Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Connection between Macroscopic Kinetic Measurables and the Degree of Rate Control

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Numerical results at low oxygen concentrations

The numerical examples shown in the main text concern methane oxidation over Pd(100) in oxygen excess. Here we describe the case of methane oxidation during rich conditions where H_2O formation competes with H_2 formation.

Figure S1 shows the Turnover Frequency (TOF) for CO_2 and H_2 as a function of temperature with $pCH_4 = 61$ mbar and $pO_2 = 30.6$ mbar. The formation of H_2 is substantial, in particular, at temperatures above 900 K. The large amount of produced H_2 demonstrates that the favored reaction path is different as compared to the situation with oxygen excess.

The reaction orders for methane combustion during rich conditions are shown in Figure S2. The results from the full microkinetic model and the results from Equation (8) in the main text match closely. A slight deviation is, however, observed around 900 K due to the rapidly changing kinetics.

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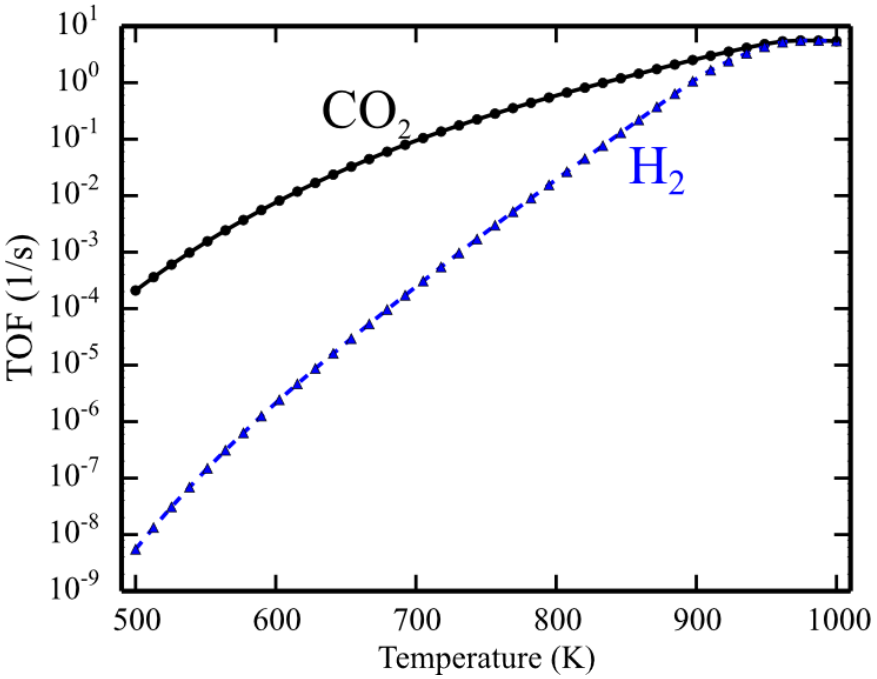

Figure S1: Turnover Frequency for CO_2 and H_2 formation as a function of temperature. $pCH_4 = 61$ mbar and $pO_2 = 30.6$ mbar.

The corresponding apparent activation energies are shown in Figure S3. Also in this case, the results from the full microkinetic model match the results from the analytical expressions. The slight deviation at 900 K is also here due to the rapidly changing kinetics. The major part of the deviation originates from large derivatives of the reaction orders which makes the results numerically sensitive to the pressure-dependent term in equation (19) of the main text.

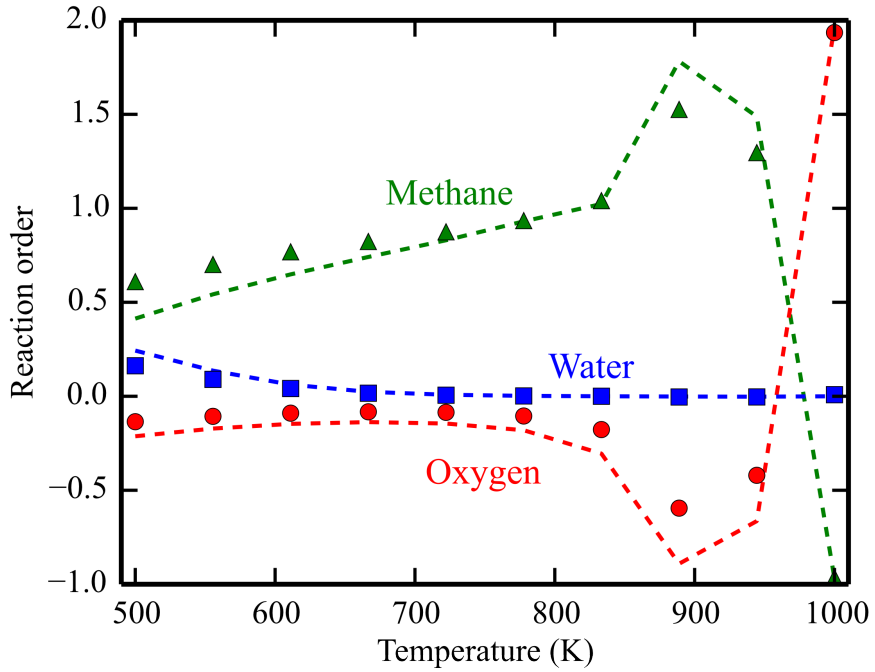

Figure S2: Reaction orders as a function of temperature. The dashed lines are evaluated by Eq. (8) in the main text, whereas the points are obtained from the total rate of the full microkinetic model. $pCH_4 = 61$ mbar and $pO_2 = 30.6$ mbar.

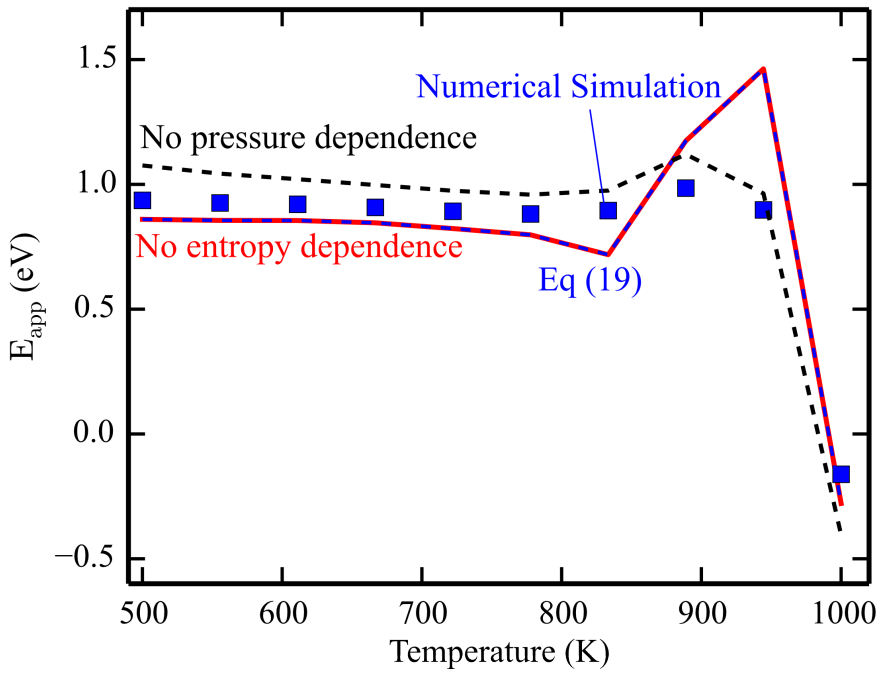

Figure S3: Apparent activation energy as a function of temperature. The dashed line are calculated using Eq. (19) in the main text, whereas the points correspond to results from the full microkinetic model. The results from Eq. (19) and the simulations with no entropy dependence coincide. $pCH_4 = 61$ mbar and $pO_2 = 30.6$ mbar.