Supporting Information

A Bioinspired Molybdenum Catalyst for Aqueous Perchlorate Reduction

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Materials and Methods

Reagents and materials

Sodium molybdate dihydrate (Na₂MoO₄•2H₂O), ammonium molybdate tetrahydrate [(NH₄)₆Mo₇O₂₄•4H₂O], molybdenum(IV) oxide (MoO₂), and molybdenum(II) acetate dimer [Mo₂(OCOCH₃)₄] were purchased from Sigma–Aldrich. The nitrogen ligands were purchased from Alfa Aesar, Ark Pharm, Combi-Blocks, Oakwood Chemical, Sigma-Aldrich, and TCI. Inorganic salts (e.g., NaClO₄, NaCl, and Na₂SO₄) in ≥99% purities were purchased from Fisher Chemical. Sulfuric acid solution (2 N standard) was purchased from Alfa Aesar. Triphenylphosphine (PPh₃, 99%) and trisodium triphenylphosphine-3,3',3"-trisulfonate (TPPTS, \geq 95%) were purchased from Sigma-Aldrich. All chemicals were used as received. Aqueous solutions were prepared with deionized (DI) water (resistivity >18.2 M Ω cm). The 5 wt% Pd/C (Sigma–Aldrich, catalog #330116) was wet sieved to obtain the <37 µm fraction, dried under air at 110°C for 2 h and heated under H₂ flow at 250°C for 1 h.¹ The treated Pd/C had the surface area of 860 m² g_{cat}^{-1} , the pore volume of 0.67 cm³ g^{-1} , the average pore size of 3.1 nm, and the Pd surface area of 6.9 m² g_{cat}^{-1} (Pd dispersion of 31% and average Pd particle size of 3.7 nm).² Control experiments suggest that the (L)MoO_x-Pd/C catalysts prepared from the Pd/C with and without the sieving and reducing treatments showed very similar performance in ClO₄⁻ reduction. The activated carbon without Pd³ was purchased from Alfa Aesar (Norit GSX; steam activated and acid-washed; surface area 1300 m² g⁻¹) and used as received.

$(L)MoO_x$ -Pd/C catalyst preparation

This procedure describes the *in situ* preparation of the typical 0.2 g L⁻¹ loading of $[(NH_2)_2bpy]MoO_x-Pd/C$ catalyst with 5 wt% Mo and the same molar amount of the $(NH_2)_2bpy$ ligand. A 50-mL round bottom flask was sequentially loaded with 49 mL of DI water (pH adjusted to 3.0 with H₂SO₄), 10 mg of Pd/C powder, 0.5 mL of Na₂MoO₄ stock solution (containing 0.5 mg or 5.2 µmol of Mo), 0.5 mL of aqueous $(NH_2)_2bpy$ stock solution (containing 5.2 µmol of ligand), and a magnetic stir bar. The flask was sealed with a rubber stopper and sonicated for 1 min, and then placed in the fume hood. H₂ gas (99.999%, Airgas) was supplied by two 16-gauge (diameter) and 6-inch (length) stainless steel needles penetrating the stopper as the gas inlet and outlet, respectively (**Figure A1**). The aqueous suspension was stirred at 1600 rpm under 1 atm H₂ headspace for 1 h to afford the suspension of $[(NH_2)_2bpy]MoO_x-Pd/C$ catalyst. All parameters such as Mo concent, catalyst loading, solution pH, and ligand structure can be readily adjusted.



Figure A1. The catalyst reactor in operation.

Perchlorate reduction

The reduction of the typical 1 mM ClO_4^- was initiated by adding 0.25 mL of NaClO₄ stock solution (200 mM) into the catalyst suspension. For the initial ClO_4^- concentration of 100 mM, 612.5 mg of solid NaClO₄ was added into the suspension. All reactions were carried out at room temperature (20°C) and under 1 atm H₂ atmosphere. The flow rate of H₂ was about 1–2 bubbles per second coming out from the 16-gauge needle tip to maintain a slightly positive pressure of the H₂ headspace inside the flask. The solution pH remained at pH 2.9–3.0 throughout the reaction because the reduction of ClO_4^- does not consume H⁺. Aliquots were collected through the H₂ outlet needle with a 3-mL plastic syringe and immediately filtered through a 0.22- μ m cellulose membrane to quench reactions.

Aqueous sample analysis

The quantitation of ClO_4^- and Cl^- was conducted by ion chromatography (Dionex ICS-5000 system with a conductivity detector and a 25 μ L sample injection loop). Samples from the reduction of 100 mM of ClO_4^- were diluted 100 times before analysis. A Dionex IonPac AS16 analytical column was used at 30 °C, with 65 mM KOH at the flow rate of 1 mL min⁻¹ as the eluent. The concentration of total Mo in aqueous samples was analyzed by inductively coupled plasma–mass spectrometry (ICP–MS, Agilent 7700). The concentration of free N ligand in aqueous samples was quantified by high-performance liquid chromatography (HPLC) with a photodiode array (PDA) detector (Shimadzu Nexera XR).

Catalyst collection and characterization

After disconnection from the H₂ supply, the flask was kept sealed by the rubber stopper and immediately transferred into an anaerobic glove bag (Coy Laboratories, filled with 98% N₂ and 2% H₂) to avoid artifacts from air exposure. The catalyst suspension was filtered through a ceramic funnel covered with filter paper (Whatman qualitative) under vacuum. The filter paper was transferred into a 20-mL scintillation vial and dried in a sand bath at 110 °C to remove moisture. The dried catalyst powder was collected and stored in the glove bag until XPS and XAS analysis (see below). For microscopy analysis, the catalyst powder was re-dispersed in distilled water and sonicated for 30 min. A drop of the suspension was loaded onto the copper microgrids and dried under vacuum. The distribution of Mo, Pd, N, O, and C elements was characterized by high-angle annular dark-field (HAADF) imaging with scanning transmission electron microscopy (STEM, FEI Titan Themis 300, operated at 300 kV) at the UC Riverside Central Facility for Advanced Microscopy and Microanalysis (CFAMM).

X-ray photoelectron spectroscopy (XPS)

Inside the glove bag, the dried powder was loaded onto a copper conductive tape on the XPS sample holder and stored in an anaerobic chamber secured with Klein Flange before transferring to the XPS facility at the UC Irvine Materials Research Institute (IMRI). All XPS experiments were performed on the Kratos AXIS Supra surface analysis instrument. The sp² C 1s peak (284.5 eV) of the carbon support was used for binding energy (BE) calibration. The BE of Mo^{II}, Mo^{IV}, and Mo^{VI} standards were acquired in our previous study.² Spectra in the resolution of 0.1 eV were fit using CasaXPS (version 2.3.19). Spectra of Mo 3d (30 scans) were fit with the constrained peak separations (3.15 eV) and the constrained ratio of peak areas (3:2) of 3d spin-orbital coupling doublets.

X-ray absorption spectroscopy (XAS)

The preparation and transfer of XAS samples are the same as mentioned above. Mo Kedge EXAFS data were collected at beamlines 4–1 and 2–2 at Stanford Synchrotron Radiation Light source. The sample chamber was purged with N₂ during data collection to minimize the artifact caused by atmospheric O₂. Both transmission and fluorescence signals were acquired. A Mo metal foil reference was concomitantly measured with the samples for energy calibration (E₀ = 20000 eV). Zirconium (Z–2) metal foil was used as the filter for collecting fluorescence signals. *Athena* was used for energy calibration, raw spectra average, post-edge normalization, and background removal.² *Artemis* was used to obtain the structural parameters by fitting k^3 -weighted EXAFS spectra to the standard EXAFS equation using several single-scattering paths. The fittings were over a *k* range of 3–13 Å⁻¹ and an *R* range of 1.0–3.0 Å for the catalyst sample, a *k* range of 3–12 Å⁻¹ and an *R* range of 0.9–2.0 Å for (NH₄)₆Mo₇O₂₄ standard as reported previsouly.² Phase and amplitude functions for the scattering paths were generated using FEFF6⁴ based on the structures of MoO₂, MoO₃, and monomolybdate. In all fittings, the number of independent variables included was fewer than the number of independent data points. The Hanning window was used for the Fourier transform of the EXAFS data.

Synthesis and testing of model Mo-ligand complexes

The synthesis of the Mo : $(NH_2)_2bpy = 1 : 1$ complex and the reported complex Mo₈O₂₂(OH)₄((*t*-Bu)₂*bpy*)₄ (Mo : $(NH_2)_2bpy = 1 : 0.5$) followed the literature method.⁵ Briefly, MoO₃ (68 mg, 0.48 mmol), $(NH_2)_2bpy$ or (*t*-Bu)₂*bpy* (0.48 mmol), and deionized water (5 mL) were loaded in a Teflonlined stainless steel autoclave. The autoclave was heated in an oven at 160°C for 3 days. The resulting products were light pink crystalline solid and amorphous white powder from the use of (*t*-Bu)₂*bpy* and $(NH_2)_2bpy$, respectively. The products were collected by filtration and washed with deionized water and diethyl ether. ¹H NMR characterization and other experiments found that the complexes fully decomposed to free ligands upon dissolution (See **Figures S12–S16** and figure captions for details).

Electrochemical study

Samples for electrochemical studies were prepared by immobilizing Na₂MoO₄, free $(NH_2)_2bpy$, and the 1:1 mixture of $(NH_2)_2bpy + Na_2MoO_4$ onto activated carbon powder with the same adsorption procedures used for the *in situ* preparation of $[(NH_2)_2bpy]MoO_x$ —Pd/C. The activated carbon did not contain Pd because Pd⁰ nanoparticles can catalyze the hydrogen evolution reaction⁶ and interfere with the reduction of $[(NH_2)_2bpy]MoO_x$. Catalyst ink was prepared by dispersing 5 mg of each carbon powder sample in the mixture of 5 ml Nafion, 500 ml ethanol, and 250 ml deionized water. Aliquots of 2 ml of the catalyst ink were applied twice onto the glassy carbon electrode. After the ink was dried in air, the working electrode was ready for use. The electrochemical cell was purged with Ar gas before measurement to prevent the artifacts from atmospheric oxygen. Cyclic voltammetry was performed at pH 3.0 using an Ag/AgCl reference electrode and platinum wire counter electrode.

Texts S1 and S2 Referred in the Main Text

Text S1. Langmuir-Hinshelwood Mechanism

The kinetic data of $[(NH_2)_2 bpy]MoO_x - Pd/C$ catalyst was analyzed with the Langmuir-Hinshelwood (LH) model. Previous works suggest that the reduction of ClO_4^- to ClO_3^- by the active sites is the rate-limiting step.⁷⁻⁸ The surface reactions can be simplified with the one-site model⁹ shown in **Scheme S1**. At the water-catalyst interface, aqueous ClO_4^- reversibly coordinates with the surface Mo center in the first step (i.e., the adsorption of ClO_4^-). The carbon surface has a very low affinity to ClO_4^- . Then, the reduction of Mo-coordinated ClO_4^- is enabled by the twoelectron oxygen atom transfer (OAT) reaction, resulting in the formation of Mo=O and the dissociation of ClO_3^- .

$$\begin{array}{c} \text{CIO}_{4^{-}}(aq) + \text{Mo}^{\text{IV}}(s) \xleftarrow[k_{-1}]{k_{-1}} & \text{Mo}^{\text{IV}} \text{--} \text{CIO}_{4^{-}}(s) \xrightarrow[k_{2}]{k_{2}} & \text{Mo}^{\text{VI}} \text{=-} \text{O}(s) + \text{CIO}_{3^{-}}(aq) \\ \textbf{A} & \textbf{S}_{\text{empty}} & \textbf{AS} & \textbf{S}_{\text{used}} \end{array}$$

Scheme S1. Langmuir-Hinshelwood model for ClO_4^- reduction by $[(NH_2)_2bpy]MoO_x-Pd/C$. The catalytic reduction proceeds on the surface of the solid catalyst. First, aqueous phase ClO_4^- (A) reversibly coordinates with the unoccupied Mo^{IV} active sites (S_{empty}), forming a Mo^{IV}-ClO₄⁻ (AS) intermediate. Then, the OAT reaction affords the reduction of ClO_4^- and the formation of Mo^{VI}=O (Sused). The following assumptions are made: (i) the reduction of ClO_4^- is the rate-limiting step, (ii) the regeneration of Sused by Pd/C and H₂ is fast and complete; therefore, the number of total active sites (S) is approximately equal to the summation of Sempty and AS (i.e., the surface concentration of Sused is close to zero), (iii) there is no activity loss of the Mo sites, and (iv) the adsorption of ClO_4^- on activated carbon is minimal.

The global reaction rate (r) is defined by

$$r = k_2[AS] = k_2\theta[S] \tag{1}$$

where [S] and [AS] denote the surface concentration of total active sites and occupied sites, respectively. θ is the surface coverage, which is defined as $\theta = [AS]/[S]$. Because the adsorption and desorption of ClO₄⁻ are assumed to be fast, the steady-state approximation is applied to AS. Therefore, the concentration variation of AS with respect to time is expressed as

$$\frac{d[AS]}{dt} = k_1[A][S](1-\theta) - k_{-1}[S](\theta) - k_2[S](\theta) = 0$$
(2)

 θ is solved as

$$\theta = \frac{k_1[A]}{k_1[A] + k_{-1} + k_2} \tag{3}$$

Because the OAT reaction is assumed to be the rate-limiting step (i.e., $k_2 \ll k_1[A]$ and k_{-1}), θ can be simplified to

$$\theta = \frac{k_1[A]}{k_1[A] + k_{-1}} \tag{4}$$

From Eq. 4 and Eq. 1, r can be expressed in terms of [A] and [S] by

$$r = \frac{K_1 k_2 [A] [S]}{K_1 [A] + 1} \tag{5}$$

in which $K_1 = k_1/k_{-1}$ is the equilibrium constant and [A] is the aqueous concentration of ClO₄⁻ at any given time. Based on the kinetic results, we notice that the observed rate constant, k_{obs} , varies in terms of the initial concentration of ClO₄⁻ (i.e., [A₀]). Hence, we define a new term φ , in which $\varphi = [A]/[A_0]$, and replace [A] with $\varphi[A_0]$ in Eq. 5.

$$r = \frac{K_1 k_2 [A_0] [S] \varphi}{K_1 [A_0] \varphi + 1}$$
(6)

At *high initial concentrations*, in which $K_1[A_0]\varphi \gg 1$, Eq. 6 can be further simplified to

$$r = k_2[S] \tag{7}$$

Eq. 7 demonstrates that the reaction is <u>zeroth-order</u> with respect to ClO_4^- . This rate law is in good agreement with our kinetic results, in which zeroth-order fitting provides >0.99 R² values (i.e., coefficient of determination) for 1, 10 and 100 mM ClO_4^- reduction by the $[(NH_2)_2bpy]MoO_x$ –Pd/C catalyst (**Figure S6**). Furthermore, the concentration variations of ClO_4^- can be described by

$$\frac{d[A]}{dt} = -k_2[S] \tag{8}$$

Upon integration and rearrangement, we can obtain the following kinetic equation:

$$\varphi = -\frac{k_2[S]}{[A_0]}t + 1 \tag{9}$$

Eq. 9 shows that $k_{obs} = k_2[S]/[A_0]$ at high ClO₄⁻ concentrations. This kinetic pattern agrees with our experimental observations. When the initial concentration of ClO₄⁻ increased from 1 to 100 mM and the catalyst loading remained constant (i.e., [S] does not change), the k_{obs} decreased from 2.01 to 0.043 mM h⁻¹ (**Figure S6**, panels **a**–**c**). In addition, k_{obs} values were almost identical when we scaled up the reaction proportionally (e.g., reduction of 10 mM ClO₄⁻ by 0.2 g L⁻¹ catalyst and reduction of 100 mM ClO₄⁻ by 2 g L⁻¹ catalyst, **Figure S6**, panel **c** versus **d**).

At *low initial concentrations*, in which $K_1[A_0]\varphi \ll 1$, Eq. 6 becomes

$$r = K_1 k_2 [A_0] [S] \varphi$$
 (10)

Now the reaction is <u>first-order</u> in φ (i.e., first-order in [ClO₄⁻]). Similarly, the reduction of ClO₄⁻ can be described by

$$\frac{d[A]}{dt} = -K_1 k_2 [A_0] [S] \varphi$$
(11)

And the following equation holds for low concentrations scenarios

$$\varphi = e^{-K_1 k_2[S]t} \tag{12}$$

Eq. 12 shows that k_{obs} is not a function of $[A_0]$. In other words, k_{obs} remains constant regardless of $[A_0]$. This kinetic pattern agrees with our experimental results, in which k_{obs} remained the same when the initial concentration of ClO₄⁻ varied from 0.1 to 0.01 mM (**Figure. S7**, panels **a**–**c**).

Text S2. Mass Transfer Analysis

A prerequisite of the LH kinetic model is the assumption that surface reactions constitute the rate-limiting step. This assumption implies that the diffusion of ClO_4^- from the bulk solution phase to the liquid-solid interface is much faster than the chemical reactions on the surface. Therefore, evaluations of external and internal mass transfer are essential to verify the assumption.

To evaluate the effect of pore diffusion resistance (i.e., *internal mass transfer*) on the measured reaction rates, we applied Weisz-Prater (WP) criterion for the system under consideration here.¹⁰⁻¹¹ In general, the WP criterion and WP parameter (C_{WP}) are described below:

If $C_{WP} = \frac{k_{obs} \tau R^2}{D\theta} < 1$, the internal mass transfer limitation is negligible

If $C_{WP} = \frac{k_{obs} \tau R^2}{D\theta} > 1$, the internal mass transfer limitation is significant

In the expression of $C_{WP} = \frac{k_{obs}\tau R^2}{D\theta}$, k_{obs} is the observed pseudo-first-order rate constant of heterogeneous reaction (min^{-1}) , R is the radius of the catalyst particle (m), τ is the tortuosity factor of the catalyst particle, θ is the porosity of the catalyst particle, and D is the diffusion coefficient of reactant in bulk solution $(m^2 s^{-1})$.

To conservatively evaluate C_{WP} , we used the largest observed reaction rate (i.e., 0.185 min⁻¹) from this study. The diameter of the catalyst particle is 37 μm because the commercial Pd/C powder was wet-filtered through a 400-mesh sieve before use.¹ Previous studies suggest that the parameters τ and θ are typically in the range of 2–10 and 0.2–0.7, respectively.¹²⁻¹³ In our conservative calculation, 10 and 0.2 were used as the estimated values for τ and θ , respectively. The diffusion coefficient of ClO₄⁻ is $(D_{ClO_4^-})$ is 1.79 × 10⁻⁹ $m^2 s^{-1}$ in bulk solution.¹⁴ Therefore, C_{WP} is calculated as

$$C_{WP} = \frac{k_{obs}\tau R^2}{D\theta} = \frac{0.185\ min^{-1} \times 10 \times \left(\frac{37}{2} \times 10^{-6}\ m\right)^2}{1.79 \times 10^{-9}\ m^2\ s^{-1} \times 60\ s\ min^{-1} \times 0.2} = 0.029 < 1$$

The above calculation shows that the WP criterion is satisfied for the system under consideration. Therefore, <u>the pore diffusion resistance is negligible</u>.

The evaluation of the *external mass transfer* rate is conducted following our recently reported method.² First, we calculated the Sherwood number (*Sh*) and used it to estimate the mass transfer coefficient ($k_{ag/s}$) of ClO₄⁻ between the aqueous solution and the catalyst surface.¹⁵⁻¹⁶

$$Sh = \left[2 + 0.4 \left(\frac{\varepsilon d_p^4}{\nu^3}\right)^{0.25} Sc^{0.33}\right] \cdot \phi_c$$
(13)

$$k_{aq/s} = \frac{D_{\text{CIO}_3^-}}{d_p} \cdot Sh \tag{14}$$

In Eq. 13, ε is the rate of flow energy supply per unit mass of liquid $(m^2 s^{-3})$, d_p is the diameter of the catalyst particle (m), ν is the kinematic viscosity of water $(\nu_{H_2O} = 1.003 \times 10^{-6} m^2 s^{-1})$ at 20°C), *Sc* is Schmidt number, and ϕ_c is Carman's surface factor (assume the catalyst particle is spherical, $\phi_c = 1$). We evaluated *Sc* and ε with the following equations:

$$Sc = \frac{v_{H_2O}}{D_{ClO_4^-}} = \frac{1.003 \times 10^{-6} \ m^2 \ s^{-1}}{1.79 \times 10^{-9} \ m^2 \ s^{-1}} = 560.34$$
$$\varepsilon = \frac{N_p \cdot l^5 \cdot n^3}{V} = \frac{5 \times (3 \ cm)^5 \times (27 \ s^{-1})^3}{50 \ cm^3} = 48 \ m^2 \ s^{-3}$$

where N_p is the power number (normally $N_p \approx 5.0$)¹⁷, *l* is the length of the stir bar ($l \approx 3 \text{ cm}$), *n* is the rotating speed of the stir bar ($n = 1600 \text{ round min}^{-1} = 27 \text{ round s}^{-1}$), and *V* is the volume of the reactor ($V = 50 \text{ cm}^3$). Thus, ε has the value of $48 \text{ m}^2 \text{ s}^{-3}$.

With the calculated values for Sc and ε , the Sherwood number was calculated as

$$Sh = \left[2 + 0.4 \left(\frac{48 \ m^2 \ s^{-3} \times (3.7 \times 10^{-5} \ m)^4}{(1.003 \times 10^{-6} \ m^2 \ s^{-1})^3}\right)^{0.25} 560.34^{0.33}\right] \cdot 1 = 11.944$$

And $k_{aq/s}$ was estimated by Eq. 14.

$$k_{aq/s} = \frac{D_{\text{ClO}_3^-}}{d_p} \cdot Sh = \frac{1.79 \times 10^{-9} \, m^2 \, s^{-1}}{3.7 \times 10^{-5} \, m} \times 11.944 = 5.78 \times 10^{-4} \, m \, s^{-1}$$

The geometric surface area of the catalyst per volume of solution $(a)^{18}$ is calculated as

$$a = \frac{SA_p \times M}{\rho_p \times V_p} \times \frac{1}{V_R} = \frac{4\pi \times (18.5 \times 10^{-6} \ m)^2 \times 0.01 \ g}{2 \times 10^6 \ g \ m^{-3} \times \frac{4\pi}{3} (18.5 \times 10^{-6} \ m)^3} \times \frac{1}{50 \times 10^{-6} \ m^3} = 16.22 \ m^{-1}$$

in which SA_p is the geometric surface area of one catalyst particle (m^2) , M is the mass of catalyst in the reduction test $(0.01 \ g)$, V_p is the volume of one catalyst particle (m^3) , and V_R is the volume of the reactor $(50 \ mL)$.

The mass transfer rate was then calculated by taking the product of the mass transfer coefficient and the geometric surface area of the catalyst per volume of the solution:

$$k_{aq/s} \cdot a = 5.78 \times 10^{-4} \, m \, s^{-1} \times 16.22 \, m^{-1} = 9.375 \times 10^{-3} \, s^{-1} = 0.563 \, min^{-1}$$

The above estimation indicates that the external mass transfer rate is larger than the observed rate constant $k_{obs} = 0.185 \ min^{-1}$ for ClO₄⁻ reduction. Therefore, the impact of external mass transfer on the reaction rates is negligible.

Figures S1–S16 Referred in the Main Text



Figure S1. The adsorption of (**a**) Mo and (**b**) ligand during the preparation of the $[(NH_2)_2bpy]MoO_x$ -Pd/C catalyst. All dotted lines start from 0% adsorption at 0 h. Results show that under air (legend *without ligand or H*₂ and *without Mo or H*₂) >95% of either Mo or ligand can be adsorbed onto Pd/C within 30 min. When all components (i.e., 1 atm H₂, Mo, and ligand) were supplied together for *in situ* catalyst preparation (legend *with ligand and H*₂ and *with Mo and H*₂), the adsorption of Mo and ligand reached >99 and >99.5%, respectively, within 1 h. Reaction condition: 0.2 g L⁻¹ Pd/C, 0.1 mM Mo from Na₂MoO₄ (for 5 wt% Mo in catalyst), 0.1 mM (NH₂)₂*bpy*, pH 3.0, 1 atm H₂, 20 °C.



Figure S2. Profiles for aqueous ClO_4^- reduction by (*L*)MoO_x-Pd/C catalysts using bipyridine derivative ligands. Reaction conditions: 0.5 g L⁻¹ of (*L*)MoO_x-Pd/C (5 wt% Mo in 5 wt% Pd/C, the molar ratio of *L*:Mo=1:1), 1 mM ClO₄⁻, pH 3.0, 1 atm H₂, 20 °C. Panel **b** used 0.2 g L⁻¹ of catalysts.



Figure S3. Profiles for aqueous ClO_4^- reduction by (*L*)MoO_x-Pd/C catalysts using various ligands. Reaction conditions: 0.5 g L⁻¹ of (*L*)MoO_x-Pd/C (5 wt% Mo in 5 wt% Pd/C, the molar ratio of *L*:Mo=1:1), 1 mM ClO₄⁻, pH 3.0, 1 atm H₂, 20 °C. In panel e, the molar ratio between the monodentate pyridine and Mo was 2:1.



Figure S4. The pH titration curve for $(NH_2)_2 bpy$ in aqueous solution $(0.4 \text{ g L}^{-1}, \text{ or } 2.15 \text{ mM})$. Due to the limited solubility of $(NH_2)_2 bpy$ in water, the titration started from pH 1.60 where both the pyridyl N and $-NH_2$ were protonated. The $(NH_2)_2 bpy$ concentration higher than 0.4 g L⁻¹ resulted in precipitation when pH went higher. The titration stopped at pH 12 as the high end of accurate measurement by the pH electrode. The low concentration of $(NH_2)_2 bpy$ as the buffer made it challenging to locate the pH turning points as pK_a . However, the comparison with the calculated pH (assuming the absence of buffer) suggested that pK_{a1} (deprotonation from $-NH_3^+$) is below 3.0 to delay the pH rising and pK_{a2} (deprotonation from pyridyl $-NH^+=$) is above 5.0 to reduce the slope of the steep pH increase. This estimation agrees with the reported pK_{a1} of 2.2 and pK_{a2} of 6.7 for the analogous 6,6'-diamino-2,2'-bipyridine.¹⁹



Figure S5. The reduction of 1 mM ClO₄⁻ by the freshly prepared (*cycle 1*) and reused (*cycle 10*, with nine previous spikes of 1 mM ClO₄⁻) [(NH₂)₂*bpy*]MoO_{*x*}-Pd/C catalyst. The 0th order fittings were conducted with all data points at C/C₀ > 0.2. Due to the low catalyst loading (0.2 g L⁻¹) and the inevitable loss of catalyst powder from each filtration-redispersion procedure, the continuous spike experiments were conducted. Each ClO₄⁻ spike was allowed at least 2 h to achieve complete reduction into Cl⁻. The ten spikes took two days to finish because no experimentation was performed during the night. The dataset *control* indicates an experiment using the freshly prepared catalyst in the presence of 9 mM NaCl, which simulated the scenario of complete reduction of nine spikes of 1 mM ClO₄⁻. The almost overlapping time profiles of the three data sets suggest that the catalyst performance is insensitive to <10 mM of Cl⁻ and resistant to the acidic and hydrogenating aqueous environment. Reaction condition: 0.2 g L⁻¹ catalyst (5 wt% Mo in 5 wt% Pd/C), 1 mM ClO₄⁻ per spike, pH 3.0, 1 atm H₂, 20 °C.



Figure S6. Catalytic reduction of high concentrations ($C_0 = 1$, 10, and 100 mM) of ClO_4^- by the $[(NH_2)_2bpy]MoO_x$ -Pd/C catalyst (5 wt% Mo in 5 wt% Pd/C, pH 3.0, 1 atm H₂, 20 °C). Panels **a**, **b**, and **c** used 0.2 g L⁻¹ catalyst. Panel **d** used 2.0 g L⁻¹ catalyst. The data with C/C₀ > 0.2 were fit with both 0th- and 1st-order models. The better fit has the equation highlighted in bold. The slope of the linear fitting (in the unit of h⁻¹) indicates the 0th-order rate constant (mM h⁻¹) divided by C₀ (mM). The discussion in the **Text S1** regarding $k_{obs} = k_2[S]/[A_0]$ corresponds to the slopes shown in these figures (i.e., $C_0 = [A_0]$). The first highlight is the decreasing k_{obs} with the increasing $[A_0]$ for ClO_4^- (panels **a**-**c**). Since the overall reaction model is simplified, the decrease of k_{obs} is not strictly in proportion with the increase of $[A_0]$. The second highlight is the very similar k_{obs} for the reduction of 10 mM ClO_4^- using 0.2 g L⁻¹ catalyst and the reduction of 100 mM ClO_4^- using 2.0 g L⁻¹ catalyst (i.e., the same ratio of $[S]/[A_0]$) shown in panels **b** and **d**. See **Text S1** for more details.



Figure S7. Catalytic reduction of low concentrations ($C_0 = 1, 0.5, 0.1, and 0.01 \text{ mM}$) of ClO_4^- by 0.2 g L⁻¹ of [(NH₂)₂*bpy*]MoO_x–Pd/C catalyst (5 wt% Mo in 5 wt% Pd/C, pH 3.0, 1 atm H₂, 20 °C). The data with C/C₀ > 0.2 were fit with both 0th- and 1st-order models. The better fit has the equation highlighted in bold. The power of the exponential fitting indicates the first-order rate constant (min⁻¹, independent from C₀). The highlight is the consistent 1st-order k_{obs} values when the kinetics cannot be fit by the 0th-order model (i.e., R²<0.98 when C₀ = 0.1 and 0.01 mM). See **Text S1** for more details.



Figure S8. Inhibition of ClO_4^- reduction using $[(NH_2)_2bpy]MoO_x^-Pd/C$ (panels **a** and **b**) and of ClO_3^- reduction using ligand-free MoO_x^-Pd/C (panels **c** and **d**) by chloride and sulfate anions. Dotted lines indicate the 0th- or 1st-order fittings using the data with $C/C_0>0.2$. Fitting results and catalyst activity comparisons are shown in **Table S2**. Reaction conditions: 0.2 g L⁻¹ catalyst (5 wt% Mo in 5 wt% Pd/C), 1 mM ClO_4^- or ClO_3^- , pH 3.0, 1 atm H₂, 20 °C. "DI" indicates control solutions without additions of NaCl or Na₂SO₄.



Figure S9. The change of CIO_4^- reduction activity by (a) $[(NH_2)_2bpy]MoO_x-Pd/C$ and (b) $Re(hoz)_2-Pd/C^1$ before and after air exposure for 1 h. Reaction conditions: 0.2 g L⁻¹ catalyst (5 wt% Mo or 5 wt% Re on the same 5 wt% Pd/C material), 1 mM CIO_4^- , pH 3.0, 1 atm H₂, 20 °C. The preparation of both catalysts took 1 h under 1 atm H₂. After air exposure, the catalyst suspensions were treated under 1 atm H₂ for another 1 h before adding CIO_4^- .



Figure S10. Mo K-edge X-ray absorption near-edge structure (XANES) spectra of the reduced $[(NH_2)_2bpy]MoO_x-Pd/C$ and Mo^{II} , Mo^{IV} , and Mo^{VI} references.



Figure S11. Mo K-edge extended X-ray absorption fine structure (EXAFS) spectra (dotted lines) of the reduced $[(NH_2)_2bpy]MoO_x-Pd/C$, Mo^{II} and Mo^{IV} references, and their shell-by-shell fits (solid lines).



Figure S12. ¹H NMR (CD₃CN, 600 MHz) spectra of (**a**) 4,4'-di-*tert*-butyl-2,2'-bipyridine [(*t*-Bu)₂*bpy*] ligand and (**b**) Mo^{VI}₈O₂₂(OH)₄[(*t*-Bu)₂*bpy*]₄ from hydrothermal synthesis. The same spectra indicate complete dissociation of the complex into the free (*t*-Bu)₂*bpy* ligand upon dissolution in acetonitrile. The NMR data is consistent with the original report on Mo^{VI}₈O₂₂(OH)₄[(*t*-Bu)₂*bpy*]₄,²⁰ suggesting that the original study also observed free (*t*-Bu)₂*bpy* ligand rather than a dissolved Mo^{VI}₈O₂₂(OH)₄[(*t*-Bu)₂*bpy*]₄ structure.



Figure S13. Aqueous ClO_4^- reduction using (*L*)MoO_x–Pd/C catalysts prepared from different Mo+*L* precursors. Reaction conditions: 0.2 g L⁻¹ catalyst (5 wt% Mo in 5 wt% Pd/C), 1 mM ClO₄⁻, pH 3.0, 1 atm H₂, 20 °C. Before adding ClO₄⁻, all catalysts were prepared by stirring the mixture of Pd/C and Mo precursors in water suspension for 12 h under 1 atm H₂ at 20 °C.

In panel **a** where $L = (t-Bu)_2 bpy$, the hydrothermal synthesis product was reported as $Mo^{VI}_8O_{22}(OH)_4[(t-Bu)_2 bpy]_4$ with Mo : $(t-Bu)_2 bpy = 1 : 0.5.^{20}$ The $(L)MoO_x$ –Pd/C catalyst prepared directly from 1:1 Na₂MoO₄ and $(t-Bu)_2 bpy$ showed a much higher activity. The addition of another 0.5 equivalent of $(t-Bu)_2 bpy$ together with the hydrothermal product also yielded a similarly higher activity. These results confirm that the pre-synthesized $Mo^{VI}_8O_{22}(OH)_4[(t-Bu)_2 bpy]_4$ complex decomposed upon dissolution in water. The Mo^{VI} species and free $(t-Bu)_2 bpy$ reassembled in Pd/C, similar to the direct use of Na₂MoO₄ + $(t-Bu)_2 bpy$. The extra $(t-Bu)_2 bpy$ filled the 50% of ligand deficit in the pre-synthesized complex to match the optimal 1:1 ratio between Mo and L (also compare **Figure 2b** in the main text). In panel **b** where $L = (NH_2)_2 bpy$, the use of the pre-synthesized $[(NH_2)_2 bpy]Mo \ Complex achieved the same <math>CIO_4^-$ reduction activity as the standard preparation from Na₂MoO₄ + $(NH_2)_2 bpy$ at 1:1 ratio. Although the structure of the hydrothermally synthesized $[(NH_2)_2 bpy]Mo \ Complex product remained unknown, the 1:1 ratio between Mo^{VI} and <math>(NH_2)_2 bpy$ in the product is confirmed by this kinetic comparison. The direct use of hydrothermally synthesized $[(t-Bu)_2 bpy]Mo \ Complex S14$ and S16).



Figure S14. ¹H NMR spectra (CD₃CN, 600 MHz) demonstrating the oxygen atom transfer from pre-synthesized Mo^{VI}₈O₂₂(OH)₄[(*t*-Bu)₂*bpy*]₄ to PPh₃ and the lack of ligand coordination in solution after the reaction with excess PPh₃ in acetonitrile at 70 °C for 12 h. The formation of OPPh₃ is attributed to the reduction of Mo^{VI} into Mo^{IV} via oxygen atom transfer. The lack of resonances for other (*t*-Bu)₂*bpy* species suggests that all pre-synthesized [(*t*-Bu)₂*bpy*]Mo structures decomposed into free (*t*-Bu)₂*bpy* ligand upon dissolution. After LiClO₄ addition and heating at 70 °C for another 8 h, no significant change of OPPh₃ : PPh₃ ratio was observed, indicating no ClO₄⁻ reduction. The same experimental approach using the hydrothermally synthesized [(NH₂)₂*bpy*]MoO_x complex observed a much lower amount of OPPh₃ and no resonance of (NH₂)₂*bpy* ligand because both the complex and free (NH₂)₂*bpy* ligand dissolved poorly in acetonitrile.

<u>Experimental details</u>: In an anaerobic glove bag (97% N₂ and 3% H₂), a 15 mL glass reaction tube was sequentially loaded with 5 mg of the pre-synthesized white powder of $Mo^{VI}_8O_{22}(OH)_4[(t-Bu)_2bpy]_4$, 27.5 mg of PPh₃, 6 mL of acetonitrile, and a magnetic stir bar. The resulting suspension thus contained 3.0 mM of Mo^{VI}, 1.5 mM of (t-Bu)_2bpy, and 17.5 mM of PPh₃. The suspension was sealed with a Teflon screw cap and heated in a 70 °C oil bath for 12 h to yield a yellow solution. LiClO₄ (1 mM) was then added, and homogeneous ClO₄⁻⁻ reduction was monitored by measuring PPh₃ versus OPPh₃ for another 8 h at 70 °C. Aliquots of 1 mL solution were collected at 0 and 8h, dried under vacuum, and redissolved in CD₃CN (1 mL) for ¹H NMR characterization.



Figure S15. Synthesis of phosphine-reduced $[(NH_2)_2bpy]Mo^{IV}$ complex in the aqueous environment. Tube 1 started from Na₂MoO₄, $(NH_2)_2bpy$, and trisodium triphenylphosphine-3,3',3"-trisulfonate (TPPTS). Tube 2 started from the pre-synthesized Mo^{VI} : $(NH_2)_2bpy = 1 : 1$ complex (by hydrothermal method) and TPPTS. Tube 3 only contained TPPTS for comparison as a clear solution. In Tube 1, the mixing of Na₂MoO₄ and $(NH_2)_2bpy$ at the beginning yielded a white suspension, which gradually turned green at 70 °C. The the pre-synthesized $[(NH_2)_2bpy]Mo$ complex needed a much longer time to turn green. The photo on the right side shows the final product as a green powder and colorless liquid. The green powder did not dissolve in common solvents. At pH 3.0, this suspension could not reduce ClO₄⁻ (see **Figure S16a**).

<u>Experimental details</u>: In the anaerobic glove bag, a 15 mL glass reaction tube was sequentially loaded with 2.9 mg of Na₂MoO₄•2H₂O, 2.3 mg of (NH₂)₂bpy, 37 mg of TPPTS, 6.5 mL of deionized water, and a magnetic stir bar. For tube 2, 4.3 mg of the hydrothermally pre-synthesized Mo^{VI} : (NH₂)₂bpy = 1 : 1 complex (assumed as Mo^{VI}₂O₆[(NH₂)₂bpy]₂) was used instead of Na₂MoO₄ and (NH₂)₂bpy. The resulting white suspension thus contained 2 mM of Mo^{VI}, 2 mM of (NH₂)₂bpy, and 10 mM of TPPTS. The suspension was sealed with a Teflon screw cap and heated in a 70 °C oil bath. After 8 h, the pH was adjusted to 3.0 by H₂SO₄ and added with NaClO₄ (0.5 mM) to monitor ClO₄⁻ reduction for another 24 h at 70 °C. Aliquots of 2 mL solution were collected at intervals. Samples were immediately analyzed by ion chromatography.



Figure S16. Time profiles for aqueous ClO_4^- reduction by TPPTS using different Mo sources with and without carbon support. The three settings in panel **a** correspond to the three reaction tubes described in **Figure S15**. The same three settings in panel **b** were added with activated carbon (no Pd nanoparticles or H₂) at the beginning of catalyst preparation. Panel **c** shows the chlorine mass balance for the ClO_4^- reduction enabled by Na₂MoO₄ + (NH₂)₂*bpy* + TPPTS + carbon at 70°C. The background chloride ion at 0 h (0.24 mM) was from the impurity in carbon (3.5 g L⁻¹ in water).

<u>Experimental details</u>: The reaction settings in panel **a** followed the method described for **Figure S15**. For the settings in panel **b**, 23 mg of activated carbon was added in each tube. The corresponding Mo content if fully immobilized on the carbon support was 5 wt%. The loading of the whole Mo/C catalyst in water was approximately 3.5 g L^{-1} .



Figure S17. Original HAADF-STEM imaging and EDX mapping of another μ m-sized particle of the [(NH₂)₂*bpy*]MoO_x-Pd/C catalyst. This particle shows the heterogeneity of metal distribution in the porous carbon (see **Figures 3i-3l** in the main text).



Figure S18. Cyclic voltammograms (CVs) of $[(NH_2)_2bpy]MoO_x/C$ (no Pd) in the absence and presence of NaClO₄. The working electrode was prepared by drop-casting $[(NH_2)_2bpy]MoO_x/C$ onto the glassy carbon electrode. The cyclic voltammetry was performed at pH 3.0 using a Ag/AgCl reference electrode and Pt wire counter electrode. Two cathodic peaks (labeled as c₁ and c₂, at -0.15 V and -0.8 V) were observed from the scanning in the negative direction. These two peaks are similar to the CVs of aqueous molybdate anions.²¹ The anodic counterpart (a₁) of c₁ was observed at 0.0 V. The large potential difference between a₁ and c₁ (0.15 V) indicates the electrochemical irreversibility. After the addition of 0.01 M NaClO₄ into the electrolyte (black trace), there was no formation of a new reduction peak, nor a significant change in current densities at c₁ and c₂. Therefore, electrochemical ClO₄⁻ reduction with $[(NH_2)_2bpy]MoO_x/C$ is unlikely to occur. The reduction using H₂+Pd or phosphine seems necessary to enable ClO₄⁻ reduction.



Figure S19. CVs of $[(NH_2)_2bpy]MoO_x/C$, MoO_x/C , and $(NH_2)_2bpy/C$ in 0.1 M NaClO₄. The results confirm that the reduction peak c_1 in **Figure S18** arises mainly from the reduction of MoO_x and the reduction peak c_2 is a combination of the reduction of MoO_x and $(NH_2)_2bpy$.

Tables S1–S4 Referred in the Main Text

Table S1. Performance of Abiotic Metal-Catalyzed Perchlorate Reduction Systems.

Entry	Catalyst	Catalyst loading	Reaction medium	Reductant	Moisture sensitivity	Air sensitivity	[ClO4 ⁻]0 (mM)	TON	TOF ^{<i>a</i>} (h ⁻¹)	Apparent rate constant or ClO4 ⁻ conversion	Ref.	
	Heterogeneous Catalysts- Mo and Re											
1							0.01	0.4	4.2	$11.1 \ h^{-1}$		
2	$[(NH_{a})_{a}h_{a}h_{a}]M_{a}O = Pd/C$	$0.2 \text{ g I}^{-1, b}$	Water	На	No	No ^e	1	38.5	106	$2.8 \ h^{-1}$	this	
3		0.2 g L	(pH 3.0)	(1 atm)	NO	110	10	385	137	$3.5 \text{ mM } h^{-1, h}$	study	
4						100	3850	165	$4.3 \text{ mM } h^{-1, h}$			
5	ReO _x -Pd/C	2.0 g L ^{-1, c}	Water (pH 2.7)	H ₂ (1 atm)	No	Yes ^f	2	13	4.2	$0.33 \ h^{-1}$	22	
6	[Re(O) ₂ (Me ₂ Npy) ₄] -Pd/C	$1.0 \text{ g L}^{-1, d}$	Water (pH 2.7)	H ₂ (1 atm)	No	N/A	2	40	31	$0.80 \ h^{-1}$	7	
7	$R_{P}(\Omega)(h_{QZ})_{2} - Pd/C$	0 5 g I ^{-1, b}	Water	H_2 (1 atm)	No	Ves	1	30	72	$2.5 \ h^{-1}$	1	
8		0.5 g L	(pri 5.0)	(1 aun)			10	300	64	$0.22 \ h^{-1}$	23	
	Homogeneous Catalysts- Re and Fe											
9	$[\operatorname{Re}(\mathrm{O})(hoz)_2(\mathrm{OH}_2)]^+$	0.03 equiv	CH ₃ CN/H ₂ O (v/v 95/5)	CH ₃ SCH ₃ (5.4 equiv)	No	No	92	31	7.8	100% after 4h	24	
10		1	CUCN				0.02	2	0.10	750/ after 16h	25	
10	[N(afa ^{Cy}) ₃ Fe(OTf)] ⁺	1 equiv	(anhydrous)	Diphenylhydrazine	Yes	Yes	0.03	3	0.19	/5% after 16h	20	
11		0.05 equiv	THF (anhydrous)	(4.0 equiv)			0.02	76 ⁱ	3.2	86% after 24h	26	

^a Turnover frequencies are either calculated using the degradation of the first 5% of the initial ClO₄⁻ concentration or as reported in the cited literature.

^b These catalysts contained ~5 wt % Mo or Re, and 5 wt % Pd.

^c This catalyst contained 5.7 wt% Re and 5 wt% Pd. ReO_x catalysts were prepared from KReO₄.

^d This catalyst contained 3.7 wt% Re and 5 wt% Pd. The catalyst can also be prepared in situ with 2:1 molar ratio of Me₂Npy:KReO₄ added into Pd/C.

^e Air exposure oxidized the reduced Mo, but metal leaching was minimal (<1.5%) and the catalytic activity was fully restored upon the re-application of 1 atm H₂. See Figure S9a.

^f Air exposure oxidized the reduced Re and caused significant leaching (>50%), but the catalytic activity was fully restored upon the re-application of 1 atm H₂.²⁷

^g Air exposure caused irreversible decomposition of the Re(*hoz*)₂ complex into ReO₄⁻ and free *hoz* ligand. The activity could not be restored. See Figure S9b.

^{*h*} Zero-order kinetics shown at high ClO_4^- concentrations. See **Text S1** for details.

^{*i*} TON was increased from entry 10 due to the addition of [N(afa^{Cy})₃Zn(OTf)]⁺ as a sacrificial agent to remove Cl⁻ from the poisoned catalyst, [N(afa^{Cy})₃FeCl]⁺.

Salt added	It added fitting equation		rate constant	relative activity						
ClO_4^- reduction by [(NH ₂) ₂ bpy]MoO _x -Pd/C										
DI	y = 0.9932 - 0.0305x	0.9985	0.0305 mM min ⁻¹	1						
0.1 M NaCl	y = 0.9955 - 0.0175x	0.9983	0.0175 mM min ⁻¹	0.57						
2.0 M NaCl	y = 0.9975-0.0016x	0.9628	0.0016 mM min ⁻¹	0.052						
1.0 M Na ₂ SO ₄	y = 1.0099 - 0.0111x	0.9985	$0.0111 \text{ mM min}^{-1}$	0.36						
ClO_3^- reduction by MoO_x –Pd/C										
DI	$y = 1.0126e^{-0.114x}$	0.9996	$0.114 { m min}^{-1}$	1						
2.0 M NaCl	$y = 1.0106e^{-0.062x}$	0.9978	0.062 min^{-1}	0.54						
1.0 M Na ₂ SO ₄	$y = 0.9858e^{-0.045x}$	0.9988	$0.045 \ { m min}^{-1}$	0.39						

Table S2. Salt Inhibition of Mo Catalysts with and without the Organic Ligand.^a

^{*a*} Source data are shown in **Figure S8**.

Table S3. Mo K-edge EXAFS Shell-by-Shell Fitting Parameters of Mo Standards and Mo–Pd/C Catalyst Samples.

Sample	shell	CN^a	\mathbf{R} (Å) ^b	$\sigma^2 (\text{\AA}^2)^c$	$\Delta E (eV)^d$	R-factor
MoO ₂	Mo-O	6	1.99 (0.01)	0.002 (0.001)	-1.4 (2.0)	0.023
	Mo-Mo	1	2.52 (0.01)	0.001 (0.001)		
	Mo-Mo	1	3.12 (0.01)	0.002 (0.001)		
	Mo-Mo	8	3.70 (0.01)	0.004 (0.001)		
(NH ₄) ₆ Mo ₇ O ₂₄	Mo-O	4	1.74 (0.01)	0.004 (0.002)	-4.0 (3.3)	0.012
[(NH ₂) ₂ <i>bpy</i>]MoO _x -Pd/C	Mo-O	1.1 (1.1)	1.67 (0.03)	0.002 (0.006)	-6.1 (4.9)	0.055
	Mo-O	5.1 (3.1)	1.99 (0.03)	0.012 (0.008)		
	Mo-Mo	0.9 (0.5)	2.57 (0.02)	0.002 (0.002)		
MoO _x -Pd/C	Mo-O	0.4 (0.3)	1.67 (0.04)	0.002^{e}	-4.1 (2.9)	0.030
	Mo-O	6.1 (1.9)	2.03 (0.02)	0.010 (0.004)		
	Mo-Mo	1.7 (0.6)	2.56 (0.01)	0.005 (0.002)		

^a Coordination number; ^b Interatomic distance; ^c Debye-Waller factor; ^d Energy shift; ^e Fixed during the fitting.

Table S4. Mo K-edge EXAFS Shell-by-shell Fitting Parameters of $[(NH_2)_2bpy]MoO_x-Pd/C$ Using a Mo-Pd Shell. Values Highlighted with Asterisks are Problematic.

Fitting Method	shell	CN ^a	\mathbf{R} (Å) ^b	$\sigma^2 (\text{\AA}^2)^c$	$\Delta E (eV)^d$	R-factor
1	Мо-О	0.5 (16.5)*	1.64 (0.80)	0.001 (0.135)		
	Мо-О	1.2 (26.3)*	1.95 (0.17)	-0.00002 (0.081)*	-10.2 (25.6)*	0.046
	Mo-Pd	1.5 (25.3)*	1.92 (0.70)	0.015 (0.166)		
	Mo-Mo	1.0 (1.8)	2.55 (0.08)	0.002 (0.009)		
2	Мо-О	-3.1 (43.5)*	1.76 (0.46)*	0.031 (0.233)*		
	Mo-Pd	2.4 (5.0)*	1.84 (0.04)	0.014 (0.014)	-13.9 (6.5)*	0.121*
	Mo-Mo	1.1 (0.8)	2.54 (0.02)	0.002 (0.003)		
3	Mo-Pd	2.5 (1.1)	1.83 (0.02)	0.014 (0.004)	-17.6(3.1)*	0.132*
	Mo-Mo	0.9 (0.5)	2.53 (0.01)	0.002 (0.003)		

^aCoordination number; ^bInteratomic distance; ^cDebye-Waller factor; ^dEnergy shifts.

References

1. Liu, J.; Choe, J. K.; Wang, Y.; Shapley, J. R.; Werth, C. J.; Strathmann, T. J. Bioinspired complex-nanoparticle hybrid catalyst system for aqueous perchlorate reduction: Rhenium speciation and its influence on catalyst activity. *ACS Catal.* **2015**, *5*, *511-522*.

2. Ren, C.; Yang, P.; Gao, J.; Huo, X.; Min, X.; Bi, E. Y.; Liu, Y.; Wang, Y.; Zhu, M.; Liu, J. Catalytic reduction of aqueous chlorate with MoO_x Immobilized on Pd/C. *ACS Catal.* **2020**, *10*, 8201-8211.

3. Gao, J.; Ren, C.; Huo, X.; Ji, R.; Wen, X.; Guo, J.; Liu, J. Supported palladium catalysts: A facile preparation method and implications to reductive catalysis technology for water treatment. *ACS ES&T Eng.* **2021**, *1*, 562–570.

4. Zabinsky, S.; Rehr, J.; Ankudinov, A.; Albers, R.; Eller, M. Multiple-scattering calculations of X-ray-absorption spectra. *Phys. Rev. B* **1995**, *52*, 2995-3009.

5. Amarante, T. R.; Neves, P.; Paz, F. A. A.; Pillinger, M.; Valente, A. A.; Gonçalves, I. S. A dinuclear oxomolybdenum(VI) complex, $[Mo_2O_6(4,4'-di-tert-butyl-2,2'-bipyridine)_2]$, displaying the $\{MoO_2(\mu-O)_2MoO_2\}^0$ core, and its use as a catalyst in olefin epoxidation. *Inorg. Chem. Commun.* **2012**, *20*, 147-152.

6. Ghasemi, S.; Hosseini, S. R.; Nabipour, S.; Asen, P. Palladium nanoparticles supported on graphene as an efficient electrocatalyst for hydrogen evolution reaction. *Int. J. Hydrog. Energy* **2015**, *40*, 16184-16191.

7. Hurley, K. D.; Zhang, Y.; Shapley, J. R. Ligand-enhanced reduction of perchlorate in water with heterogeneous Re–Pd/C catalysts. *J. Am. Chem. Soc.* **2009**, *131*, 14172-14173.

8. McPherson, L. D.; Drees, M.; Khan, S. I.; Strassner, T.; Abu-Omar, M. M. Multielectron atom transfer reactions of perchlorate and other substrates catalyzed by rhenium oxazoline and thiazoline complexes: Reaction kinetics, mechanisms, and density functional theory calculations. *Inorg. Chem.* **2004**, *43*, 4036-4050.

9. Ainsworth, S. Michaelis-Menten Kinetics. In *Steady-State Enzyme Kinetics;* Macmillan Education UK: London, 1977; pp 43-73.

10. Shuai, D.; Choe, J. K.; Shapley, J. R.; Werth, C. J. Enhanced activity and selectivity of carbon nanofiber supported Pd catalysts for nitrite reduction. *Environ. Sci. Technol.* **2012**, *46*, 2847-2855.

11. Weisz, P.; Prater, C. Interpretation of measurements in experimental catalysis. *Adv. Catal* **1954**, *6*, 60390-60399.

12. Satterfield, C. N. *Mass Transport in Heterogeneous Catalysis;* MIT Press: Cambridge, MA, 1970.

13. Davie, M. G.; Reinhard, M.; Shapley, J. R. Metal-catalyzed reduction of N-nitrosodimethylamine with hydrogen in water. *Environ. Sci. Technol.* **2006**, *40*, 7329-7335.

14. Heil, S. R.; Holz, M.; Kastner, T. M.; Weingärtner, H. Self-diffusion of the perchlorate ion in aqueous electrolyte solutions measured by ³⁵Cl NMR spin–echo experiments. *J. Chem. Soc. Faraday Trans.* **1995**, *91*, 1877-1880.

15. Sänger, P.; Deckwer, W.-D. Liquid—solid mass transfer in aerated suspensions. *Chem. Eng. J.* **1981**, 22, 179-186.

16. Sano, Y.; Yamaguchi, N.; Adachi, T. Mass transfer coefficients for suspended particles in agitated vessels and bubble columns. *J. Chem. Eng. Japan* **1974**, *7*, 255-261.

17. Bates, R. L.; Fondy, P. L.; Corpstein, R. R. Examination of some geometric parameters of impeller power. *Ind. Eng. Chem. Process. Des. Dev.* **1963**, *2*, 310-314.

18. Liu, B.; Yao, H.; Song, W.; Jin, L.; Mosa, I. M.; Rusling, J. F.; Suib, S. L.; He, J. Ligand-free noble metal nanocluster catalysts on carbon supports via "soft" nitriding. *J. Am. Chem. Soc.* **2016**, *138*, 4718-4721.

19. Kishii, N.; Araki, K.; Shiraishi, S. The changes in conformation and complexability of 6,6'-diamino-2,2'-bipyridine by protonation. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2121-2126.

20. Amarante, T. R.; Neves, P.; Tomé, C. t.; Abrantes, M.; Valente, A. A.; Paz, F. A. A.; Pillinger, M.; Gonçalves, I. S. An octanuclear molybdenum(VI) complex containing coordinatively bound 4,4'-di-tertbutyl-2,2'-bipyridine, [Mo₈O₂₂(OH)₄(di-*t*Bu-bipy)₄]: Synthesis, structure, and catalytic epoxidation of bioderived olefins. *Inorg. Chem.* **2012**, *51*, 3666-3676.

21. You, J.; Wu, D.; Liu, H. Electrochemical studies of molybdate and thiomolybdates. *Polyhedron* **1986**, *5*, 535-537.

22. Hurley, K. D.; Shapley, J. R. Efficient heterogeneous catalytic reduction of perchlorate in water. *Environ. Sci. Technol.* **2007**, *41*, 2044-2049.

23. Liu, J.; Han, M.; Wu, D.; Chen, X.; Choe, J. K.; Werth, C. J.; Strathmann, T. J. A new bioinspired perchlorate reduction catalyst with significantly enhanced stability via rational tuning of rhenium coordination chemistry and heterogeneous reaction pathway. *Environ. Sci. Technol.* **2016**, *50*, 5874-5881.

24. Abu-Omar, M. M.; McPherson, L. D.; Arias, J.; Béreau, V. M. Clean and efficient catalytic reduction of perchlorate. *Angew. Chem.* **2000**, *112*, 4480-4483.

25. Ford, C. L.; Park, Y. J.; Matson, E. M.; Gordon, Z.; Fout, A. R. A bioinspired iron catalyst for nitrate and perchlorate reduction. *Science* **2016**, *354*, 741-743.

26. Drummond, M. J.; Miller, T. J.; Ford, C. L.; Fout, A. R. Catalytic perchlorate reduction using iron: Mechanistic insights and improved catalyst turnover. *ACS Catal.* **2020**, *10*, 3175-3182.

27. Choe, J. K.; Shapley, J. R.; Strathmann, T. J.; Werth, C. J. Influence of rhenium speciation on the stability and activity of Re/Pd bimetal catalysts used for perchlorate reduction. *Environ. Sci. Technol.* **2010**, *44*, 4716-4721.