Observation and rationalization of nitrogen oxidation enabled only by coupled plasma and catalyst

Hanyu Ma1, Rakesh K. Sharma2, Stefan Welzel2, Mauritius C. M. van de Sanden2,3, Mihalis N. Tsampas2✉ & William F. Schneider1,4 ✉

Heterogeneous catalysts coupled with non-thermal plasmas (NTP) are known to achieve reaction yields that exceed the contributions of the individual components. Rationalization of the enhancing potential of catalysts, however, remains challenging because the background contributions from NTP or catalysts are often non-negligible. Here, we first demonstrate platinum (Pt)-catalyzed nitrogen (N2) oxidation in a radio frequency plasma afterglow at conditions at which neither catalyst nor plasma alone produces significant concentrations of nitric oxide (NO). We then develop reactor models based on reduced NTP- and surface-microkinetic mechanisms to identify the features of each that lead to the synergy between NTP and Pt. At experimental conditions, NTP and thermal catalytic NO production are suppressed by radical reactions and high N2 dissociation barrier, respectively. Pt catalyzes NTP-generated radicals and vibrationally excited molecules to produce NO. The model construction further illustrates that the optimization of productivity and energy efficiency involves tuning of plasma species, catalysts properties, and the reactor configurations to couple plasma and catalysts. These results provide unambiguous evidence of synergism between plasma and catalyst, the origins of that synergy for N2 oxidation, and a modeling approach to guide material selection and system optimization.

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1 Department of Chemical and Biomolecular Engineering, University of Notre Dame, Notre Dame, IN 46556, USA. 2 Dutch Institute for Fundamental Energy Research (DIFFER), De Zaale 20, 5612 AJ Eindhoven, The Netherlands. 3 Department of Applied Physics, Eindhoven University of Technology (TU/e), 5600 MB Eindhoven, The Netherlands. 4 Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN 46556, USA.

✉email: m.tsampas@DIFFER.nl; wschneider@nd.edu
The ability of a nonthermal plasma (NTP) and heterogeneous catalyst combination to achieve reaction yields that exceed the contributions of the individual components is well documented. Often reactions are explored at conditions at which NTP or thermal catalytic yields are non-negligible. Disentangling the gain achieved by combining NTP and catalyst from the background contributions of NTP and catalyst alone, and inferring the origins of yield enhancements, are thus significant practical challenges. Here, we demonstrate NTP-catalytic nitrogen oxidation:

\[ \text{N}_2(g) + \text{O}_2(g) \leftrightarrow 2\text{NO}(g) \]  

in a reactor configuration and at conditions in which neither catalyst nor NTP yields a significant product. Observed NO production is thus the result of the mutual action of NTP and catalyst. Further, we demonstrate a modeling strategy to integrate and isolate NTP and catalyst contributions to observed performance. These models recover and rationalize the observed productivity and provide a foundation for system optimization.

Results and discussion

**Plasma-catalytic N\textsubscript{2} oxidation experiments.** We measured NO production via N\textsubscript{2} oxidation in a radio frequency plasma reactor at low O\textsubscript{2}-to-N\textsubscript{2} pressure ratios, with and without downstream catalyst. The reactor consists of an inductive coil connecting to a radio frequency power supply and a matching network and a quartz tube with a heating mantle (Fig. 1a). A porous Pt film deposited on a tubular YSZ membrane is used as the catalyst. Catalyst microstructure consists of a network of percolated particles of the order of microns (Fig. 1b) with the thickness of approximately 14 micron (Fig. 1c). N\textsubscript{2}-O\textsubscript{2} mixtures are introduced to the reactor at 100 SCCM, 5 mbar, and ambient temperature.

The N\textsubscript{2}-O\textsubscript{2} plasma is generated in the area near the coil and activated species flow toward the heating mantle, which is kept at 873 K. Figure 1d reports observed NO concentrations in the absence and presence of catalyst as a function of inlet O\textsubscript{2} mole fractions from 10\textsuperscript{-4} to 10\textsuperscript{-2}. Also reported is the thermodynamic equilibrium production of NO at 873 K. NO production at zero plasma power (i.e. thermal catalysis) is zero within the detection limit of the instrument. Thus thermal catalysis is ineffective at these operating conditions. Moreover, NO production via plasma (80 W) is also ineffective. NO concentrations are less than 20 and 60 ppm without and with the YSZ tube with a standard deviation of 40–50%.

However, NO production increases significantly upon placing a Pt catalyst in the middle of the heating mantle (Fig. 1d). NO concentrations exceed thermal equilibrium across the entire gas composition range explored and vary nonlinearly with O\textsubscript{2} mole fraction, maximizing near 5 \times 10\textsuperscript{-4} and decreasing at lower or higher O\textsubscript{2} concentrations. The results provide unambiguous evidence of NO production dependent upon both plasma and Pt catalyst and sensitivity to exact plasma composition. X-ray diffraction (Supplementary Fig. 3a) and X-ray photoelectron spectroscopy (Supplementary Fig. 3b) observations confirm that...
the bulk and surface of the Pt catalyst are unmodified at all tested O₂ mole fractions in Fig. 1 by a plasma exposure of 30 min for each measurement.

Plasma-catalytic N₂ oxidation models. To rationalize plasma-catalytic NO production and its unusual dependence on O₂ mole fraction, we created microkinetic models for the thermal catalytic, non-thermal plasma, and coupled systems. Figure 2 illustrates the relevant physical processes in each case, including surface activation of thermalized gas molecules, reactions of vibrationally excited molecules and of radicals present in an NTP, and reactions at the interface between the two, respectively. Catalytic reactions occur at surfaces and thus are characterized by rates per surface site, or turnover frequency. Plasma-phase reactions occur in an (inhomogeneous) bulk phase. The relative contributions of the two to observed product concentrations are thus dependent on the relative number of active site and volume of the reactor. Here, we first consider intrinsic rates over a catalyst in the absence and presence of relevant concentrations of plasma-generated, excited species. We then couple the two through an integral reactor series parameterized to be representative of the reactor of Fig. 1a and incorporating plasma-only and plasma-catalytic steps.

Intrinsic catalytic rates. Catalytic N₂ oxidation is the reverse of the more widely studied catalytic NO decomposition reaction. The overall reaction energy and free energy are both about 1.8 eV because the reaction conserves molecules and therefore ΔS° ≈ 0.

Thermal catalytic N₂ oxidation is therefore endergonic. We adopt the thermal catalytic mechanism reactions indicated to be relevant to NO decomposition on Pt²²–²⁴. Figure 3a summarizes the potential energy surfaces for N₂ oxidation over models for a Pt terrace (Pt(111)) and a step (Pt(211)), extracted from previously reported DFT results²⁴. The initial N₂ activation step is both endothermic and has high barrier on terraces and even step sites on Pt. We supplement this reaction scheme with two additional steps to incorporate the potential adsorption of plasma-generated radicals, consistent with their observed relevance to plasma-wall chemistry¹⁵,²⁵:

\[
N(g) + * \leftrightarrow N^* \quad (2a)
\]

\[
O(g) + * \leftrightarrow O^* \quad (2b)
\]

where * represents a surface active site. Kinetic parameters for all surface reaction steps are detailed in Supplementary Table 1.

We parametrize a mean-field microkinetic model to predict the intrinsic steady-state NO turnover frequency (TOF) over Pt at conditions consistent with experiment (Fig. 1). TOFs are computed at fixed N₂, O₂, N, and O pressures and at zero conversion²⁶,²⁷. N radical densities are estimated from N₂ dissociation fractions measured at similar plasma conditions and O₂ dissociation fractions assumed to be one order of magnitude greater than N₂²⁸–³². N₂ and O₂ are assumed to have the same vibrational temperature, and the vibrational energy distributions and the consequent effects on the kinetics of N₂ and
O\textsubscript{2} dissociative adsorption are modeled following Mehta et al. (Supplementary Methods and Supplementary Fig. 4)\textsuperscript{33}.

Figure 3b compares TOFs at a Pt step as a function of conditions. Thermal TOFs (black line) over Pt(211) increases with T but are vanishingly small at even the highest temperature. Oxygen atoms are the most abundant surface intermediate across this regime (Supplementary Fig. 5a), and by degree of rate control\textsuperscript{34} analysis (Supplementary Fig. 6a), N\textsubscript{2} dissociative adsorption is rate-controlling, both consistent with the high N\textsubscript{2} dissociation barrier. The green region of Fig. 3b shows TOFs at N\textsubscript{2} and O\textsubscript{2} vibrational temperatures from 3000 to 10,000 K. TOFs are increased substantially relative to thermal-only catalysis, especially at the lowest bulk temperatures, i.e. gas and catalyst temperatures, and apparent activation energies are diminished. Predicted surface coverages are unchanged from the thermal case (Supplementary Fig. 5b) but the rate-controlling step changes to NO desorption at lower bulk and O\textsubscript{2} adsorption at higher bulk temperatures (Supplementary Fig. 6b), consistent with N\textsubscript{2} dissociation rates enhanced by vibrational excitation. The orange region of Fig. 3b shows TOFs at N radical density artificially set to 2 to 8 orders of magnitude less than the N\textsubscript{2} density and O/O\textsubscript{2} fraction to 10N/N\textsubscript{2}. N and O radicals have a similar to even greater enhancing impact on NO TOFs, most notably at the lowest bulk temperatures. NO is the most-abundant surface species at bulk temperatures below 800 K (Supplementary Fig. 5c), and NO desorption becomes rate controlling (Supplementary Fig. 6c), both reflecting the assumed barrierless accommodation of O and N by the Pt surface. At higher bulk temperatures, surface coverages tend to zero and rates become controlled by oxygen adsorption. Both vibrational excitation and radical adsorption relax the rate limitations of N\textsubscript{2} dissociation and are particularly effective at lower bulk temperatures.

Rates derived from kinetic parameters appropriate to a Pt terrace lead to similar general observations (Supplementary Fig. 7). Absolute Pt terrace TOFs, however, are significantly less than Pt steps at all but the highest vibrational temperatures or N densities, consistent with the greater reaction barriers on the terrace.

**Plasma vs plasma-catalytic NO production.** The above microkinetic models predict absolute, per active site rates at given conditions\textsuperscript{35}. Experiments most directly provide access to product concentrations rather than reaction rates. To compare plasma-only to plasma-catalytic productivity, we develop well-mixed, isothermal integral reactor models appropriate to the plasma afterglow region and the Pt catalyst bed, respectively (Fig. 4a and b and see details in Supplementary Methods)\textsuperscript{26}. Bulk temperatures of the gas and catalyst are assumed to be 873 K to correspond with experiments.

We describe noncatalytic NO oxidation in the afterglow (Fig. 4a) using the Zeldovich mechanism, consistent with previous experiments and simulations of nonthermal radio frequency, gliding arc, and microwave N\textsubscript{2}/O\textsubscript{2} plasmas\textsuperscript{10–12,15,16,28,36}:

\[
\text{N}_2(g) + O(g) \leftrightarrow \text{NO(g)} + N(g) \quad (3a)
\]

\[
\text{O}_2(g) + N(g) \leftrightarrow \text{NO(g)} + O(g) \quad (3b)
\]

Rate constants are from experimental measurements (Supplementary Table 3)\textsuperscript{15,37,38}. To capture the influence of vibrational excitations on the rate of Reaction (3a), we reduce the reaction barrier by an amount commensurate with the degree of plasma-induced vibrational excitation (Fig. 2, middle)\textsuperscript{16}. We take the reactor length to be consistent with the length of the heating mantle and flow rates consistent with experiment.

To describe NO concentrations generated by the plasma and porous Pt catalyst together (Fig. 4b), we treat this region as a sum of coupled contributions of a noncatalytic bulk-phase, described using the same Zeldovich parameters, and a surface-catalytic phase, described using the Pt step parameters. The relative contributions of these two phases is a function of the reactor volume and number of active sites (Supplementary equation (11)). The total volume is taken to be that of the porous Pt catalyst bed, and flow rate and free volume-to-active site ratios are taken to be consistent with the experimental setup.

Figure 4c reports the plasma-only, noncatalytic NO concentrations, plotted as NO concentration for ready comparison to experiment, as a function of assumed vibrational temperature and inlet atomic N density as descriptors because of their relevance in plasma N\textsubscript{2} oxidation\textsuperscript{10–12,15,16,28,36,39}. Wide ranges of T\textsubscript{vib} and P\textsubscript{N} are included to represent different plasma characteristics. The partial pressures of other species are reported in Supplementary Table 3. NO concentrations increase monotonically with T\textsubscript{vib} and...
and N radical partial pressures. Pressures of N\textsubscript{2} and O\textsubscript{2} are 4.995 and 0.005 mbar, respectively.

Because the rate of the second reaction is more sensitive to vibrational temperature and N radical density, increasing N radical densities and vibrational temperatures. In contrast, NO concentrations are of similar orders of magnitude overall but less sensitive to vibrational temperatures, conditions typical of low-P radio frequency and microwave plasmas\textsuperscript{11,29,30}.

The origins of this catalytic influence are revealed by an analysis of relative steady-state reaction fluxes normalized to the overall NO production rate\textsuperscript{26,40}. Figure 5 reports these fluxes at four representative conditions corresponding to the four corners of Fig. 4d, focusing on pathways involving nitrogen. At a relatively low vibrational temperature and N radical density (Fig. 5c and lower left of Fig. 4d), the absolute TOF is only 5.3 \times 10^{-9} \text{ s}\textsuperscript{-1} and is primarily limited by the rate of generation and adsorption of N radicals. At a much greater vibrational temperature and low N radical density (Fig. 5d and lower right of Fig. 4d), N\textsubscript{2} dissociative adsorption dominates surface accommodation of nitrogen and the absolute TOF increases to 4.5 \times 10^{-7} \text{ s}\textsuperscript{-1}. Both of these regimes are blue in Fig. 4e because the Zeldovich reaction in the larger homogeneous volume is more effective at producing NO than in the smaller catalyzed volume. At high vibrational temperature and N radical density (Fig. 5b and upper right corner of Fig. 4d), the absolute catalyzed TOF reaches its maximum of 0.22 s\textsuperscript{-1}. Catalyzed rates are dominated by the large fluxes of N radicals to the catalyst and their subsequent reactions to NO or recombination to N\textsubscript{2}. These surface reactions become more effective at directing N into channels that produce NO than is the homogeneous phase, where the reverse Zeldovich reaction depletes NO. As a result, this regime is yellow in Fig. 4e. At high N radical density but lower vibrational temperature (Fig. 5a and upper left corner of Fig. 4d), surface reactions remain dominated by N adsorption and reaction to NO or N\textsubscript{2}. Despite the fact that the TOF in this quadrant (0.13 s\textsuperscript{-1}) is less than in the upper right, the plasma-catalyst combination is most effective in yielding NO, because the catalyst is most effective here in shunting N radicals away from the unproductive reverse Zeldovich reaction.

NO concentrations are maximized at high T\textsubscript{vib} and high N radical densities in the plasma-only and plasma-catalytic reactors, respectively (Fig. 4). In both of these regimes, a large fraction of plasma-generated N radicals ultimately return to N\textsubscript{2} either homogeneously or at the catalyst surface, diminishing the energy efficiency of NO production. To compare the theoretical energy consumption of the two reactors as a function of reaction species, we calculate the enthalpy required to reach T\textsubscript{vib} and P\textsubscript{N} from reactants at the bulk gas temperature, and normalize the energy to the NO production (details in Supplementary Methods). Supplementary Fig. 11 shows the plasma-only reactor is the most energy-efficient at higher T\textsubscript{vib}, consistent with previous reports\textsuperscript{16}. The catalyzed plasma reactor is more energy-efficient overall and is particularly efficient at low T\textsubscript{vib} and intermediate P\textsubscript{N}, where the energy deposited into dissociated N\textsubscript{2} is most effectively directed into NO. The predicted energy consumption is two orders of magnitude lower than plasma only in this regime. The minimum predicted energy consumption is 2.9MJ/mol\textsubscript{NO} at T\textsubscript{vib} = 1000 K and P\textsubscript{N} = 10\textsuperscript{4}, which exceeds the minimum energy (about 0.3MJ/mol\textsubscript{NO}) using established estimates of the efficiencies of known processes in a N\textsubscript{2}-O\textsubscript{2} NTP\textsuperscript{16,41,42}. These results illustrate that the quest for optimal NO productivity and optimal energy efficiency may lead to different target plasma regimes.

**Optimal plasma-catalytic N\textsubscript{2} oxidation regimes.** Thermal N\textsubscript{2} oxidation rates and thus NO production are negligibly small at the conditions of Fig. 4. The results of Fig. 4e, then, highlight the existence of regimes in which plasma-catalytic N\textsubscript{2} oxidation is expected to be much more effective than plasma-only or thermal catalytic N\textsubscript{2} oxidation, qualitatively consistent with the results of

![Figure 3 Microkinetic N\textsubscript{2} oxidation rates. a DFT-reported potential energy surfaces for thermal N\textsubscript{2} oxidation on Pt(211) and Pt(111). b Reaction rates vs. reciprocal temperature on Pt(211) at various vibrational temperatures and N radical partial pressures. Pressures of N\textsubscript{2} and O\textsubscript{2} are 4.995 and 0.005 mbar, respectively.](image-url)
Fig. 4 Plasma vs plasma-catalytic NO production. Schematic representations of integral reactor models for (a) plasma reactions and (b) plasma catalytic reactions, respectively. Outlet NO concentrations (ppm) of (c) plasma reactions and (d) plasma catalytic reactions against $T_{ve}$ and $P_n$ at 873 K, where the inlet pressures of N$_2$ and O$_2$ are 4.995 and 0.005 mbar, respectively. The residence times are 0.28 s and 6.4 $\mu$s in (a) and (b), respectively. The number of active Pt sites is 230 nmol.

The relationship between NO productivity and gas composition is weakly sensitive to these variations and tracks the impact on the plasma-only NO productivity; the largest impacts are on the composition at maximum NO production, which varies from $P_{O_2}/(P_{O_2} + P_{N_2}) = 10^{-3.3}$ to $10^{-2.9}$, and total NO production at the maximum, which varies from $10^{2.3}$ to $10^3$ ppm. Given this weak dependence, we focus the narrative on the simplest model, shown in Fig. 6; conclusions are insensitive to this choice.

Figure 6b compares the NO concentration vs O$_2$ fraction between the reactor series of Fig. 6a (red line) and the plasma-only model of Fig. 4a (blue line), plotted on a log scale. NO concentrations from both reactors exceed thermal N$_2$-O$_2$ equilibrium and generally increase with O$_2$ content. The reactor series captures the non-monotonic increase in NO concentration and better predicts the peak in concentration than does the single reactor model of Fig. 4b. The Pt catalyst enhances NO production substantially at O$_2$ fractions less than $3 \times 10^{-3}$; NO concentrations are sensitive to catalyst site number, but this effect saturates at about 10 nmol, above which NO production varies minimally. At greater O$_2$ mole fractions, however, NO concentrations converge to those of the uncatalyzed reactor. To validate this prediction, we performed experiments at high O$_2$ pressures, combined with those of Fig. 1, and plotted on a logarithmic scale in Fig. 6c. The experimental observations are consistent with the series reactor predictions across a wide range of N$_2$-O$_2$ compositions, including the evident advantages of the catalyzed reactor, sensitivity to composition, and convergence to the plasma-only productivity at highest O$_2$ mole fractions. The series reactor model successfully captures the obvious drop of NO concentration after reaching the maximum at intermediate O$_2$ mole fractions and the increasing NO concentration at high O$_2$ mole fractions, which are not observed in the plasma catalytic model alone (Supplementary Fig. 12a). Models and experiments appear to differ in predicted plasma-only NO concentration sensitivity to O$_2$ mole fraction in...
the dilute limit, likely the result of some combination of experimental uncertainty in NO concentration at these very low levels and uncertainties in the reactor model details. The prominent role of catalyst in promoting NO production is robust to these details.

This loss in catalyst effectiveness can be understood from Supplementary Fig. 12b and d. Catalyzed NO production is maximized at conditions that balance the coverage of adsorbed N and O. At sufficiently high O₂ concentrations, the catalyst surface becomes O-covered and NO productivity decreases. That the same phenomenon is at play in the series reactor model is shown in Supplementary Fig. 13. As a result, the catalyst is less effective in promoting (or inhibiting) NO production, as observed in the experiments. X-ray photoelectron spectra of the Pt catalyst following exposure to plasmas from 1 to 15% O₂ overlap with fresh metallic Pt (Supplementary Fig. 3b), suggesting Pt remains metallic in a wide range of O₂ mole fractions. Deconvolution of the X-ray photoelectron spectrum of the Pt catalyst following exposure to the 20% O₂ plasma (Supplementary Fig. 3c) reveals features attributable to metallic Pt (13%) and oxidized Pt (1%).

**Fig. 5 Reaction fluxes vs plasma conditions.** Steady-state reaction flux of N₂ oxidation on Pt (211) in a integral reactor at 873 K with (a) P₀ = 2 × 10⁻²P_N₂ and T_vib = 1000 K, (b) P₀ = 2 × 10⁻²P_N₂ and T_vib = 10000 K, (c) P₀ = 2 × 10⁻¹P_N₂ and T_vib = 1000 K, and (d) P₀ = 2 × 10⁻¹P_N₂ and T_vib = 10000 K, presented as Sankey diagrams, in which each segment indicates a reaction and the corresponding segment width qualitatively indicates the value of the rate normalized to the NO production rate. Solid lines represent reactions involving catalytic sites and dotted lines represent plasma processes. Blue, gold and red mean intermediate, productive and unproductive routes, respectively. The reaction conditions are consistent with the four corners of Fig. 4d.

Fig. 6 Composition sensitivity. a Series of three integral reactors to describe the reactor of Fig. 1. b NO production as a function of O₂ pressure in plasma-only and plasma-catalytic reactor series at P₀ = 2 × 10⁻³P_N₂, T_vib = 6000 K, and bulk temperature 873 K. Red solid line represents a Pt active site number of 230 nmol and dashed and dotted line represent order-of-magnitude variations in that number. c Observed NO production vs O₂ pressure ratio. Maximum represents all O₂ coverts to NO. Total reactor pressure is 5 mbar. The error bars represent the standard deviation of at least three measurements.
The catalyst (porous Pt film) is prepared on yttria-stabilized zirconia (YSZ) tube (Ortech, 2 mm thickness, 25 mm diameter, and 245 mm length) by brush painting the Pt precursor (25 wt% Pt/C) followed by a heat treatment at 900 °C for 2 h in air. The crystal structure and purity of the catalyst were determined by X-ray diffraction (XRD, Bruker, Cu Kα radiation, λ = 1.54056 Å) in the Bragg-Brentano configuration. Diffractograms were collected at a scan rate of 0.02° in the 20 range of 20–90°. The surface composition of the Pt film was investigated by X-ray photoelectron spectroscopy (XPS, Thermo Scientific). The surface morphology of the as prepared catalyst (Pt/YSZ) was characterized using a scanning electron microscope (FEI Quantax 3D FEG instrument) at an acceleration voltage of 3–5 keV (Fig. 1b and c). The Pt film has a porous structure and consists of a network of percolated particles. The thickness of the microfilm is around 14 μm. SEM micrographs before and after plasma experiments show no difference since the Pt catalyst is 15 cm far from the tail of the active plasma area. This is in good agreement with the minimal temperature increase on the catalyst (i.e. 1–2 °C) upon plasma ignition. The visible tail of the active plasma area decreased with O2 mole fractions and remained away from the substrate (Supplementary Fig. 2). We estimated the time for gas-phase species to travel from the tail of the coil to the heating mantle to be 0.2 s. N and O densities in similar low-pressure N2-O2 discharge afterglows have previously been found to persist at least 1 s. Vibrational temperatures, in contrast, are observed to decrease over this timescale in a low-pressure N2 afterglow48. We estimated vibrational temperatures to be 10000 K in the radio frequency plasma29 and select Tvib = 6000 K as representative of the temperature drop expected during flow to the catalyst. The catalyst geometrical area is 20 cm², while the loading is 5 mg of Pt per cm². The surface area of the catalyst was determined by hydrogen adsorption with potential deposition method50 and it was found to be 230 nmol of Pt adsorption sites.

The experiments were performed by co-injecting and co-activating 5 mbar N2 and O2 (100 standard cubic centimeters per minute) by RF plasma source with plasma power as 80 W while maintaining 0 W reflected power through a tunable matching network. The calibrations to quantify the NO production and O2 consumption were carried out by N2 (99.99% purity) and 1000 ppm in He and 100 ppm in O2 in He and O2 cylinders, respectively. In each case, the standard gas mixture was used without dilution and with He dilution in the levels of 25% and 50% keeping the flow rate constant. In all the cases, a linear relation between the signal level and amount of the gas in study, has been observed. The concentration of NO produced during plasma experiments is in good agreement (5%) with the oxygen level decrease. Experiments were repeated three times. N2O and NOC concentrations are negligibly small in both plasma-only and plasma-catalytic experiments across O2 fraction from 10⁻⁴ to 0.2 (Supplementary Fig. 1b).

The reaction and activation energies of nitrogen oxidation were collected from literature, where the calculations were performed using DACAPW with core electrons described by Vanderbilt ultrasoft pseudopotentials and exchange and correlation effects described by the RPBE functional24. The standard entropies of gas molecules are from NIST-JANAF thermochemical tables35 and entropies of adsorbrates on Pt were estimated with harmonic oscillator model52. The rate constants of adsorption, surface and desorption reactions were estimated with transition state theory33. The steady-state surface coverages and rates were solved with a mean-field microkinetic model, as detailed in Supplementary Methods53. The steady-state surface coverages and rates were solved with a mean-field microkinetic model, as detailed in Supplementary Methods53. The steady-state surface coverages and rates were solved with a mean-field microkinetic model, as detailed in Supplementary Methods53. The steady-state coverage of the nitrous oxide was included because of the depopulation of highly excited levels. See details in Supplementary Methods. The adsorption of N2 and O (Reaction (2a) and (2b)) were included in the plasma catalysis model. The dissociation of NO oxidation is observed to be about one order of magnitude higher than the N2-O2 plasma oxidation.31,32,34,35 Experimentally measured forward rate constants for reactions in the Zeldovich mechanism were used (Supplementary Table 3). The backward rate constants were calculated with standard free energy to enforce thermal consistency51. The calculated backward rate constants in agreement with experimental measurements37,38. Vibrational excitation of N2 and O2 are included using the same methods in the plasma catalytic model. Integral reactor models to predict the NO concentrations of plasma reactions and coupled plasma and catalysts are detailed in Supplementary Methods. The modeling approach is validated by experiments in which the flow is well mixed. The ordinary equation of gas compositions and surface coverages were solved simultaneously. We also elaborate this modeling approach for materials selection in nitrogen oxidation36.
Data availability
The experimental and simulation data in this study have been deposited in the Zenodo database [https://doi.org/10.5281/zenodo.4624272]19. The experimental data is also included in both the Excel file and the Python scripts for figure creation.

Code availability
The code in this study have been deposited in the Zenodo database [https://doi.org/10.5281/zenodo.5571134 (2021)].55 The repository includes Python scripts to generate the simulation data and the figures. Other utility functions to generate potential energy surfaces, catalytic turnover frequencies and product concentrations are also included.

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Author contributions
All authors contributed to the conception of the research problem and approach. H.M. developed the microkinetic models. R.K.S. performed the experiments. H.M., R.K.S., S.W., M.C.M.v.d.S., M.N.T. and W.F.S. co-wrote the manuscript.

Competing interests
The authors declare no competing interests.

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Correspondence and requests for materials should be addressed to Mihalis N. Tsampas or William F. Schneider.

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