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COMMUNICATION

Surface-like NO_x Reduction at an Atomically-Precise Tricopper Cluster

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Abstract: The combustion of nitrogen-containing fuels and increasing use of nitrogen-rich fertilizers is accumulating NO_x pollutants in the environment. Copper is an attractive catalyst material for reductive NO_x remediation, yet ambiguity persists regarding the elementary bond-making and bond-breaking steps occurring at the catalyst interface. Starting from a molecular tricuprous μ_3-oxo complex (**1**), an unusually reduced and highly reactive surface-like cluster (**2**) has been prepared. Characterization data and electronic structure calculations are consistent with **2** featuring σ-aromaticity that primes the tricopper core for two-electron chemistry. Cluster **2** mediates catalytic reductive coupling of NO to N_2, proceeding through N_2O, *via* sequential oxygen atom transfer steps. Stoichiometric reduction of NO_3^- and NO_2^- is also disclosed, mapping the complete denitrification cycle at an atomically-precise molecular cluster.

Toxic nitrogen oxide (NO_x) pollutants are amassing in aquatic and atmospheric ecosystems as a result of the combustion of nitrogen-containing fuels and the widespread application of nitrate (NO_3^-) fertilizers.[1] These highly bioavailable contaminants have detrimental effects on human health and lead to harmful eutrophication in rivers and lakes.[2] In nature, the geochemical denitrification cycle employs a series of metalloenzymes to reduce NO_3^- to benign dinitrogen (N_2).[2b,3] Anthropogenically, copper has emerged as a promising material to catalyse the electrochemical reduction of NO_x reagents both to N_2 and, under acidic conditions, ammonia (NH_3).[4] Notwithstanding, challenges remain in elucidating reaction mechanism(s) and controlling the elementary steps requisite for these complex multi-proton, multi-electron reductions.[3]

Prevailing NO_x reduction mechanisms involve nitrate binding, followed by sequential deoxygenation events (either oxygen atom transfer or proton-coupled electron transfer), generating adsorbed nitric oxide (NO) species (**Figure 1**, top).[4e,5] Notably, NO is a conserved intermediate in both biological[6] and synthetic NO_x reduction schemes.[7] In heterogeneous systems, NO demonstrates remarkably diverse surface reactivity,[5c,7b,8] and precedes the key N–N coupling step controlling product selectivity.[9] At low surface concentrations, NO adsorbs molecularly at hollow sites, but as monolayers begin to form, NO oligomerization is observed *en route* to nitrous oxide (N_2O), N_2, and the formation of copper oxides.[10] Surface-bound NO is postulated to maintain radical character, and Eley-Rideal-type mechanisms for hyponitrite generation have likewise been

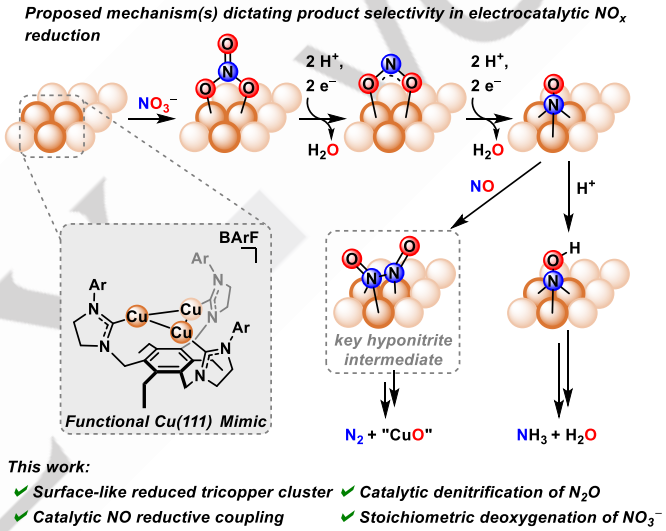


Figure 1. Surface NO coverage, and the subsequent proclivity to form NO dimers via N–N coupling, dictates selectivity in copper-catalysed NO_x reduction; catalytic surface-like NO denitrification is achieved from a highly reduced molecular tricopper platform.

proposed.[11] The structure of this key hyponitrite intermediate is not well established, yet bridging binding modes across multiple metal centres are commonly invoked.[7b,12] Whereas numerous studies have explored bioinorganic mechanism(s) for NO reduction and coupling via molecular mimicry,[7c,13] there is a dearth of surface-relevant model chemistry.[7b] To this end, developing functional structural models of surface active sites remains a key challenge in catalysis science.

Discrete copper clusters featuring metallic copper character and unsupported Cu–Cu bonding interactions remain rare,[14] due to the high d-electron count and weak cohesive energy of copper.[15] Polycopper systems that either leverage multiple monometallic units or pre-template copper centres in proximity are known to form hyponitrite ($[N_2O_2]^{2-}$) ligands via the reductive coupling of NO, recapitulating the key elementary N–N bond-forming step.[7a,7b,7e,16] Once the N–N bond is forged, however, an exogenous chemical stimulus (*eg.* acid or reductant) is generally required to release nitrous oxide (N_2O).[7a,7c,13b,13c,17] To our knowledge, discrete molecular copper catalysts for NO reduction are not known.[18] Despite its strong oxidizing potential, the

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relative kinetic inertness of N_2O leaves it recalcitrant to further reduction chemistry.[19] Few homogeneous copper complexes are competent for N_2O reduction[13b,20] and only recently have molecular copper catalysts capable of even this final denitrification step been disclosed.[19b,21]

We report here the synthesis and characterization of a highly reduced tricopper complex supported by a chelating tris(carbene) ancillary ligand. The electrons stored in the core of this cluster predispose it to readily accept an oxygen atom equivalent, reactivity that can be utilized for the catalytic reduction of NO and N_2O. The N–N bond forming step in NO reduction is hypothesized to be facilitated by the multinuclear nature of the cluster, as is the oxygen atom transfer (OAT) chemistry, which affords a functional model system for catalytic NO reduction at copper electrode surfaces (**Figure 1**). Cluster **2** is capable of stoichiometric deoxygenation of NO_3^- and NO_2^-, demonstrating a well-defined molecular platform competent for each step in the global denitrification pathway.

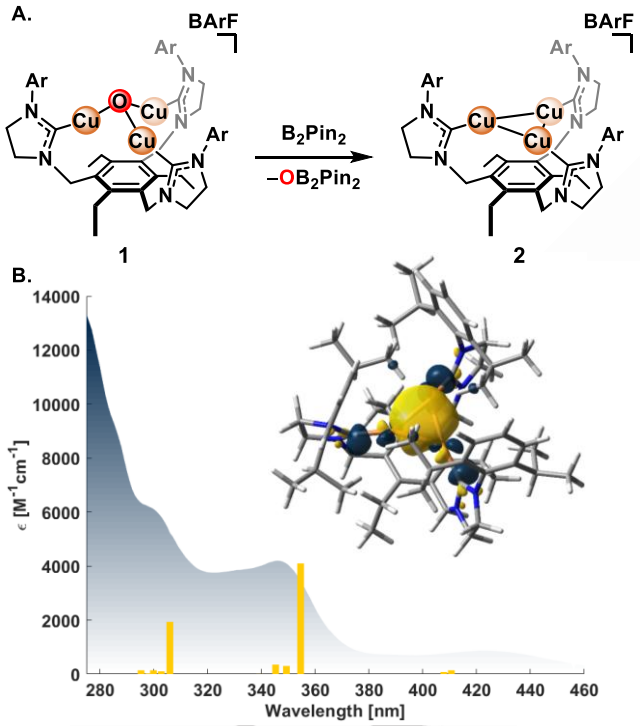


Figure 2. Synthesis of surface-like tricopper cluster **2** (A). Experimental (blue) and calculated (yellow) UV-Visible spectra and computed HOMO (0.04 eÅ^{-3} isosurface) for **2** (B); optimization and TD-DFT were conducted at the uM06L-D3(0)/def2-SVPD(Cu,N)│def2-SVP(C,H) level of theory in the gas phase. Ar = 2,6-diisopropylphenyl; BArF = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate.

Targeting a low-valent tricopper cluster, we adapted the deoxygenative reduction protocol reported by Bertrand and coworkers for closely related untethered cyclic(alkyl)(amino) carbene (CAAC) complexes.[22] Addition of bis(pinacol) diboron (B_2Pin_2) to a solution of μ_3-oxo cation **1**[23] results in formation of a bright yellow diamagnetic product (**Figure 2A**). Multinuclear NMR spectroscopy supports both a C_{3v} symmetric solution structure, suggesting an intact cluster compound, and stoichiometric generation of diboroxane ($O(BPin)_2$), consistent

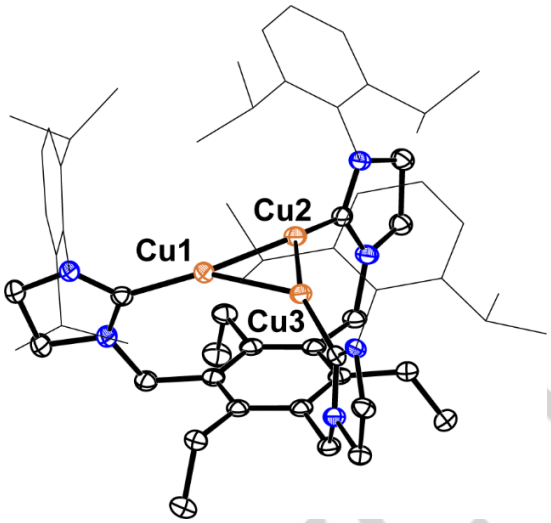


Figure 3. Solid-state structure of **2** shown with thermal anisotropic displacement ellipsoids displayed at a 50% probability level. Hydrogen atoms and the BArF counterion are omitted for clarity.

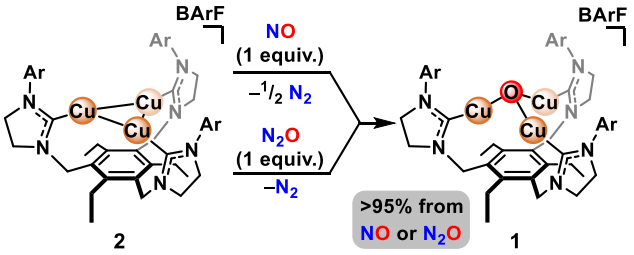
with deoxygenation of the tricopper core. The constitution of this species was corroborated by single crystal X-ray diffraction (SCXRD), evidencing generation of cluster **2** (**Figure 3**).[24] The Cu–Cu distances are roughly symmetric, averaging to 2.3688(4) Å. These are slightly contracted relative to both the computed equilibrium distances of a Cu(111) surface (*ca.* 2.41 Å) and the CAAC-supported analogue (*cf.* 2.373 Å).[22] The centroid of the tricopper plane resides 2.89 Å above that of the central arene linker, precluding the involvement of a copper-arene interaction in stabilizing this unusually reduced species.

These structural parameters were reproduced with high fidelity in a computational model of **2**, which supports σ-aromaticity in a mixed-valent $Cu^0_2Cu^I$ core (**Figure 2B**). The computed HOMO of **2** is consistent with charge delocalization across all three copper centers, corroborated by the symmetry observed experimentally in the solid-state.[25] This three-center, two-electron (3c2e) bonding situation is conserved across known examples of coinage metal $[M_3]^+$ clusters.[22,26] The TD-DFT simulated electronic absorption spectrum shows close agreement to the experimental UV-visible spectrum of **2**. The three primary absorption features are attributable to $Cu_3(\sigma) – L(\pi^*)$ MLCTs (301, 348, and 425 nm), underscoring the highly Lewis-basic nature of the complex. We envisioned leveraging these reducing 3c2e Cu–Cu bonding electrons for the reductive catenation of NO.

Treating a degassed d_8-THF solution of **2** with gaseous NO (2.2 equiv.) results in immediate bleaching and complete conversion to the oxo cluster **1**, as evidenced by ^{1}H NMR spectroscopy. Repeating this reaction with a single equiv. of NO gas likewise afforded quantitative formation of **1**, a result that suggests **2** is competent for both reduction of NO to N_2O and further deoxygenation *en route* to N_2. Independent addition of N_2O gas to **2** confirmed this inferred reactivity (**Scheme 1**). Despite longstanding interest in N_2O reduction chemistry at multicopper clusters, motivated by the Cu_Z site of N_2O reductase,[20,27] well-defined multicopper compounds competent for N_2O reduction are rare.[20a,27a,27c,27d,28] Complex **2** is unique in its O-atom acceptor ability. The electrons stored in the trimetallic

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Scheme 1. N_xO OAT Reactivity of **2**.

core obviate the need for sacrificial reductants to complete the deoxygenation. Experimentally, no intermediates are observed, and the formation of **1** is rapid, even at cryogenic temperatures (Figure S8), irrespective of the amount of NO added to reduced cluster, **2**. This chemistry mirrors NO reductive coupling at copper surfaces in which N_2O and N_2 are generated together with copper oxide at temperatures as low as 85 K.[29]

Recognizing that the reactivity outlined above (*c.f.* **Figure 2A** and **Scheme 1**) constitutes a catalytic cycle for the reduction of NO to N_2 *via* N_2O, we pursued optimizing this process. Initial efforts focused on N_2O reduction. Paralleling stoichiometric N_2O deoxygenation chemistry, low catalyst loadings (1 mol%) of **2** were found to be competent for catalysis under remarkably mild conditions (room temperature, 1 atm N_2O; **Table 1**, Entry 1). A significant solvent dependence was observed for both the rate of the reaction and the longevity of the catalyst (Entries 1-5). Ethereal solvents showed top performance, with diethyl ether proving optimal in terms of solubilizing reaction components, expeditious initial TOF, and overall TON (Entry 5). Control experiments corroborate that N_2O reduction does not proceed in the absence of the copper catalyst, and high TON can be achieved with low catalyst loadings and extended reaction times (Entries 6 and 8, respectively).

Table 1. Denitrification of N_2O catalysed by **2**.

N_2O (1 atm) + B_2Pin_2 —(cat. [2], Solvent, Time, 25 °C)→ N_2 + $O(Bpin)_2$

Entry	Solvent	Catalyst Loading (mol %)	Time (h)	TON[a]	Initial TOF[a] (h^{-1})
1	THF	1	1	77.4	100
2	MTBE	1	1	17.8	71
3	PhF	1	1	58.5	89
4	2-MeTHF	1	1	105.0	178
5	Et_2O	1	1	98.4	244
6	Et_2O	0	24	0	0
7	Et_2O	0.4	24	235.6	226
8	Et_2O	0.2	24	383.0	231

[a]Turn over number and frequency was calculated using quantitative ^{11}B NMR spectroscopy[21] integrated against a PNPBArF (PNP = bis(triphenylphosphine)iminium) internal standard.

There are only two prior examples of molecular copper catalysts capable of this transformation. The first leverages ligand redox non-innocence to facilitate N_2O reduction via a proton-coupled electron transfer (PCET) mechanism.[19b] Quite recently, Chaplin and coworkers disclosed the efficacy of NHC-supported monocopper boryl complexes that take advantage of boron's oxophilicity to drive this reduction.[21] In the present system, deoxygenation is accomplished via OAT to the reduced Cu_3 core—chemistry that proceeds in the absence of exogenous borane reductants—and diborane serves as a terminal O-atom acceptor. This differentiates the operative mechanism from previously reported systems. Notably, **2** is a significantly more efficient catalyst at room temperature than its monocopper analogue (*cf.* TOF 244 h^{-1} vs. 4 h^{-1}, respectively)[21] under comparable reaction conditions. *In situ* spectroscopy points to the μ_3-oxo complex **1** as the resting state, consistent with rate limiting reduction by B_2Pin_2. Similar rate-determining reduction was established for the monocopper chemistry (with a cuprous boroxide resting state),[21] demonstrating that the multimetallic platform more readily undergoes chemical reduction.

Table 2. Denitrification of NO catalysed by **2**.

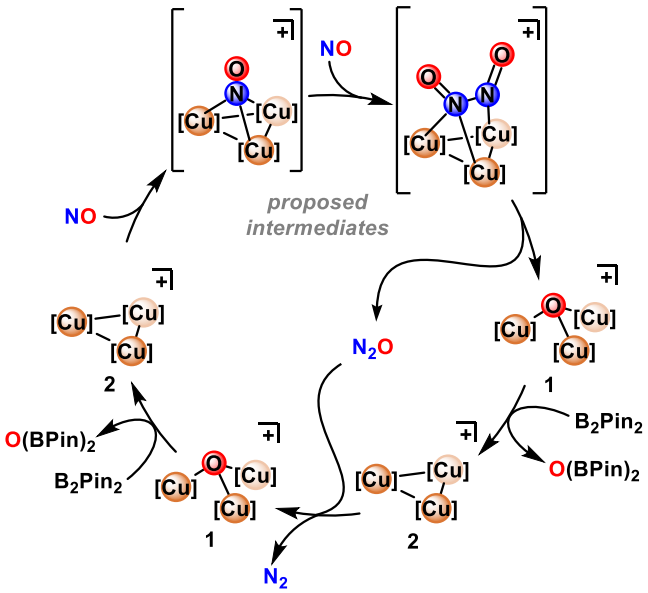
NO (1 atm) + B_2Pin_2 —(cat. [2], THF, Time, 25 °C)→ N_2 (and/or N_2O) + $O(Bpin)_2$

Entry	Catalyst Loading (mol %)	Time (h)	TON[a]	Initial TOF[a] (h^{-1})
1	1	1	37.1	60
2	1	24	84.6	60
3[b]	0.2	24	50.1	--
4	0	24	0	0

[a]Turn over number and frequency was calculated using quantitative ^{11}B NMR spectroscopy[21] integrated against a PNPBArF internal standard. For NO reactions, one turn over corresponds to one deoxygenation event—the resultant gas is a mixture of N_2O and N_2. [b]^{15}NO was used in lieu of NO.

Similar to the N_2O deoxygenation chemistry, the stoichiometric reactivity outlined above was readily extended to catalytic NO reductive coupling (**Table 2**). With a 1 mol% catalyst loading of **2**, >80 turnovers for NO reduction were achieved (Entry 2). Repeating these conditions with isotopically enriched ^{15}NO confirmed formation of both $^{15}N_2O$ (^{15}N δ_{MeNO2} = –146.8 (d) and –231.2 (d) ppm; J = 8.3 Hz)[17] and $^{15}N_2$ (^{15}N δ_{MeNO2} = –71.0 (s) ppm)[7c, 30] as the reaction products, consistent with the inferred sequential OAT mechanism (**Scheme 2**). The overall catalytic cycle involves two molecules of NO undergoing a two-electron reductive coupling/deoxygenation sequence atop the reduced

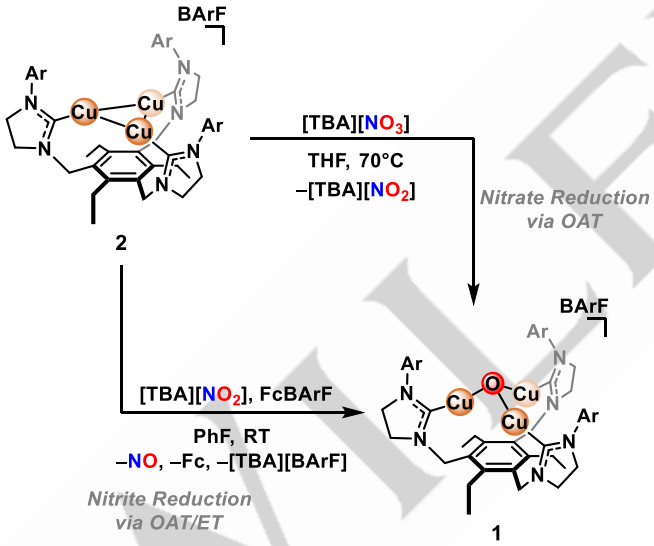
Scheme 2. Proposed Cycle for Cu-Catalysed Complete Denitrification of NO.



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tricopper core, liberating N_2O and generating the oxidized cluster **1**. We postulate that NO binding is the initial step—the lowest energy NO binding site for surfaces is the three-fold hollow site mimicked by **2**.[29b,31] Subsequent binding of a second NO unit and direct reductively coupling or N–N coupling with an outter sphere NO equivalent both have precedent in copper surface science and we are currently agnostic with regard to this elementary step.[11c, 29b] Subsequent deoxygenation of a putative hyponitrite would liberate N_2O, generating **1**. NO reduction catalysis is sluggish in comparison to the N_2O chemistry (*cf.* TOF for Table 1, Entry 1 vs. Table 2, Entry 1), despite the facility of stoichiometric NO deoxygenation (*viz.* **Scheme 1**). Spectroscopic interrogation of catalytic mixtures shows trace amounts of **1** as the only detectable diamagnet; we hypothesize that NO binding may generate open-shell off-cycle species. Preliminary IR spectroscopic probes support reversible NO binding to oxo complex **1** (ν_{NO} = 1610 cm^{-1}). Binding a strongly π-acidic NO ligand likely inhibits subsequent reduction of **1** by B_2Pin_2, resulting in the disparate rates observed for catalysis under NO and N_2O. Further, the optimal solvent conditions established for the N_2O chemistry did not translate to the NO reduction catalysis due to the insolubility of the copper clusters in Et_2O following NO addition.[32] Diborane reduction of **1** regenerates the reactive cluster **2**, which can then deoxygenate N_2O to return **1** and release benign N_2. To our knowledge, this is the first example of a base-metal molecular catalyst competent for the complete reductive denitrification of NO.



Scheme 3. OAT chemistry from NO_3^- and NO_2^-. FcBArF = ferrocenium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate; PhF = fluorobenzene; Fc = ferrocene.

Molecular copper complexes are well-known to reduce nitrite (NO_2^-) to NO.[3,13d,33] This, however, is a single electron process and is incongruent with the OAT chemistry observed for **2**.[3] We leveraged an *in-situ* oxidant to achieve net OAT reduction of NO_2^- to NO. Subjecting a fluorobenzene (PhF) solution of **2** to either a mixture of [TBA][NO_2] and ferrocenium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (FcBArF) resulted in formation of **1** after 8 hours (**Scheme 3**).[34] NO release was corroborated by irreversible chemical trapping with tetraphenylporphyrin cobalt(II).

The most recalcitrant bond activation in NO_x reduction chemistry is the scission of the first N–O bond of NO_3^-.[35] Emboldened by the successful reduction catalysis observed for both NO and N_2O, we targeted emulating the full denitrification pathway via OAT from NO_3^- and NO_2^-.[36] Treating **2** with [TBA][NO_3] in THF solution at 70 °C for 24 hours demonstrated generation of the oxidized cluster, **1**, in 90% yield (**Scheme 3**). An analogous reaction with $Na^{15}NO_3$ confirmed the NO_x byproduct as $^{15}NO_2^-$ (via colorimetric detection with Griess' reagent), mirroring the chemistry of nitrate reductase in the first step of biological denitrification.[6c] Contrasting molecular systems that leverage H-bonding to promote OAT,[33a,35,37] the multinuclear nature of **2** both delivers the requisite electrons and stabilizes the resultant oxo through metal-metal cooperativity, recapitulating essential design features of surface-mediated NO_x reduction. The tricopper core of **2** is therefore competent for each step of the denitrification pathway, completing the individual reactions required for the ten-electron reduction of two equivalents of NO_3^- to N_2.

In this report, we present the synthesis of an unusually reduced tricopper cluster, **2**. With reactive electrons in the 3c2e copper-copper bonded core, **2** is a potent oxygen atom acceptor. Cluster **2** can efficiently deoxygenate and couple NO, affording N_2O and the oxygenated cluster **1**, emulating proposed mechanistic steps for heterogeneous copper surfaces. Re-reduction with diborane reagents renders this process catalytic. Moreover, **2** is capable of reducing N_2O, demonstrating the catalytic total denitrification of NO at a surface emulating molecular cluster. Finally, **2** was shown to directly reduce NO_3^- to NO_2^- and, in the presence of an oxidant, can convert NO_2^- to NO, mapping out each step of the global denitrification pathway. Mechanistic investigations of the catalytic NO reduction chemistry and efforts to render the nitrogen oxyanion reduction catalytic are currently underway.

Acknowledgements

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Keywords: catalysis • copper • NO_xRR • nitrate reduction • oxygen atom transfer (OAT)

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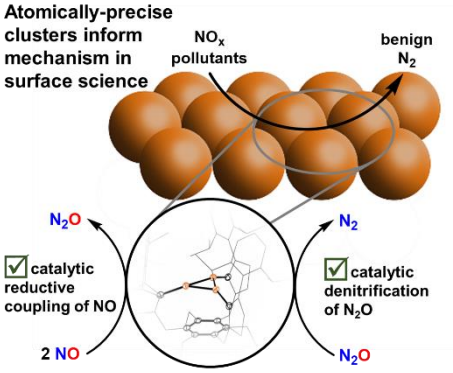
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