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 
N₂ dissociation and a weak interaction with adsorbed NH intermediate.

Plasma-induced vibrational excitations lower activation barrier for N₂ dissociation

N₂ (v)

H₂

NH₃

N₂

H₂

Microkinetic model parametrized by experimentally measured N₂, vibrational temperature

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

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

Kinetic experiments confirm rate enhancements and shift in optimal catalyst

Future challenge to disentangle other potential effects of the plasma

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) ~ 10,000 K > T(ion) = T(ambient) & T(chemistry)

Significant fraction of energy may be deposited into vibrational excitation of N₂,

Modeling rate enhancements by N₂ vibrational excitations

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

We can then write N₂ + 2hν = N₂ (v) in a series of state-specific reactions, N₂ (v) + 2hν = N₂ (v') with individual rates, r_i(v) = k_i(v) / P_i(v) and overall rate \sum r_i(v)

Vibrational populations (p) estimated from a truncated Treanor model (determined by optical emission spectroscopy measurements).

Plasma-catalytic kinetic measurements

Some NH₃ formed when N₂ and H₂ passed through plasma alone or when DBD reactor packed only with support
Rates enhanced when metal catalysts introduced

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