Supporting Information: Predicted Influence of Plasma Activation on Non-Oxidative Coupling of Methane on Transition Metal Catalysts

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In this supporting information, we provide extra documentation to complement the main article. In Section 1, we show the heat maps for the impact of bending modes on the TOFs on the (211) steps, for an alpha parameter equal to 0.5 and 0.1, to be compared with the impact of stretch modes with a Fridman-Macheret parameter shown in the main article. Section 2 shows the thermodynamic scaling relations for the (211) and (111) metal surfaces and the comparison between calculated entropies and literature values. In Section 3 we show the steady state coverages and turnover frequencies (TOFs) calculated for the metal (111) terraces, analogous to the results on the (211) stepped surfaces shown in the main article. Section 4 shows the individual net rates of each of the elementary reactions in the 3 models. Finally, in Section 5, we show the heat maps for the impact of the vibrational temperature on the TOFs on the metal (111) terraces.

<u>1. Heat maps for the effect of the vibrational temperature of the bending modes on the TOFs on metal</u> (211) steps



Figure S1: log(TOF) as a function of T_{vib} and E_b on the metal (211) steps for excitation of the bending modes with an alpha parameter equal to 0.5. Colors are assigned relative to the maximum TOF.



Figure S2: log(TOF) as a function of T_{vib} and E_b on the metal (211) steps for excitation of the bending modes with an alpha parameter equal to 0.1. Colors are assigned relative to the maximum TOF.



2. Scaling relations for reaction energies and reaction barriers on the metal (211) surfaces

Figure S3: Adsorption energies and activation barriers on metal (211) steps, as function of the CH_3 binding energy for molecular and radical adsorption. The adsorption of radical species is assumed barrierless.



Figure S4: Reaction energies and activation barriers on metal (211) steps, as function of the CH_3 binding energy for hydrogenation of CH_y and C_2H_y species.



Figure S5: Coupling energies and activation barriers on metal (211) steps, as function of the CH_3 binding energy for CH, CH_2 and CH_3 .



Figure S6: Adsorption energies and activation barriers on metal (111) terraces, as function of the CH_3 binding energy for molecular and radical adsorption. The adsorption of radical species is assumed barrierless.



Figure S7: Reaction energies and activation barriers on metal (111) terraces, as function of the CH_3 binding energy for hydrogenation of CH_y and C_2H_y species.



*Figure S8: Coupling energies and activation barriers on metal (111) terraces, as function of the CH*₃ *binding energy for CH, CH*₂ *and CH*₃*. Activation barriers were derived from BEP relations.*¹

Adsorption/desorption			γ _f	ξ _f	MAE	γa	ξa	MAE
H _(g) + *	≓	H*	0.69	-2.61	0.09	0.00	0.00	0.00
$H_{2(g)} + 2^*$	\rightleftharpoons	2H*	1.38	-0.70	0.19	1.06	0.21	0.16
C _(g) + *	≓	C*	4.04	-5.96	0.37	0.00	0.00	0.00
CH _(g) + *	≓	CH*	3.06	-5.58	0.26	0.00	0.00	0.00
CH _{2(g)} + *	≓	CH ₂ *	2.01	-3.46	0.15	0.00	0.00	0.00
CH _{3(g)} + *	\rightleftharpoons	CH ₃ *	1.00	-1.52	0.00	0.00	0.00	0.00
CH _{4(g)} + 2*	≓	CH ₃ * + H*	1.69	0.42	0.09	1.59	1.15	0.16
C ₂ H _(g) + *	≓	C ₂ H*	5.08	-4.43	0.49	0.00	0.00	0.00
C ₂ H _{2(g)} + *	≓	$C_2H_2^*$	3.87	-1.52	0.50	1.60	-0.07	0.30
C ₂ H _{3(g)} + *	\rightleftharpoons	$C_2H_3^*$	3.06	-2.50	0.26	0.09	-0.01	0.03
C ₂ H _{4(g)} + *	\rightleftharpoons	C_2H_4 *	2.01	0.06	0.15	1.94	0.09	0.17

Table S1: Surface Reaction Steps and Associated Microkinetic Parameters on the (111) terraces

$C_2H_{5(g)} + * \rightleftharpoons C_2H_5^*$	1.00	-1.25	0.00	0.00	0.00	0.00
(De)hydrogenation						
$C^* + H^* \rightleftharpoons CH^* + *$	-1.67	-0.53	0.21	-0.48	1.07	0.08
$CH^* + H^* \rightleftharpoons CH_2^* + *$	-1.73	0.35	0.21	-0.05	0.78	0.11
$CH_2^* + H^* \rightleftharpoons CH_3^* + *$	-1.70	-0.25	0.24	0.05	0.61	0.07
$C_2H^* + H^* \rightleftharpoons C_2H_2^* + *$	-1.67	-0.53	0.21	-0.21	0.47	0.00
$C_2H_2^* + H^* \ \rightleftharpoons \ C_2H_3^* + \ *$	-1.73	0.35	0.21	-0.21	0.47	0.00
$C_2H_3^* + H^* \ \rightleftharpoons \ C_2H_4^* \ + \ *$	-1.73	0.35	0.21	-0.36	0.99	0.00
$C_2H_4^* + H^* \ \rightleftharpoons \ C_2H_5^* + \ *$	-1.70	-0.25	0.24	-0.21	0.47	0.00
$C_2H_5^* + H^* \rightleftharpoons C_2H_{6(g)} + 2^*$	-1.69	-0.52	0.09	-1.10	0.89	0.00
Carbon coupling						
$2 CH^* \rightleftharpoons C_2 H_2^* + *$	-2.01	-0.60	0.15	-1.10	2.29	0.09
$2 \operatorname{CH}_2^* \rightleftharpoons \operatorname{C}_2 \operatorname{H}_4^* + *$	-2.01	-0.60	0.15	-1.01	1.26	0.07
$2 \text{ CH}_3^* \rightleftharpoons \text{C}_2 \text{H}_{6(g)} + 2^*$	-2.00	-0.87	0.00	-0.12	2.00	0.00

In Table S1, we list the scaling relations that we built for the reactions, based on reaction and activation energies computed using the RPBE functional on the (111) terraces of Pt, Rh, Pd, Ni, Cu, Au and Ag.² The linear fit parameters, γ and ξ , for the forward reaction energy and the activation barrier are listed, along with the mean absolute error (MAE). For lack of available thermodynamic data, we assumed the energy of hydrogenation of C₂H^{*} to be equal to the hydrogenation of C^{*}, the hydrogenation of C₂H₄* to be equal to the hydrogenation of C₂H₄* to be equal to the hydrogenation of CH₂*.

Table S2: Comparison between calculated entropies and literature data, S°_{500K} , in Jmol⁻¹K⁻¹

	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₂ H ₂	H ₂
Calculated	197.4	239.2	230.6	212.2	153.9
NIST	207.0	262.4	246.2	226.6	145.7

In Table S2, we compare the standard entropy at 500 K, calculated with the formula given in the main article, and the tabulated data in the database of the National Institute of Standards and Technology (<u>https://webbook.nist.gov/chemistry/</u>). The mean absolute error is 14 J mol⁻¹K^{-1.}

3. Steady state reaction rates and surface coverages



Figure S9: Steady state coverages (a) and volcano plots (b) in thermal catalytic NOCM at 500K and 0% conversion on the metal terraces (111).



Figure S10: Steady state coverages (a) and volcano plots (b) in catalytic NOCM at 500K and 0% conversion on the metal (111) terraces for vibrationally excited methane following a Boltzmann distribution at $T_{vb} = 1500K$.



Figure S11: Steady state coverages (a) and volcano plots (b) in catalytic NOCM at 500K and 0% conversion on the metal (111) terraces with reactive plasma species, characteristic for a DBD plasma.

On the x-axis, the binding energy ranges from -1 to 2 eV instead of -1 to 1 eV in previous figures, to show the shift to the weaker catalysts.

4. Net rates of the elementary reactions in the model



Figure S12: Reaction rates (s⁻¹) of every reaction in the model for thermal NOCM. If the net rate is positive it is shown in a full line, if the net rate is negative it is shown in a dashed line.



Figure S13: Reaction rates (s^{-1}) of every reaction in the model for NOCM with vibrationally excited methane. If the net rate is positive it is shown in a full line, if the net rate is negative it is shown in a dashed line.



Figure S14: Reaction rates (s^{-1}) of every reaction in the model for NOCM with plasma-generated radicals. If the net rate is positive it is shown in a full line, if the net rate is negative it is shown in a dashed line.



5. Heat map for the effect of the vibrational temperature on the TOFs on metal (111) terraces

Figure S15: log(TOF) as a function of T_{vib} and E_b on the metal (111) terraces. Colors are assigned relative to the maximum TOF.

References

- (1) Wang, S.; Temel, B.; Shen, J.; Jones, G.; Grabow, L. C.; Studt, F.; Bligaard, T.; Abild-Pedersen, F.; Christensen, C. H.; Nørskov, J. K. *Catal. Letters* **2011**, *141* (3), 370.
- (2) Hummelshøj, J. S.; Abild-Pedersen, F.; Studt, F.; Bligaard, T.; Nørskov, J. K. Angew. Chemie Int. Ed. 2012, 51 (1), 272.