Overcoming Ammonia Synthesis Scaling Relations with Plasma-enabled Catalysis

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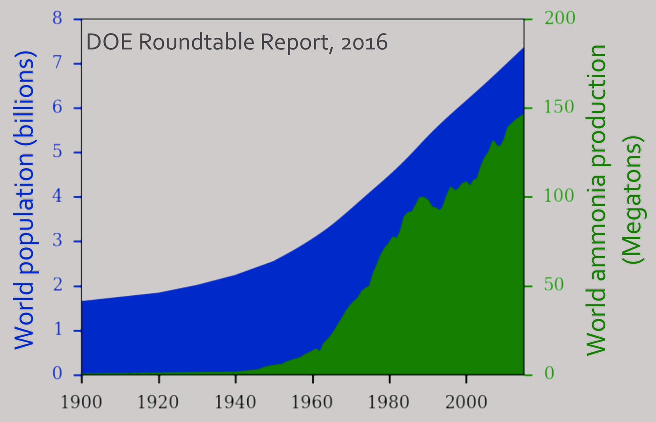
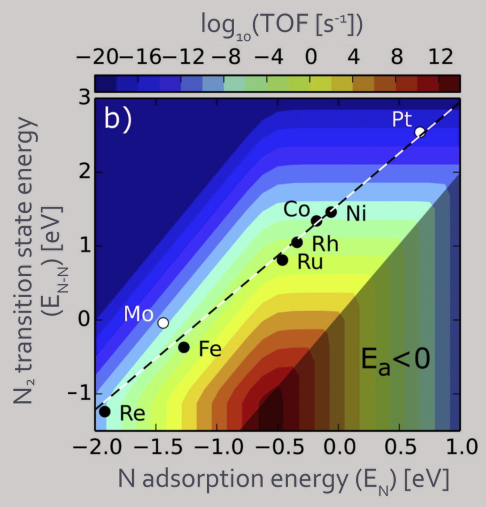
Can we make ammonia at low pressures and low temperatures?

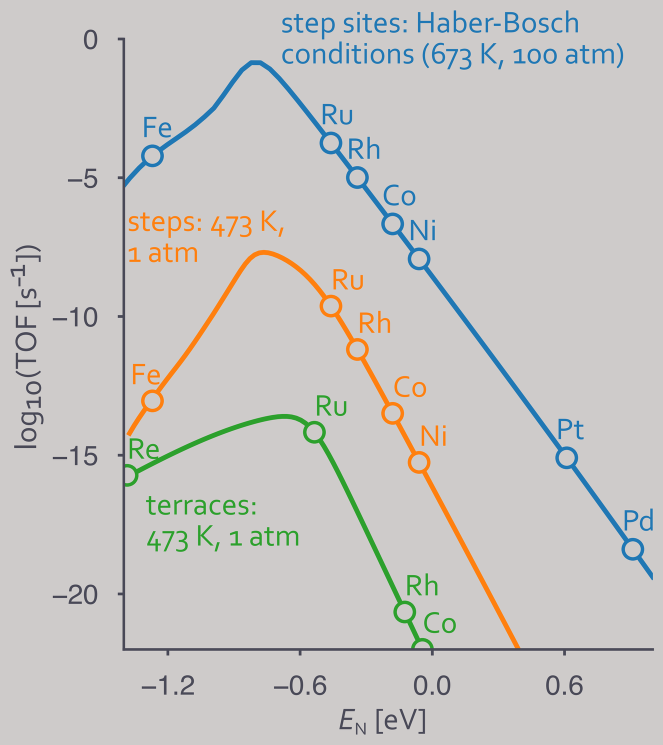


Over half the world's population relies on ammonia-based fertilizers for food

Haber-Bosch conditions:
100-200 atm, 700-800 K
Not practical for distributed small-scale production



Scaling relations limit achievable rates on conventional catalysts:
Not possible to have a low barrier for N_2 dissociation and a weak interaction with adsorbed NH_x intermediates



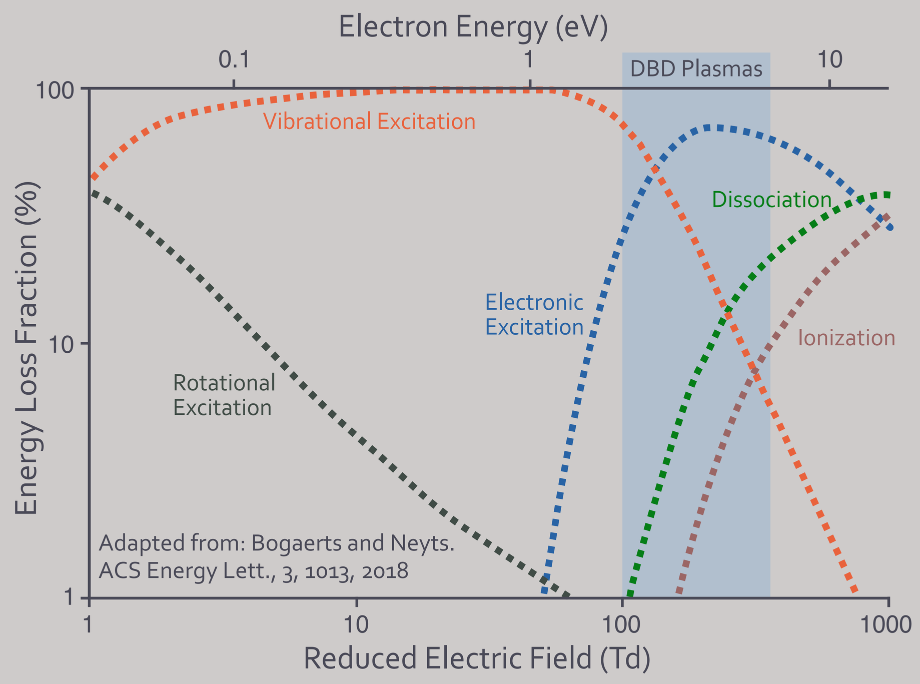
Strategy: Direct energy into target reaction steps by an extrinsic, non-thermal stimulus

Non-equilibrium dielectric barrier discharge (DBD) plasma

Gas ionized by an electric discharge

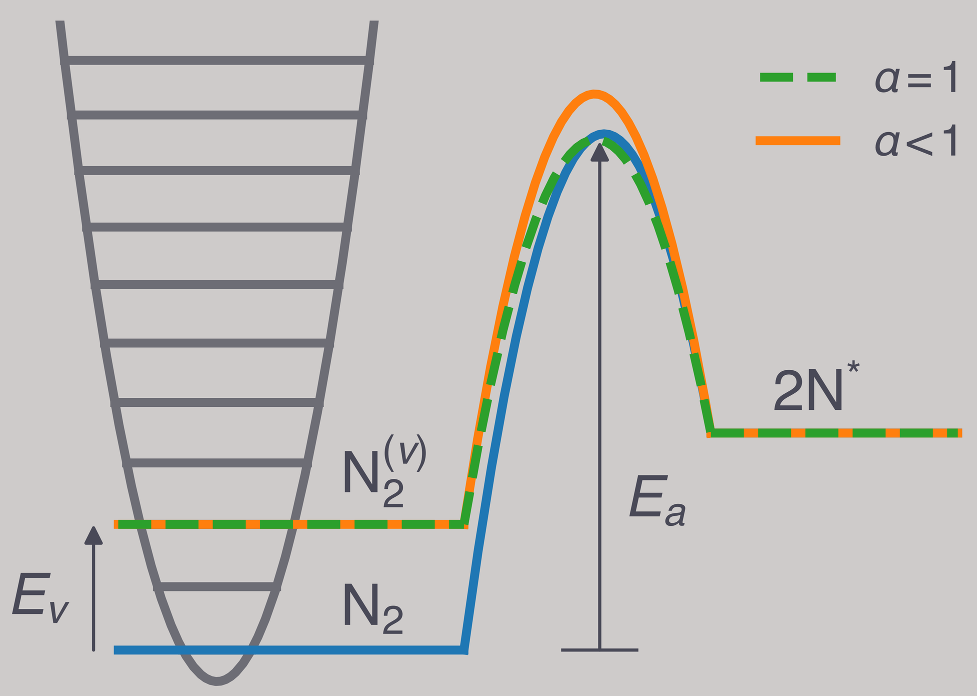
Comprised of reactive intermediates:
free electrons, vibrationally or electronically excited molecules, ions, and radicals

Characterized by thermal non-equilibrium:
$T_{electron}$ (~10000 K) > T_{vib} (~ 1000 K) > T_{rot} = T_{trans} (near-ambient)



Significant fraction of energy may be deposited into vibrational excitation of N_2

Excitation channels in a N_2 plasma



Modeling rate enhancements by N_2 vibrational excitations

Vibrational state-specific rate constants: activation energy lowered by the vibrational energy times an efficiency factor (α, estimated by Fridman-Macheret model)

$$k_v^{(f)} = A\exp\left(-\frac{E_a^{(f)} - \alpha E_v}{k_B T}\right) \qquad \alpha = \frac{E_a^{(f)}}{E_a^{(f)} + E_a^{(b)}}$$

We can then write $N_2 + 2^* \rightleftharpoons 2N^*$ as a series of state-specific reactions, $N_2^{(v)} + 2^* \rightleftharpoons 2N^*$ with individual rates,

$$r_1(v) = k_v^{(f)} p_v P_{N_2} \theta_*^2 - k_v^{(b)} \theta_N^2$$

and overall rate $\sum r_1(v)$

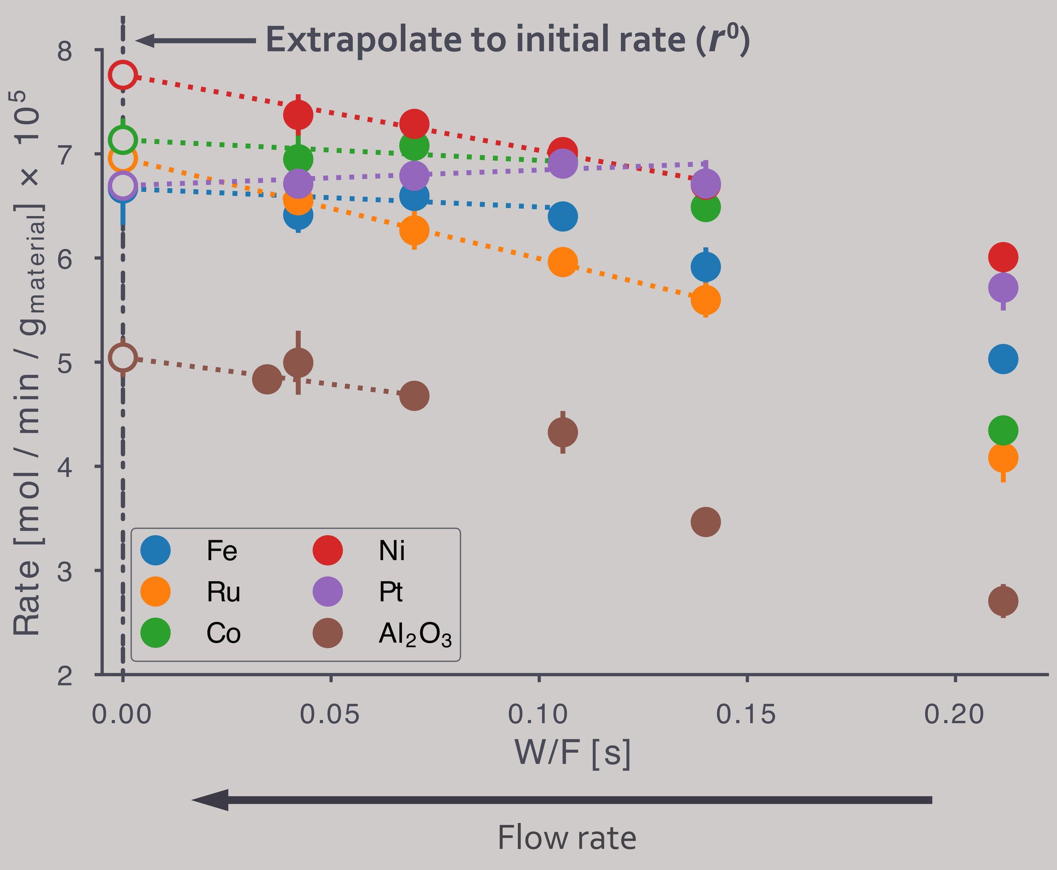
Microkinetic model details:
DFT energies for surface intermediates taken from CatApp
No rate-limiting step assumed, ODEs integrated to steady state

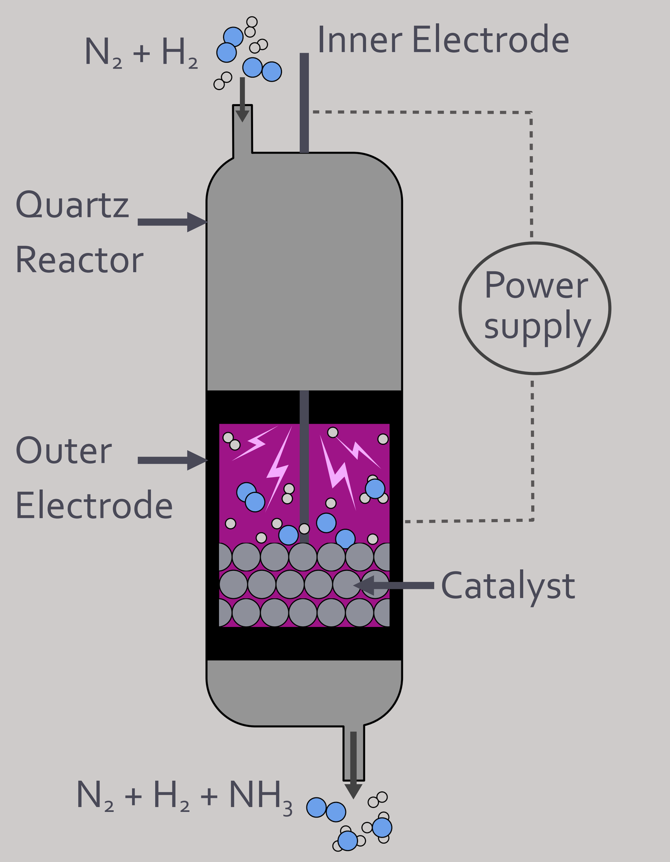
Vibrational populations (p_v) estimated from a truncated Treanor distribution at a vibrational temperature of 3000 K (determined by optical emission spectroscopy measurements)

Plasma-catalytic kinetic measurements

Some NH_3 formed when N_2 and H_2 passed through plasma alone or when DBD reactor packed only with support

Rates enhanced when metal catalysts introduced



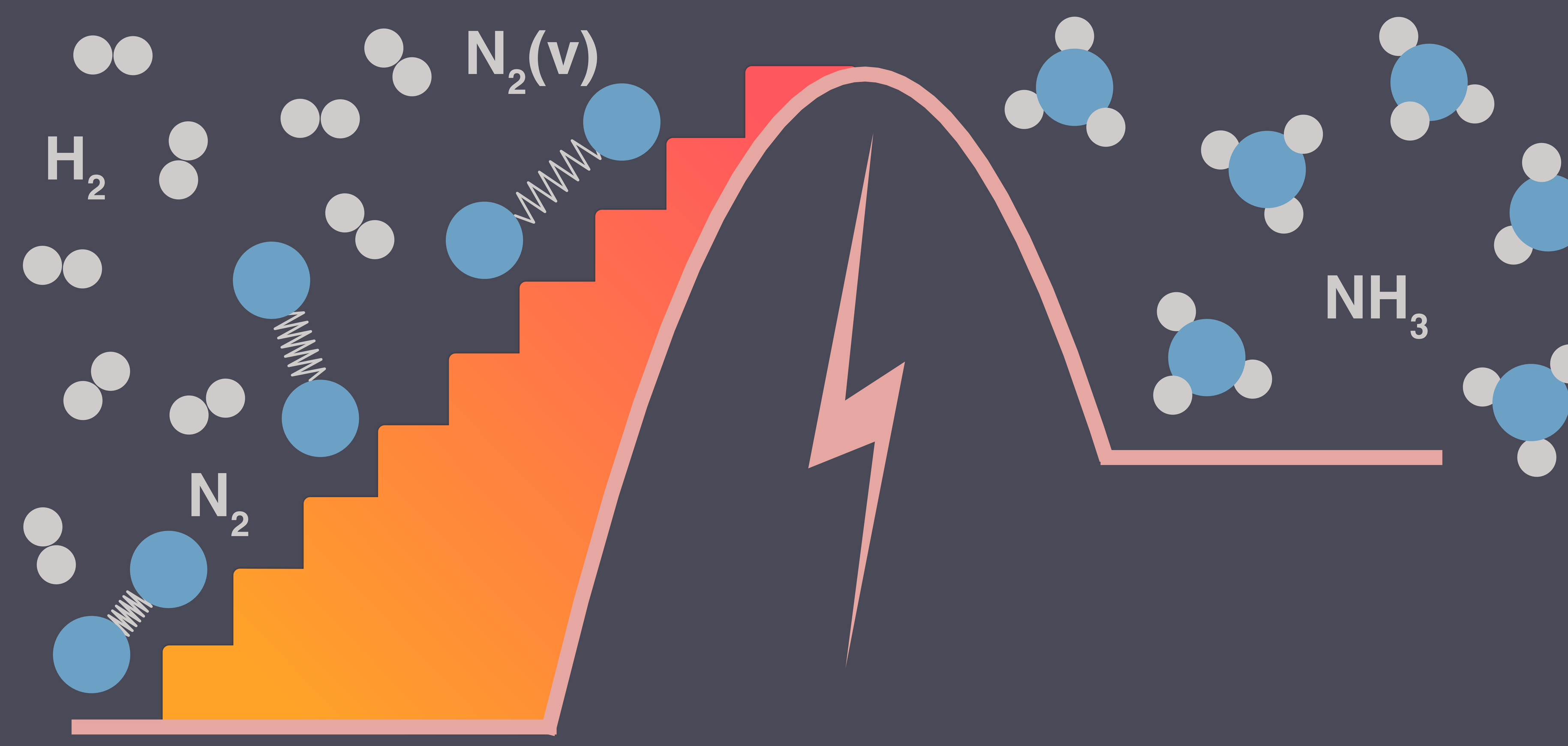


Metal catalysts supported on Al_2O_3
Power = 10 W, T = 438 K, P = 1 atm, N2:H2 = 2:1

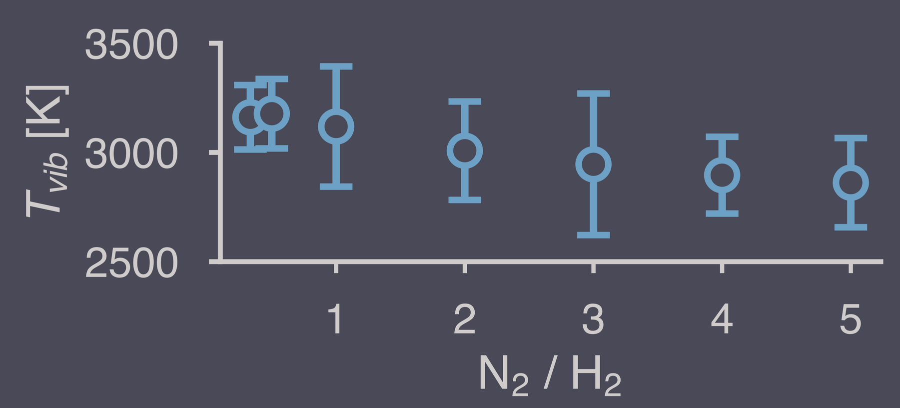
Initial rates normalized (by CO accessible sites) to obtain site-time yield (STY):

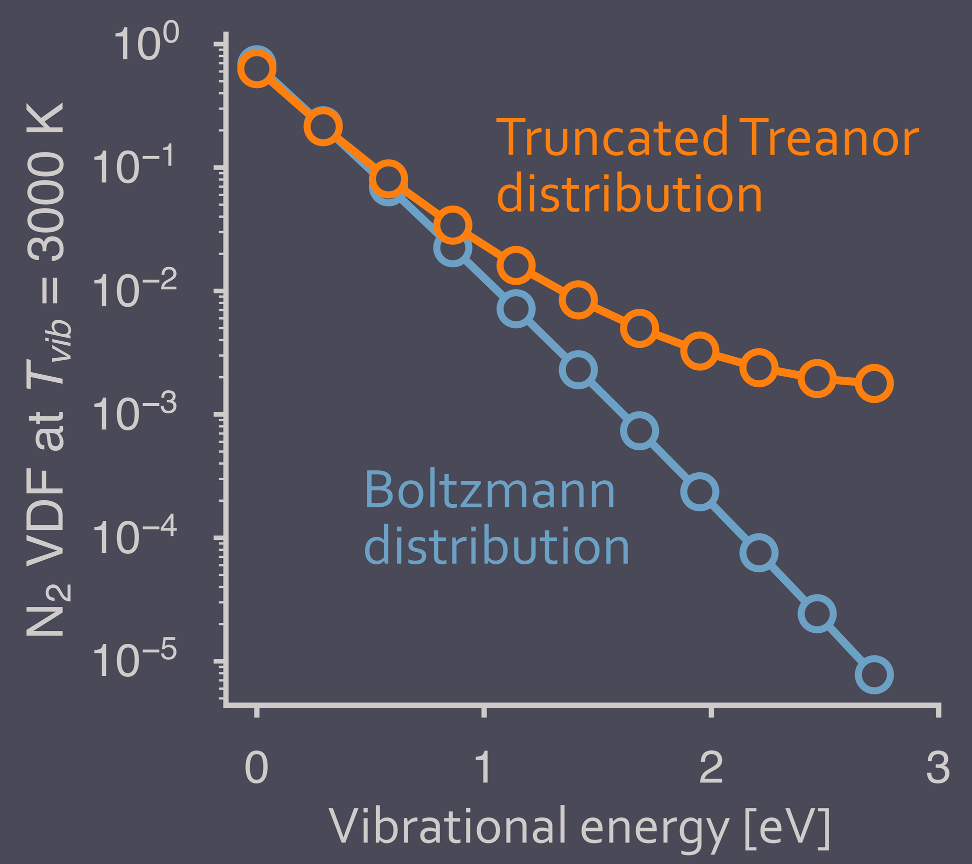
$$STY = \frac{r^0_{M/Al_2O_3+DBD} - r^0_{Al_2O_3+DBD}}{n_{sites}}$$

Plasma-induced vibrational excitations lower activation barrier for N_2 dissociation

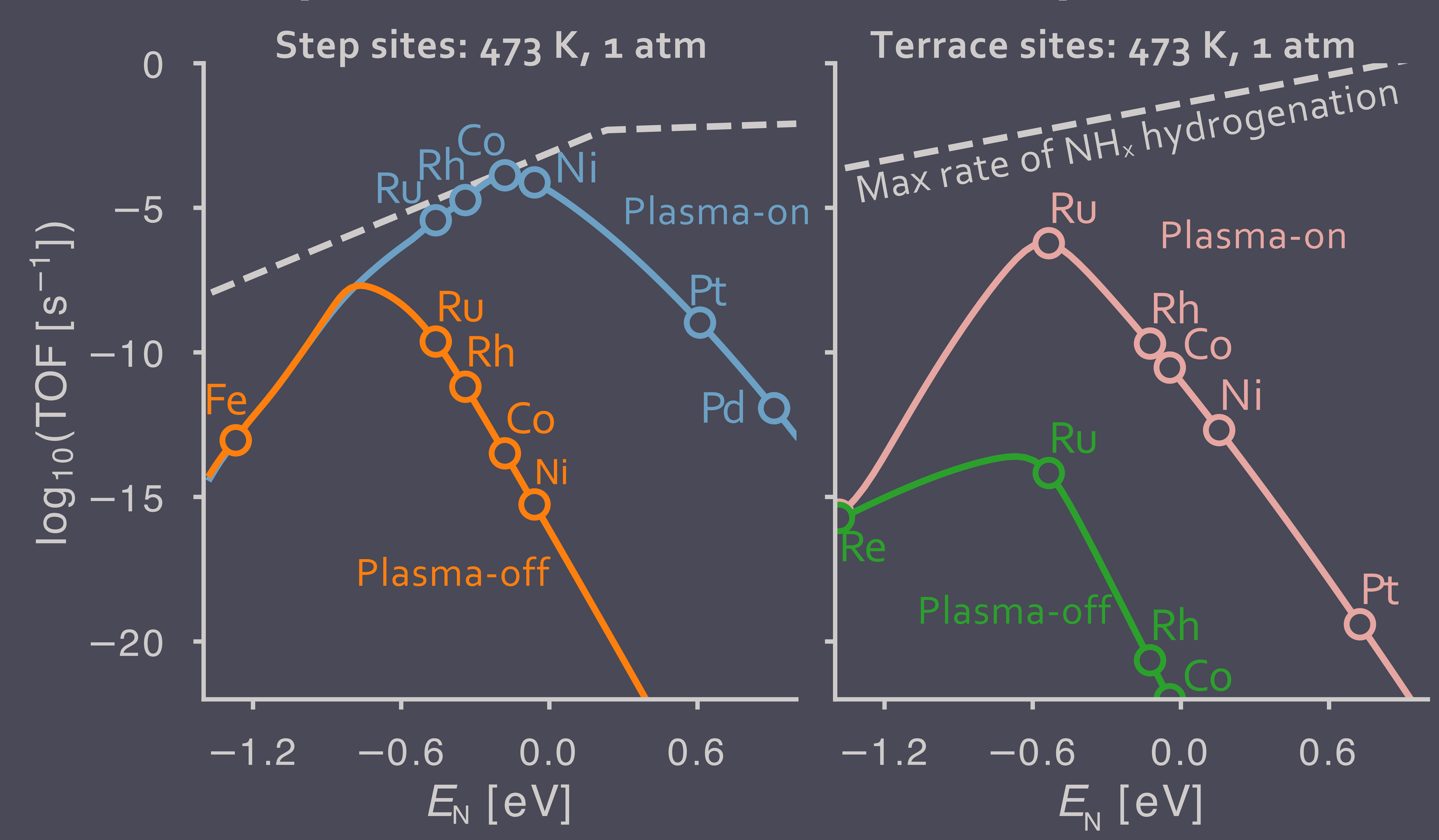


Microkinetic model parametrized by experimentally measured N_2 vibrational temperature

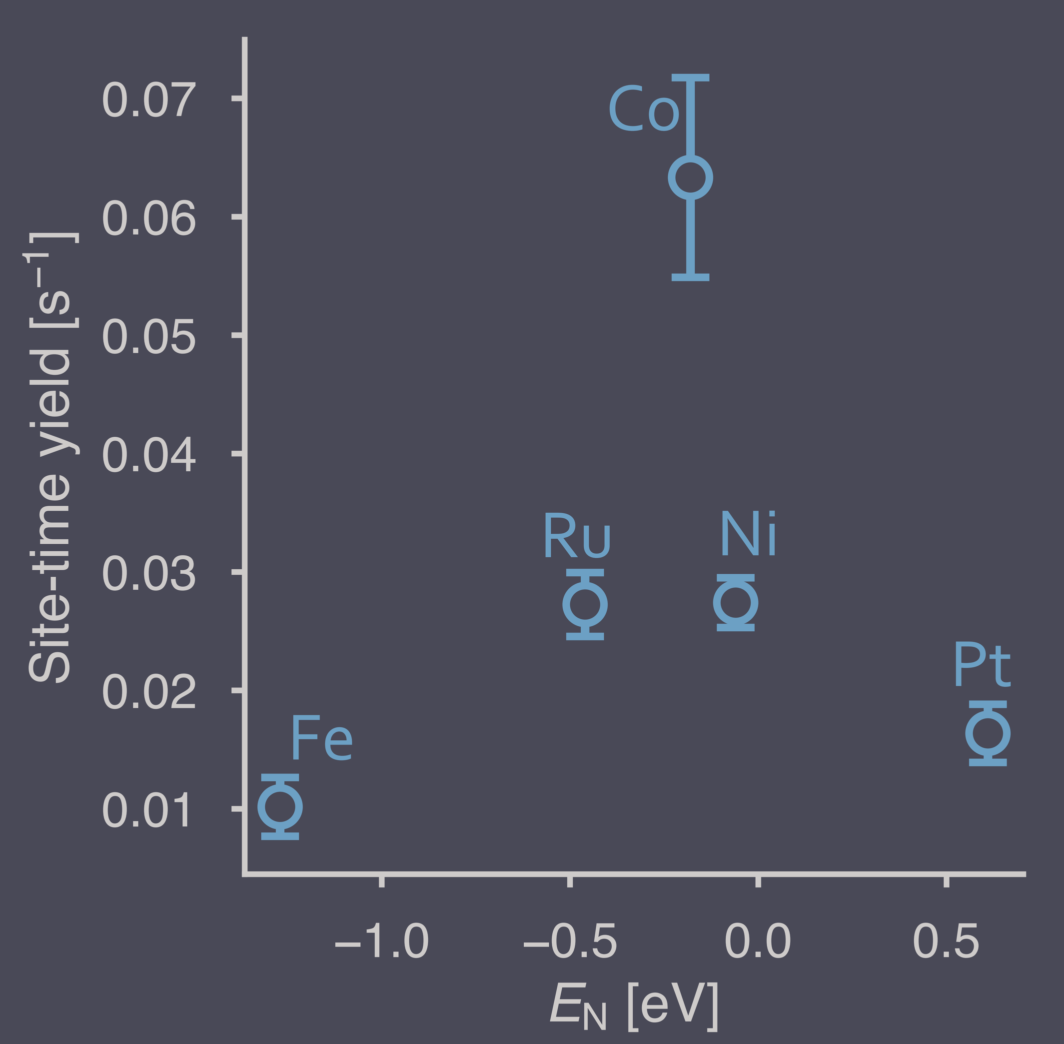




Predicted low-temperature and pressure plasma-catalytic rates well beyond those for thermal catalysis



Enhancements greater for metals that bind N less strongly than the optimal thermal catalyst. Terrace sites may become active, resulting in more atom-efficient catalysis.



Kinetic experiments confirm rate enhancements and shift in optimal catalyst

Future challenge to disentangle other potential effects of the plasma

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