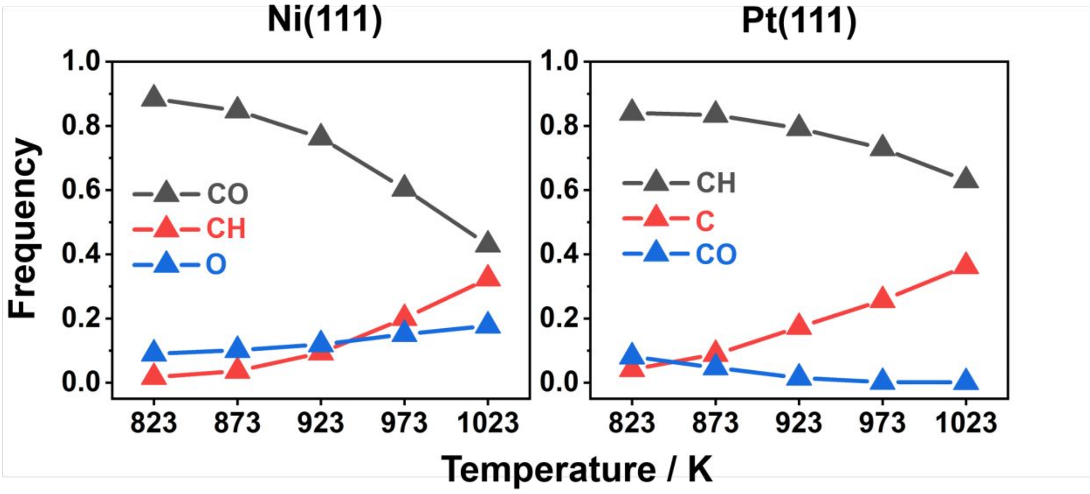
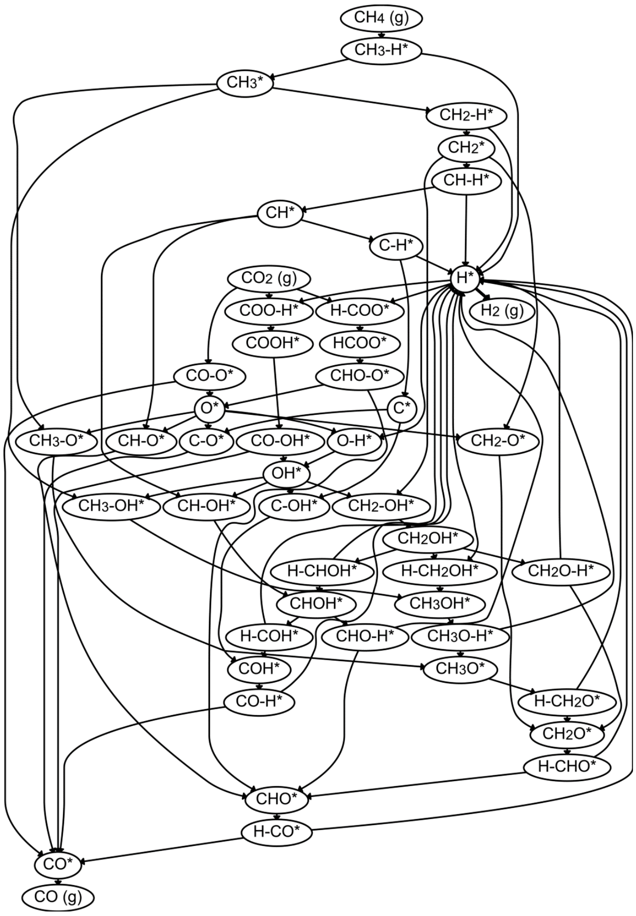


Figure S6. Frequency of species with most negative DRC on Ni(111) and Pt(111).

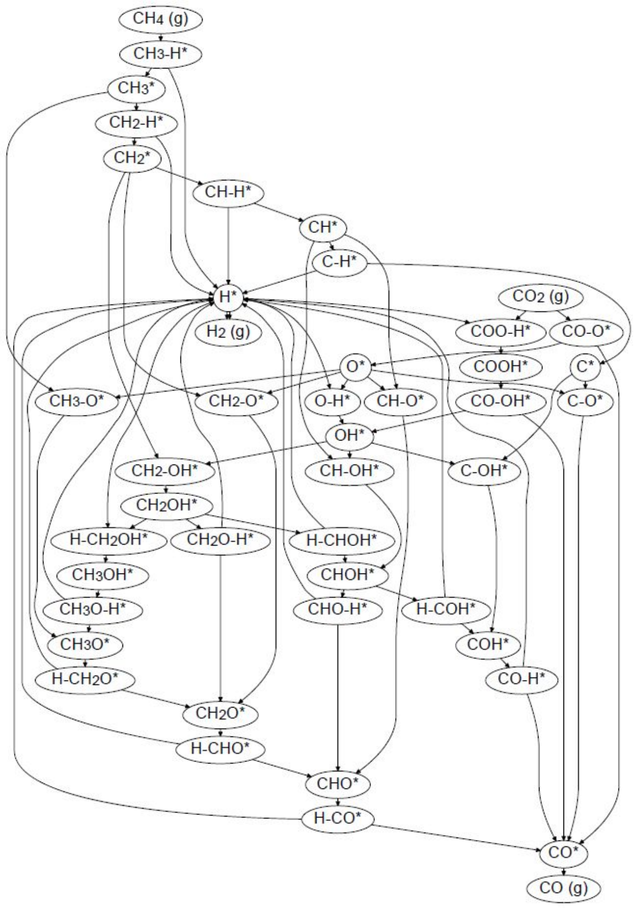
6. Example of the reaction network pruning process

Reaction condition: 923 K, 1 bar, using BEEF-vdw energies on Ni(111).

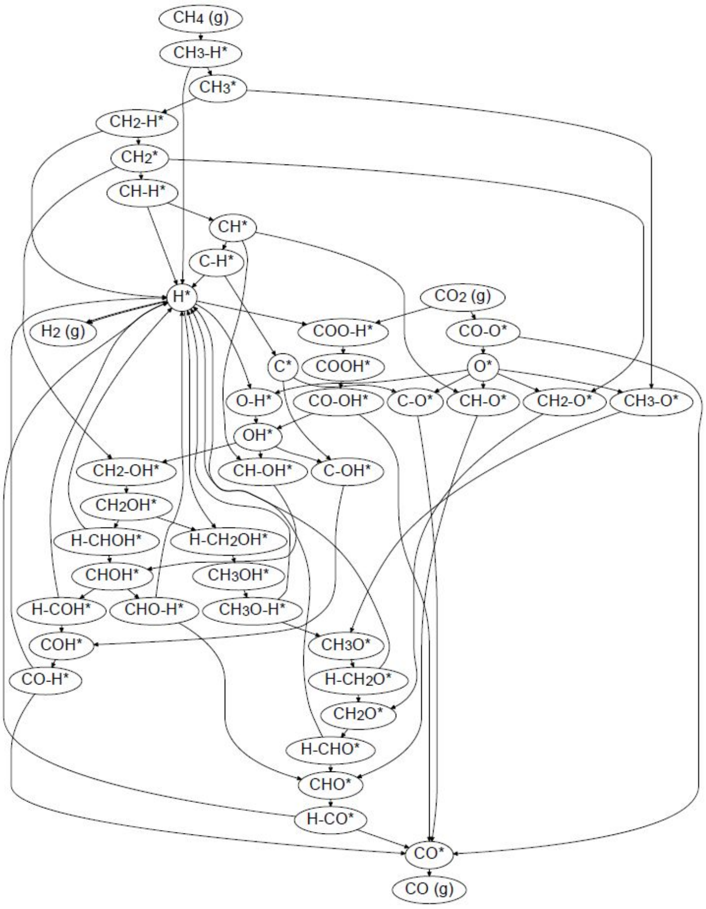
Iteration 1



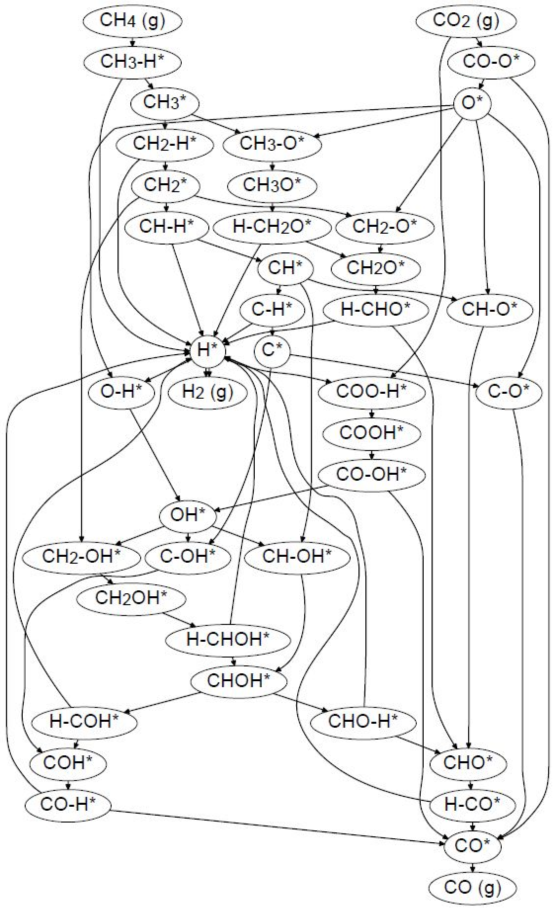
Iteration 2


CH4 (g)
CH3-H*
CH3*
CH2-H*
CH2*
CH-H*
CH*
C-H*
H*
CO2 (g)
H2 (g)
COO-H*
CO-O*
O*
COOH*
C*
CH3-O*
CH2-O*
O-H*
CH-O*
CO-OH*
C-O*
OH*
CH2-OH*
CH-OH*
C-OH*
CH2OH*
H-CH2OH*
CH2O-H*
H-CHOH*
CH3OH*
CHOH*
CH3O-H*
CHO-H*
H-COH*
CH3O*
COH*
H-CH2O*
CO-H*
CH2O*
H-CHO*
CHO*
H-CO*
CO*
CO (g)

Iteration 3

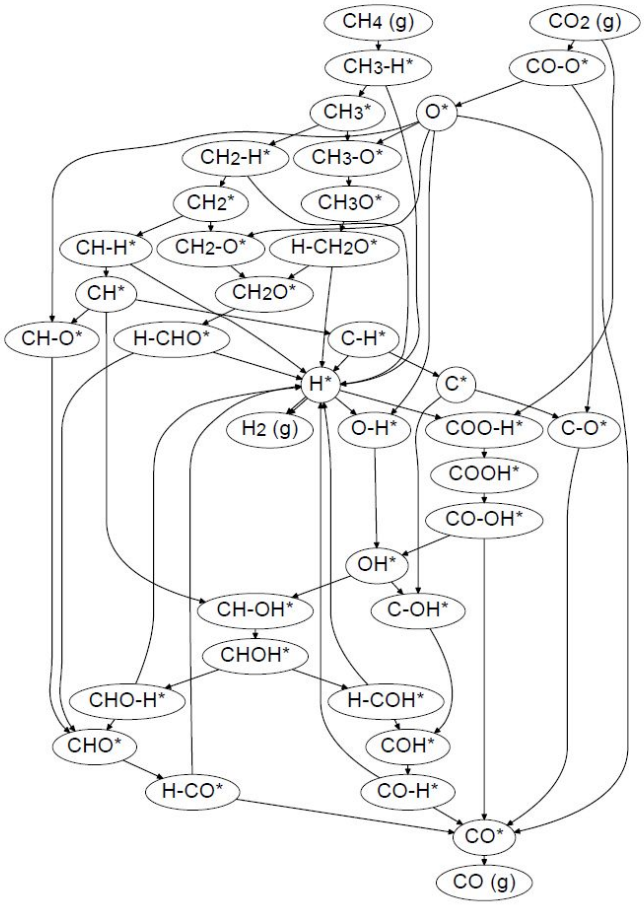

CH4 (g)
CH3-H*
CH3*
CH2-H*
CH2*
CH-H*
CH*
C-H*
H*
CO2 (g)
H2 (g)
COO-H*
CO-O*
C*
COOH*
O*
O-H*
CO-OH*
C-O*
CH-O*
CH2-O*
CH3-O*
OH*
CH2-OH*
CH-OH*
C-OH*
CH2OH*
H-CHOH*
H-CH2OH*
CHOH*
CH3OH*
H-COH*
CHO-H*
CH3O-H*
COH*
CH3O*
CO-H*
H-CH2O*
CH2O*
H-CHO*
CHO*
H-CO*
CO*
CO (g)

Iteration 4



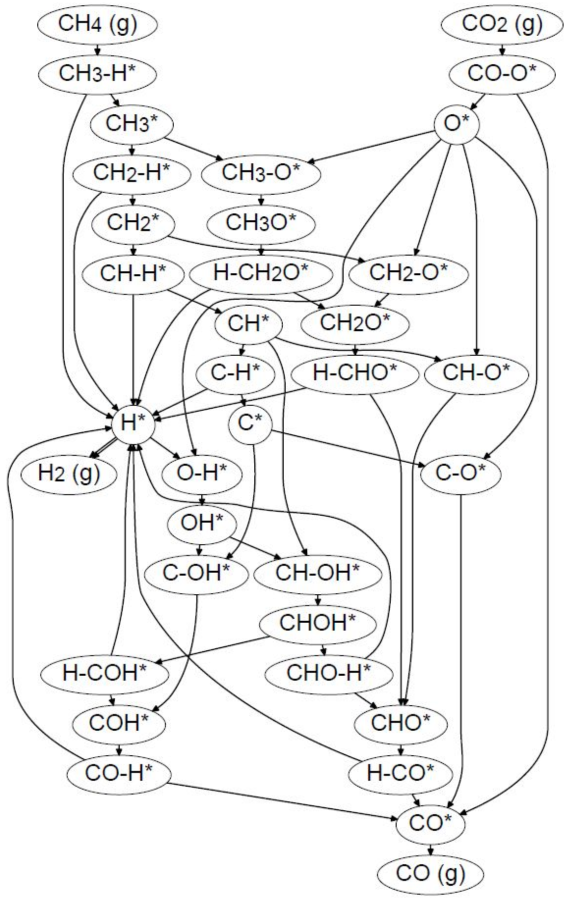
CH4 (g)
CO2 (g)
CH3-H*
CO-O*
CH3*
O*
CH2-H*
CH3-O*
CH2*
CH3O*
CH-H*
H-CH2O*
CH2-O*
CH*
CH2O*
C-H*
H-CHO*
CH-O*
H*
C*
O-H*
H2 (g)
COO-H*
C-O*
COOH*
CO-OH*
OH*
CH2-OH*
C-OH*
CH-OH*
CH2OH*
H-CHOH*
CHOH*
H-COH*
CHO-H*
COH*
CHO*
CO-H*
H-CO*
CO*
CO (g)

Iteration 5

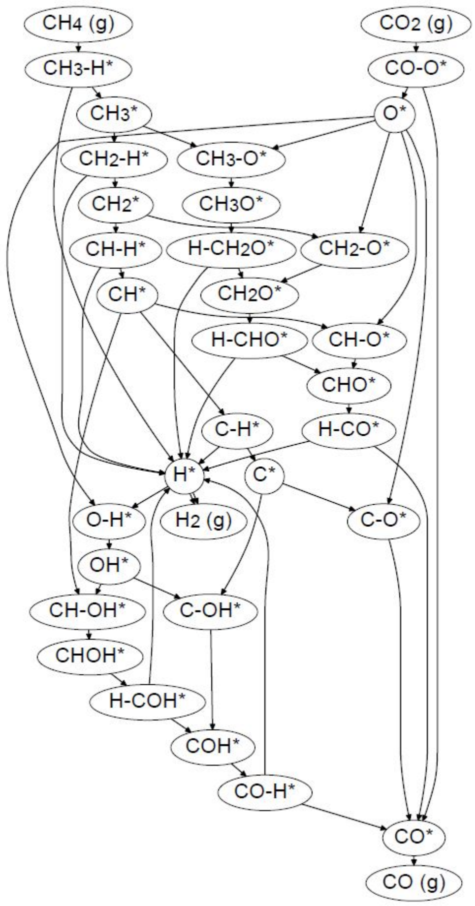


CH4 (g)
CO2 (g)
CH3-H*
CO-O*
CH3*
O*
CH2-H*
CH3-O*
CH2*
CH3O*
CH-H*
CH2-O*
H-CH2O*
CH*
CH2O*
CH-O*
H-CHO*
C-H*
H*
C*
H2 (g)
O-H*
COO-H*
C-O*
COOH*
CO-OH*
OH*
CH-OH*
C-OH*
CHOH*
CHO-H*
H-COH*
CHO*
COH*
H-CO*
CO-H*
CO*
CO (g)

Iteration 6

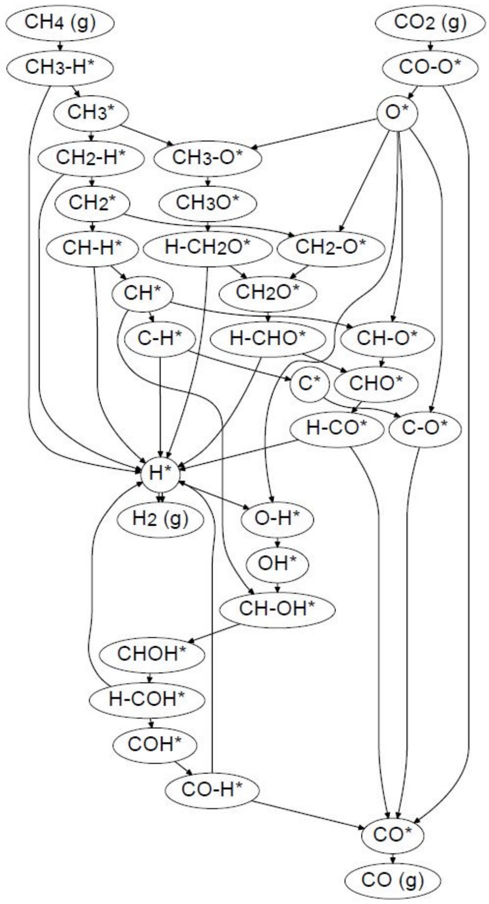

CH4 (g)
CO2 (g)
CH3-H*
CO-O*
CH3*
O*
CH2-H*
CH3-O*
CH2*
CH3O*
CH-H*
H-CH2O*
CH2-O*
CH*
CH2O*
C-H*
H-CHO*
CH-O*
H*
C*
H2 (g)
O-H*
C-O*
OH*
C-OH*
CH-OH*
CHOH*
H-COH*
CHO-H*
COH*
CHO*
CO-H*
H-CO*
CO*
CO (g)

Iteration 7



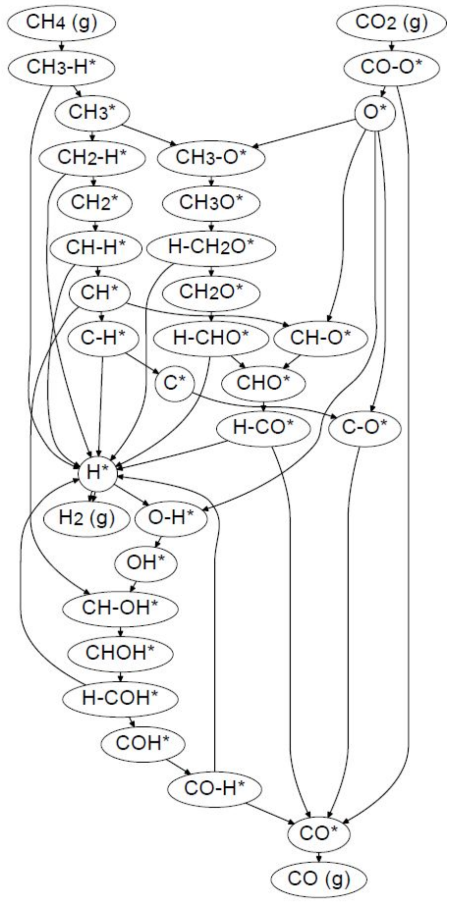
CH4 (g)
CO2 (g)
CH3-H*
CO-O*
CH3*
O*
CH2-H*
CH3-O*
CH2*
CH3O*
CH-H*
H-CH2O*
CH2-O*
CH*
CH2O*
H-CHO*
CH-O*
CHO*
C-H*
H-CO*
H*
C*
O-H*
H2 (g)
C-O*
OH*
CH-OH*
C-OH*
CHOH*
H-COH*
COH*
CO-H*
CO*
CO (g)

Iteration 8



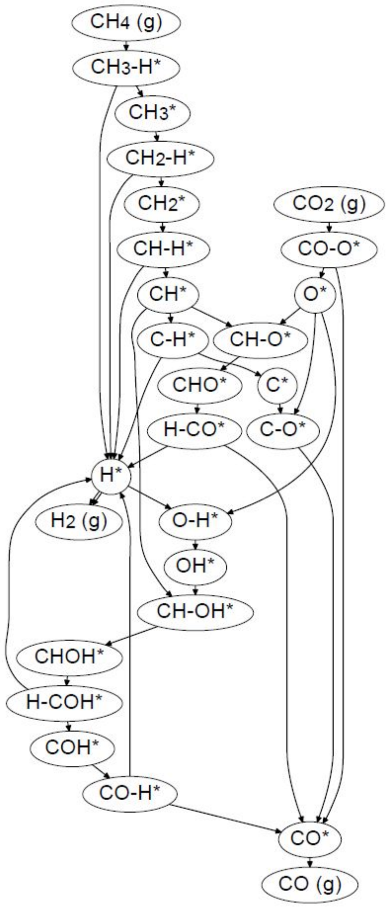
CH4 (g)
CO2 (g)
CH3-H*
CO-O*
CH3*
O*
CH2-H*
CH3-O*
CH2*
CH3O*
CH-H*
H-CH2O*
CH2-O*
CH*
CH2O*
C-H*
H-CHO*
CH-O*
C*
CHO*
H-CO*
C-O*
H*
H2 (g)
O-H*
OH*
CH-OH*
CHOH*
H-COH*
COH*
CO-H*
CO*
CO (g)

Iteration 9

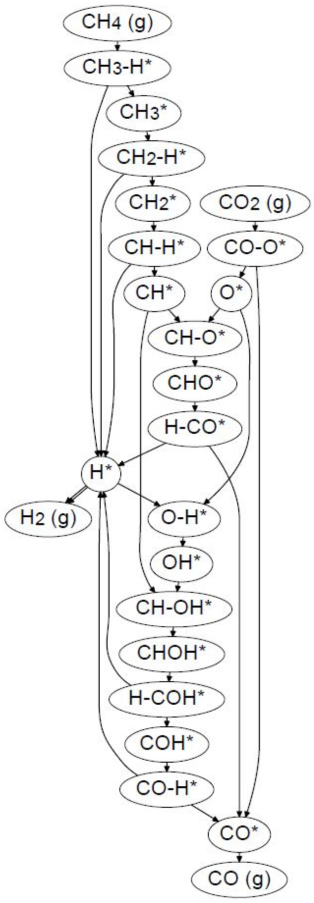


CH4 (g)
CO2 (g)
CH3-H*
CO-O*
CH3*
O*
CH2-H*
CH3-O*
CH2*
CH3O*
CH-H*
H-CH2O*
CH*
CH2O*
C-H*
H-CHO*
CH-O*
C*
CHO*
H-CO*
C-O*
H*
H2 (g)
O-H*
OH*
CH-OH*
CHOH*
H-COH*
COH*
CO-H*
CO*
CO (g)

Iteration 10



Iteration 11



Iteration 12

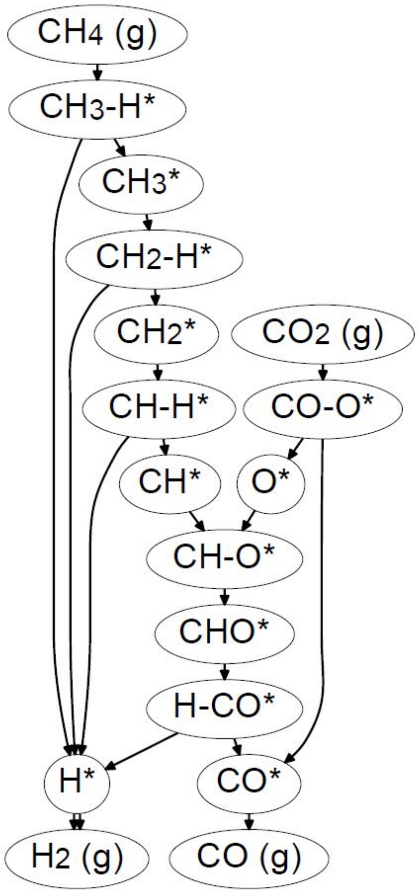


Figure S7. DRM reaction network pruning process on 923K, 1 bar, using BEEF-vdw energy on Ni(111).

References

(1) Wellendorff, J.; Lundgaard, K. T.; Mogelhoj, A.; Petzold, V.; Landis, D. D.; Norskov, J. K.; Bligaard, T.; Jacobsen, K. W.: Density functionals for surface science: Exchange-correlation model development with Bayesian error estimation. *Phys. Rev. B* **2012**, *85*, 23.