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REVIEW ARTICLE

# Catalytic reduction of water pollutants: knowledge gaps, lessons learned, and new opportunities

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## HIGHLIGHTS

- Advances, challenges, and opportunities for catalytic water pollutant reduction.
- Cases of Pd-based catalysts for nitrate, chlorate, and perchlorate reduction.
- New functionalities developed by screening and design of catalytic metal sites.
- Facile catalyst preparation approaches for convenient catalyst optimization.
- Rational design and non-decorative effort are essential for future work.

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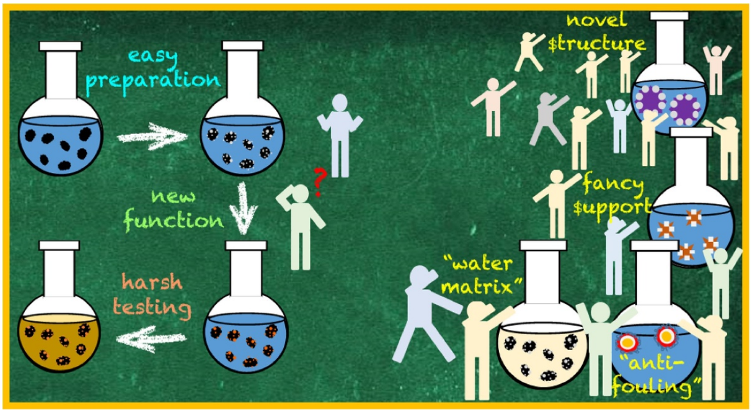
## GRAPHIC ABSTRACT



## ABSTRACT

In this paper, we discuss the previous advances, current challenges, and future opportunities for the research of catalytic reduction of water pollutants. We present five case studies on the development of palladium-based catalysts for nitrate, chlorate, and perchlorate reduction with hydrogen gas under ambient conditions. We emphasize the realization of new functionalities through the screening and design of catalytic metal sites, including (i) platinum group metal (PGM) nanoparticles, (ii) the secondary metals for improving the reaction rate and product selectivity of nitrate reduction, (iii) oxygen-atom-transfer metal oxides for chlorate and perchlorate reduction, and (iv) ligand-enhanced coordination complexes for substantial activity enhancement. We also highlight the facile catalyst preparation approach that brought significant convenience to catalyst optimization. Based on our own studies, we then discuss directions of the catalyst research effort that are not immediately necessary or desirable, including (1) systematic study on the downstream aspects of under-developed catalysts, (2) random integration with hot concepts without a clear rationale, and (3) excessive and decorative experiments. We further address some general concerns regarding using $H_2$ and PGMs in the catalytic system. Finally, we recommend future catalyst development in both "fundamental" and "applied" aspects. The purpose of this perspective is to remove major misconceptions about reductive catalysis research and bring back significant innovations for both scientific advancements and engineering applications to benefit environmental protection.

## 1 Introduction

Since the first report (Vorlop and Tacke, 1989), catalytic reduction of water pollutants has been extensively studied for over 30 years (Chaplin et al., 2012; Yin et al., 2018; Heck et al., 2019). The target pollutants include toxic oxyanions (e.g., nitrate ($NO_3^-$), nitrite ($NO_2^-$), bromate ($BrO_3^-$), chlorate ($ClO_3^-$), perchlorate ($ClO_4^-$), chromate ($CrO_4^{2-}$)), organic halides (e.g., various brominated, chlorinated, or fluorinated hydrocarbons and functional

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molecules), and nitro- and nitroso- compounds (e.g., TNT, RDX, and NDMA, Fig.1). For water treatment, hydrogen gas ($H_2$) is an ideal electron source because the byproduct is $H_2O$:

$$ClO_4^- + 4\,H_2 \rightarrow Cl^- + 4\,H_2O \tag{1}$$

$$2\,NO_3^- + 5\,H_2 + 2\,H^+ \rightarrow N_2 + 6\,H_2O \tag{2}$$

The activation of $H_2$ (into 2 $e^-$ + 2 $H^+$) at ambient temperature (e.g., 20 °C) and pressure (1 atm) is enabled by heterogeneous catalysts, which typically contain platinum-group metal (PGM) nanoparticles on high-surface-area support (e.g., activated carbon C, $\gamma$-alumina $Al_2O_3$, and porous silica $SiO_2$). The PGMs include ruthenium (Ru), osmium (Os), rhodium (Rh), iridium (Ir), palladium (Pd), and platinum (Pt).

Despite the unique advantages of reductive catalysis, especially (i) the use of $H_2$ as a clean electron source, (ii) the completion of pollutant treatment under ambient conditions, and (iii) the simplicity of catalyst preparation, reactor setting, and result interpretation, the topic of reductive catalysis for water pollutant treatment has been recently vanishing from the academic research focus. However, this trend is not caused by the technology maturity that leaves no opportunity for further innovation. It is also not caused by the development of other technologies showing better cost-effectiveness. While some criticize the use of PGM (costly) and $H_2$ gas (flammable), the recent upsurge of electrochemical reduction of nitrate ($NO_3^-$) into ammonia ($NH_3$) excludes both PGM and $H_2$ as negative factors. In those rapidly emerging studies since 2020, various PGMs are used on the electrode (Li et al., 2020; Lim et al., 2021; Chen et al., 2022), and the electrochemical systems also produce $H_2$ as an undesirable byproduct. Thus, the dramatic shift of research interest triggers curiosities, such as (i) what has

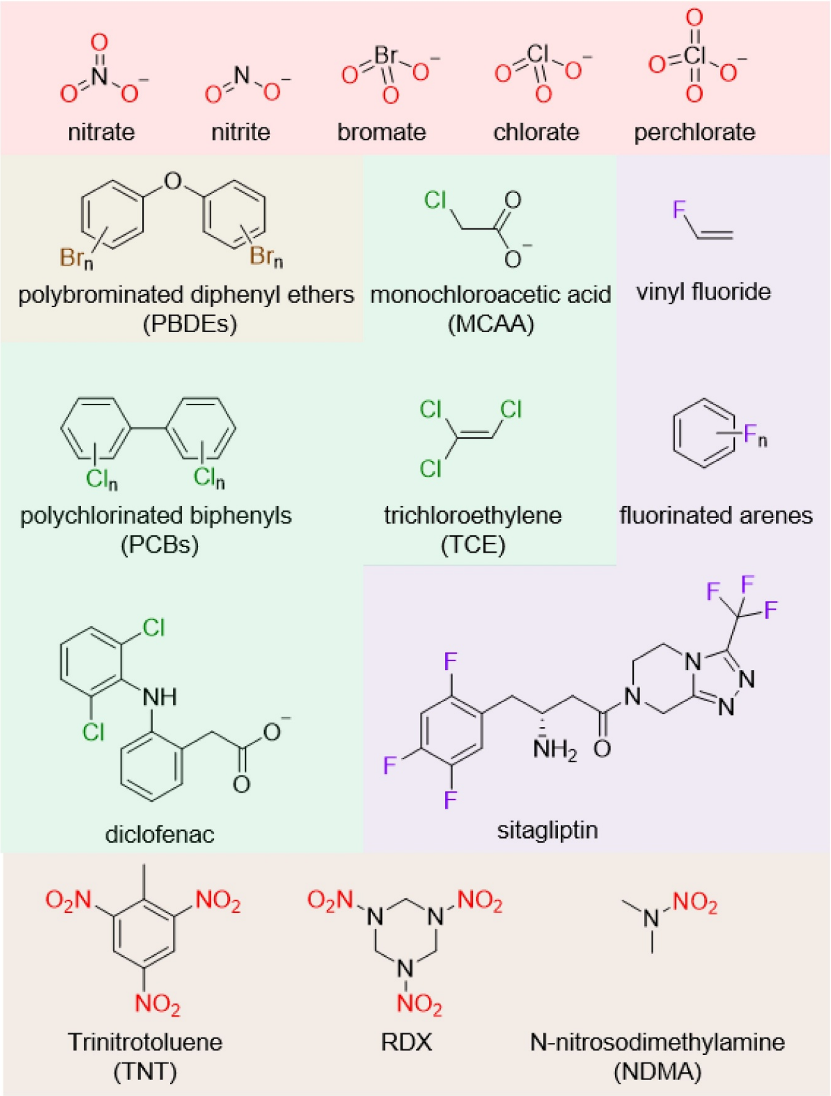

**Fig. 1** Representative pollutants reported to be degraded by reductive catalysis.

been achieved and (ii) why the direction is now considered obsolete. Moreover, young researchers are more interested in (i) what knowledge gaps need to be filled, (ii) what misconceptions and pitfalls need to be avoided, and (iii) what new opportunities are in this “mistakenly abandoned” direction.

This paper will first provide a brief review of oxyanion reduction catalyst development, then discuss the lessons learned and knowledge gaps identified. It highlights past advances (in terms of overcoming technical challenges rather than generating “academic hotspots”) and proposes new research opportunities. The discussion focuses on PGM catalysts using $H_2$ as the electron source. Although the electrochemical/electrocatalytic reduction systems are not in the scope of this paper, the two approaches have close similarities in design rationales and working mechanisms (Werth et al., 2020). References are cited to support the authors’ perspectives. Readers can find excellent comprehensive literature reviews of this field in the references (Chaplin et al., 2012; Yin et al., 2018; Heck et al., 2019).

## 2 Case studies of advances in reductive catalysis

### 2.1 Nitrate reduction catalysts toward dinitrogen ($N_2$)

The reduction of $NO_3^-$ was the original motivation for developing oxyanion reduction catalysts. This case study shows the rapid development of various aspects of a catalytic system. In stark comparison, 30 years later, the pace of catalyst innovation has been substantially slower. This phenomenon is worth reflection among the environmental catalysis research community.

The first report (Vorlop and Tacke, 1989) initiated the development of PGM catalysts to reduce $NO_2^-$ and $NO_3^-$. It explicitly pointed out that although $NO_3^-$ in drinking water can be removed by ion exchange, electrodialysis, and reverse osmosis, the concentrated oxyanions required degradation treatment for disposal. It also noted the rapid catalytic treatment of $NO_3^-$ compared to microbial reactors. The earliest report confirmed the activity of both $Pd/Al_2O_3$ and $Pt/Al_2O_3$ for $NO_2^-$ reduction. Doping various secondary metals such as copper (Cu), nickel (Ni), chromium (Cr), cobalt (Co), and iron (Fe) to $Pd/Al_2O_3$ enabled $NO_3^-$ reduction (Fig. 2). While most secondary metals converted $NO_3^-$ into $NH_3$, Cu allowed a faster rate of $NO_3^-$ reduction and a lower selectivity toward the toxic $NH_3$. In the following report (Vorlop et al., 1992), the product selectivity (i.e., $N_2$ versus $NH_3$) was attributed to metal content, support materials, and solution pH. This work also identified tin (Sn) as another secondary metal for $NO_3^-$ reduction. In the third report (Tacke and Vorlop, 1993), the Cu−$Pd/Al_2O_3$ catalyst powder was further encapsulated in alginate beads. A fluidized pilot reactor was operated for 100 days without catalyst deactivation. Detailed experimental data mentioned in the above reports in German were compiled in another paper in English (Hörold et al., 1993), which was often considered the “first report” of catalytic $NO_2^-$ and $NO_3^-$ reduction. In 1997, Prüsse et al. (1997) identified indium (In) as an even better option than Cu and Sn for both $NO_3^-$ reduction kinetics and product selectivity toward $N_2$. Systematic investigations of In−Pd, Sn−Pd, and Cu−Pd were reported in 2000 (Prüsse et al., 2000) and 2001 (Prüsse and Vorlop, 2001).

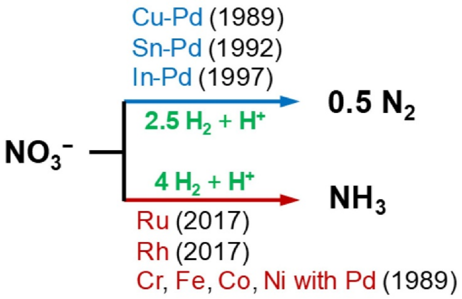

**Fig. 2** Major catalysts for nitrate reduction.

The studies of various aspects by Vorlop and colleagues built the framework for oxyanion reduction catalyst development in the following three decades: (i) the use of Pd as the primary choice of metal, (ii) the integration with a second metal to enable the reaction with challenging substrates, (iii) product selectivity (i.e., pathway control) and the influencing factors, and (iv) catalyst longevity and robustness. Around 400 papers have cited each of those publications (Hörold et al., 1993; Prüsse et al., 2000; Prüsse and Vorlop, 2001). The three bimetallic formulations also dominated the following research on $NO_3^-$ reduction toward $N_2$. A quick search of the most recent publications between 2016 and 2022 found meticulous advanced studies. Examples include spectroscopic characterization and theoretical simulations of In−Pd nanostructures (Guo et al., 2018), boosting the reaction kinetics and deactivation resistance of In−Pd by gold (Au) (Guo et al., 2022), immobilization of In−Pd onto sustainable and scalable natural fibers (Durkin et al., 2018), immobilization of Sn−Pd onto red mud (Hamid et al., 2018) and coal fly-ash-derived zeolites (Park et al., 2019). Notably, the electrochemical $NO_3^-$ reduction toward $N_2$ also adopted similar design rationales. For example, Sn−Pd was electrochemically deposited on stainless steel mesh (Su et al., 2020); the Cu−Pd was directly used as a suspension in an electrochemical chamber (Zhang et al., 2016; Chen et al., 2019).

In short, the development of nitrate reduction catalysts had rapid growth at the beginning. The first report had already included various aspects that could be covered by multiple research articles as of today. The Cu−Pd, Sn−Pd, and In−Pd formulations were first reported in 1989, 1992, and 1997, respectively. After that, the following studies have significantly improved the catalyst formulation and mechanistic understanding of the three formulations instead of identifying new metal species.

### 2.2 Nitrate reduction catalysts toward ammonia ($NH_3$)

The original studies aimed to convert $NO_3^-$ and $NO_2^-$ into $N_2$ rather than into the toxic $NH_3$ (Vorlop and Tacke, 1989). Both the Drinking Water Ordinance of Germany in 1989 (Vorlop and Tacke, 1989) and the new Standards for Drinking Water Quality issued by the Ministry of Environmental Protection of China in 2022 (Standardization Administration of China, 2022) set the limit for $NH_3$ at 0.5 mg/L. $NH_3$ in source waters is a highly challenging pollutant (Ye et al., 2022). However, in 2020, the goal of electrochemical conversion of $NO_3^-$ suddenly switched from $N_2$ to $NH_3$ because the latter is reconsidered as a value-added product. This switch is more or less astounding because it reversed the efforts made in the past three decades (1989–2019) when the production of $NH_3$ was considered a failure of catalyst development.

The discussion of the environmental significance of producing $N_2$ versus $NH_3$ is not in the scope of this perspective. However, the metal-dependent functionality is noteworthy. The initial selection of Pd as the primary PGM was from a single test during the original exploration (Hörold et al., 1993). Five metals, Pd, Pt, Ru, Ir, and Rh, on $Al_2O_3$ support were screened by $NH_3$ production from $NO_2^-$. $Pd/Al_2O_3$ showed a distinctly low $NH_3$ production, so it was further used to prepare bimetallic catalysts for $NO_3^-$ reduction. Interestingly, most subsequent studies on the reduction of $NO_3^-$ and other pollutants kept using Pd as the sole PGM for more than two decades. This situation motivated us to re-examine the five PGMs (Os is highly toxic and unsuitable for water treatment) on carbon and $Al_2O_3$ supports (Chen et al., 2017). To our surprise, both Ru/C and $Ru/Al_2O_3$ showed high activity of $NO_3^-$ reduction without using any secondary metal. The following study further confirmed nearly 100 % selectivity to $NH_3$ by Ru catalysts (Fig. 2) (Huo et al., 2017; Kong et al., 2022). Notably, Ru is also used in recent electrochemical systems for $NH_3$ synthesis from $NO_3^-$ (Li et al., 2020; Chen et al., 2022). Because electrochemical methods do not require a PGM to extract electrons from $H_2$, many other electrode materials only contained the first-row transition metals such as Fe, Co, Ni, and Cu (Chen et al., 2020; Wang et al., 2020; Wu et al., 2021; He et al., 2022; Li et al., 2022), which are consistent with the initial findings (Vorlop and Tacke, 1989; Hörold et al., 1993).

In short, the switch of PGM metal (e.g., from Pd to Ru) and the secondary metal (e.g., from In/Sn/Cu to Fe/Co/Ni) can dramatically switch the reaction pathway from yielding > 70 % $N_2$ to ~100 % $NH_3$. Despite the emerging confusion about the product preference, the two upsurges of $NO_3^-$ reduction technology in the early 1990s and the early 2020s clearly suggest abundant opportunities for catalyst innovation, including the reactivity, pathway, and functionality, from a rational selection of PGMs and the secondary metals.

### 2.3 Chlorate and perchlorate reduction catalysts

The 2022 new Standards for Drinking Water Quality of China set the concentrations of $BrO_3^-$, $ClO_3^-$, and $ClO_4^-$ at 0.01, 0.7, and 0.07 mg/L, respectively (Standardization Administration of China, 2022). $BrO_3^-$ is a carcinogen and can be generated from $Br^-$ under natural and engineered oxidation (Chen et al., 2017; Gao et al., 2021). $ClO_3^-$ is a common toxic byproduct of chlorine disinfection or electrochemical oxidation (Ren et al., 2020). $ClO_4^-$ is an endocrine-disrupting pollutant from energetic materials. Beyond the Earth, it is also a rich component in the Martian soil (Ren et al., 2021a). Detailed literature for the background information of these anion pollutants can be found in the cited research reports. Using Pd and Cu–Pd catalysts to reduce $BrO_3^-$ and $ClO_3^-$ can be traced back to a patent filed in 1994 (Becker et al., 1998). Among the three oxyanions, $BrO_3^-$ is the most labile substrate and can be rapidly reduced by various Pd-only catalysts reported since 2010 (Chen et al., 2010; Wang et al., 2014; Cerrillo et al., 2021; Gao et al., 2021). In comparison, $ClO_3^-$ is much more recalcitrant than $BrO_3^-$. While the chloralkali process has developed Rh (Van Santen et al., 2001) and Ir (Kuznetsova et al., 2012) catalysts to reduce $ClO_3^-$, which is an undesirable byproduct in the concentrated brine, academia seldom worked on $ClO_3^-$ reduction. The limited attempts confirmed the challenge of $ClO_3^-$ to Pd-only catalysts (Liu et al., 2015a; Ye et al., 2018).

Again, the enhanced degradation of recalcitrant oxyanions could be achieved by introducing specific metal species (Fig. 3). For example, we recently found that the immobilization of molybdenum (Mo) into Pd/C accelerated $ClO_3^-$ reduction by 55 times (Ren et al., 2020). The source of Mo is the common fertilizer, sodium molybdate ($Na_2MoO_4$) or ammonium molybdate [$(NH_4)_6Mo_7O_{24}$]. Under the reducing condition of Pd+$H_2$ at room temperature, the $Mo^{VI}$ precursor is reduced to a mixture of $Mo^{II}$, $Mo^{III}$, $Mo^{IV}$, and $Mo^{V}$ oxides. At pH 3.0, the $MoO_x$–Pd/C catalyst showed comparable activity to the much more expensive Rh catalysts. A more attractive feature of $MoO_x$–Pd/C is the much higher resistance to concentrated salts (e.g., $SO_4^{2-}$ and $Cl^-$ at mol/L levels) than Rh. Interestingly, tungsten (W) in similar mineral compositions, such as sodium tungstate ($Na_2WO_4$ and $Na_6W_{12}O_{39}$), showed no activity enhancement.

As for the most recalcitrant $ClO_4^-$, the activity of $MoO_x$–Pd/C catalyst was too low to provide a satisfying

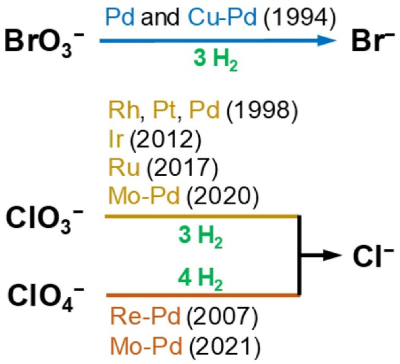

**Fig. 3** Major catalysts for bromate, chlorate, and perchlorate reduction.

reaction rate. Before we added organic ligands to enhance the $ClO_4^-$ reduction by $MoO_x$–Pd/C (see below) (Ren et al., 2021a), the technical solution had been dominated by rhenium (Re)-based $ReO_x$–Pd catalysts since 2007 (Hurley and Shapley, 2007). The reductive immobilization of perrhenate salts (e.g., $KReO_4$) in Pd/C yield a mixture of $Re^I$, $Re^{III}$, and $Re^V$ oxides (Choe et al., 2010; Choe et al., 2014). At room temperature, the reduced Re species can directly reduce $ClO_4^-$.

Using oxometallate species of Group 6 (Mo (Kolthoff, 1921; Haight and Sager, 1952) and W (Haight, 1954)), Group 7 (Re) (Abu-Omar and Espenson, 1995), and Group 8 (Os (Crowell et al., 1940)) metals to reduce $ClO_3^-$ and $ClO_4^-$ can be traced back to as early as 1921. However, the early systems required concentrated acids (e.g., 1–10 mol/L HCl or $H_2SO_4$) and toxic reducing agents (e.g., HBr, $SnCl_2$, and $H_3PO_2$). Water treatment engineering requires knowledge transfer from those seminal studies in homogenous solutions to the heterogeneous catalytic systems using $H_2$ as the clean reductant (Fig. 4). But as summarized above, common $W^{VI}$ oxometallate salts did not work with the Pd/C+$H_2$ platform. We also excluded osmate ($OsO_4^{2-}$) as a candidate due to the high cost and high toxicity of Os and the limited activity observed in our preliminary tests with $OsO_x$–Pd/C. On the Pd/C+$H_2$ platform, reduced oxophilic metal species (e.g., $Re^V$, $Mo^{IV}$) trigger the stepwise reduction of $ClO_4^-$ via a new mechanism, oxygen atom transfer (OAT) (Holm, 1987):

$$ClO_4^- + Re^V/Mo^{IV} \rightarrow ClO_3^- + Re^{VII}O/Mo^{VI}O \qquad (3)$$

Although $ClO_3^-$ and $ClO_x^-$ products can be directly reduced by PGM+$H_2$, the reduction of $ClO_4^-$ requires the OAT mechanism and is usually the rate-limiting step. The primary role of PGM+$H_2$ is to reduce the oxidized OAT metal back to the reduced state, thus forming the catalytic cycle:

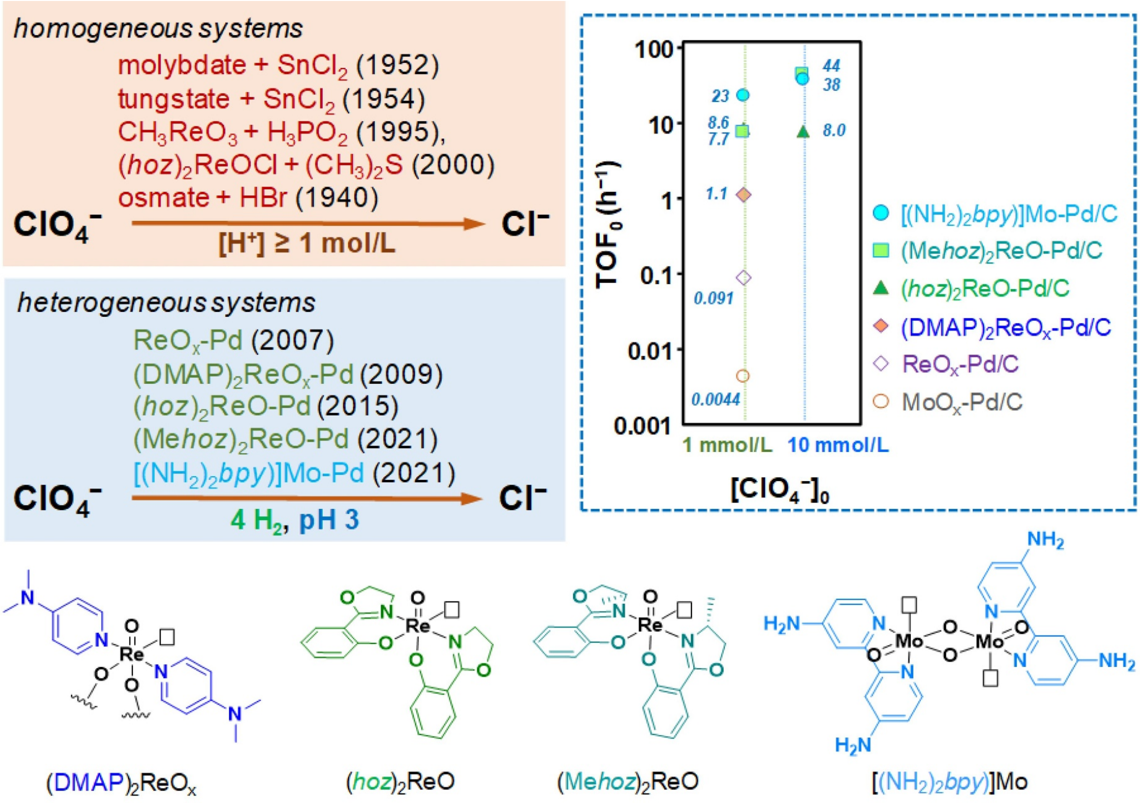

**Fig. 4** Catalytic systems for perchlorate reduction and the proposed or determined structures of organic ligand-coordinated $Re^V$ and $Mo^{IV}$ metal sites on the carbon surface.

$$\mathrm{Re^{VII}O/Mo^{VI}O + H_2 \rightarrow Re^{V}/Mo^{IV} + H_2O} \tag{4}$$

Before the ligand enhancement was systematically studied, the original $ReO_x$–Pd catalyst was directly applied to treat the waste brine from the regeneration of ion-exchange resins (Liu et al., 2013). For practical application of pollutant degradation technologies, rapid removal of oxyanions from contaminated drinking water by ion exchange is always necessary. The resin regeneration typically uses concentrated NaCl to liberate $ClO_4^-$ and $NO_3^-$ from the resin capture sites (e.g., $-NR_3^+$ functional groups). Therefore, concentrated $ClO_4^-$ and $NO_3^-$ need to be degraded in the presence of concentrated $Cl^-$ and $SO_4^{2-}$ (also captured from the groundwater). In general, one would expect the metal catalysts to be more or less inhibited by concentrated salts, but $ClO_4^-$ reduction by $ReO_x$–Pd/C was surprisingly enhanced by concentrated NaCl (Liu et al., 2013). A probable explanation is the enhanced activity of $H^+$ (i.e., $\{H^+\} > [H^+]$, activity coefficient $\gamma > 1$) in the presence of concentrated salts. Because each dissolved $Na^+$ and $Cl^-$ are theoretically solvated by six and two $H_2O$ molecules, respectively, the dissolution of > 1 mol/L NaCl would significantly reduce the $H_2O$ molecules available for $H^+$ solvation. As $ClO_4^-$ reduction is assisted by $H^+$ (an acidic pH such as 3.0 is usually required), the enhanced activity of $H^+$ due to reduced solvation might accelerate the reaction. A systematic discussion of the higher $\{H^+\}$ in concentrated salt solutions can be found in the supporting file of the report (Liu et al., 2013).

Interestingly, although $ReO_x$–Pd/C could also rapidly reduce $NO_3^-$ ($NH_3$ was the primary product), the activity for $ClO_4^-$ reduction was shut down by the $NO_3^-$ co-contaminant. To solve this challenge, we added In–Pd/$Al_2O_3$ to reduce $NO_3^-$ before using $ReO_x$–Pd/C to reduce $ClO_4^-$. This sequential process design successfully avoided $ReO_x$–Pd/C deactivation by $NO_3^-$.

In short, integrating a functional metal can help the PGM catalyst reduce challenging oxyanions. The addition of an oxometallate precursor of Group 6–8 metals utilizes the new OAT mechanism. The bimetallic system has the following advantages. First, the incorporation of the OAT metal is realized by an *in situ* reduction of the common mineral salt. Second, the substantial activity enhancement saves PGM while ensuring the same catalytic activity. Third, the rate-limiting reaction at the OAT metal site is not severely inhibited (e.g., $MoO_x$–Pd/C) or even accelerated (e.g., $ReO_x$–Pd/C) by concentrated salts.

### 2.4 Ligand-enhanced perchlorate reduction

Although $ReO_x$–Pd/C showed unique $ClO_4^-$ reduction activity as a heterogeneous catalyst, the reaction rate was still much lower than that of $BrO_3^-$ reduction by Pd-only catalysts or $ClO_3^-$ reduction by $MoO_x$–Pd/C. In general, the catalyst activity can be estimated by the following primary parameters: half-life of the oxyanion reduction (min or h), initial concentration of the oxyanion (mmol/L), catalyst loading (g/L), and metal content in the catalyst (wt%). Although the rigorous approach is to calculate the initial turnover frequency ($TOF_0$, Fig. 4) by considering the number of available metal atoms at the catalyst surface, the comparison of those kinetic parameters provides a quick estimation. The comparison is often fair because (i) the catalyst developers are responsible for maximizing the utilization of PGM, and (ii) many studies did not provide metal dispersion data to calculate $TOF_0$. For the reduction of 1 mmol/L $ClO_4^-$, the use of 2.0 g/L of $ReO_x$–Pd/C (5 wt% Re, 5 wt% Pd) showed a half-life between 2.5 and 6 h, depending on the batch of commercial Pd/C (Liu et al., 2013). In comparison, for the reduction of 1 mmol/L $ClO_3^-$, the use of 0.2 g/L of $MoO_x$–Pd/C (5 wt% Mo and 5 wt% Pd) showed a half-life of < 10 min (Liu et al., 2013). Apparently, the $ClO_4^-$ reduction activity on the catalyst surface had great room for improvement.

Ligand-enhanced catalysis was motivated by the comparison with a molecular Re(O)(*hoz*)$_2$Cl complex (Fig. 4), which contains one oxo ligand, one chloro ligand, and two N,O-bidentate ligands [$L_{O-N}$, *hoz* = 2-(2’-***h***ydroxyphenyl)-2-***o***xa***z***oline] (Abu-Omar et al., 2000). This complex showed rapid $ClO_4^-$ reduction in a homogeneous system, where acetonitrile was the solvent and dimethylsulfide was the oxygen acceptor:

$$\begin{aligned}&\mathrm{ClO}_x^- + [\mathrm{Re^V(O)}(hoz)_2]^+\\&\rightarrow \mathrm{ClO}_{x-1}^- + [\mathrm{Re^{VII}(O)_2}(hoz)_2]^+\end{aligned} \tag{5}$$

$$\begin{aligned}&[\mathrm{Re^{VII}(O)_2}(hoz)_2]^+ + \mathrm{(CH_3)_2S}\\&\rightarrow [\mathrm{Re^V(O)}(hoz)_2]^+ + \mathrm{(CH_3)_2S=O}\end{aligned} \tag{6}$$

The immobilization of the Re(O)(*hoz*)$_2$Cl complex onto Pd/C achieved rapid $ClO_4^-$ reduction by $H_2$. Using the same metrics of comparison, 0.5 g/L of Re(O)(*hoz*)$_2$–Pd/C (5 wt% Re and 5 wt% Pd) shortened the half-life of 1 mmol/L $ClO_4^-$ to ~15 min. Therefore, in comparison to $ReO_x$–Pd/C, the use of ¼ of the catalyst loading and > 10x faster reaction suggest a > 40x activity enhancement by the coordination of Re with two *hoz* ligands. The design rationale, mechanistic elucidation, and stability improvement of the Re(O)($L_{O-N}$)$_2$–Pd/C catalyst family (Zhang et al., 2011; Liu et al., 2015a; Liu et al., 2015b; Liu et al., 2016a; Liu et al., 2016b; Liu et al., 2017; Ren and Liu, 2021) are not in the scope of this paper. The concise point is that tuning the ligand structure could bring in substantial enhancement of the catalyst activity and stability at the scale of 1–2 orders of magnitude. The ligand effect is much more pronounced than other approaches for catalyst development, such as changing the catalyst support material.

Although the Re(O)(*hoz*)$_2$Cl complex is air-stable and can be immobilized onto Pd/C by adsorption, its multistep synthesis from $KReO_4$ and irreversible decomposition affected the potential application. Therefore, the *in* *situ* formation of active Re sites from the $KReO_4$ precursor and free organic ligand is an alternative route. The direct addition of *hoz* ligand (*hoz* : Re = 2:1) into $ReO_x$−Pd/C achieved merely 4x faster $ClO_4^-$ reduction kinetics, but the addition of the monodentate pyridine ligands (e.g., 4-dimethylaminopyridine) (Hurley et al., 2009) showed even better results (up to 12x) (Liu et al., 2015b). Thus, ligand selection is a key factor for activity enhancement.

A similar attempt on the $MoO_x$−Pd/C catalyst resulted in a major breakthrough. Without the addition of organic ligands, the catalyst showed little activity by reducing < 4 % of 1 mmol/L $ClO_4^-$ at a loading of 2.0 g/L after 8 h. However, various N,N-bidentate ligands significantly accelerated the reaction (Ren et al., 2021a). The best ligand was 4,4'-diamino-2,2'-bypyridine $[(NH_2)_2$*bpy*] (Fig. 4). With the addition of $(NH_2)_2$*bpy*:$Na_2MoO_4$ at 1:1, the $[(NH_2)_2$*bpy*]$MoO_x$−Pd/C catalyst at 0.2 g/L loading shortened the half-life of 1 mmol/L $ClO_4^-$ to ~15 min. The coordination of the $(NH_2)_2$*bpy* ligand with the $Mo^{IV}$ site thus led to a > 6200x enhancement of the reactivity with $ClO_4^-$. Interestingly, in the case of Mo catalysts, monodentate pyridine ligands resulted in very limited enhancement. The ligand adaptability for $MoO_x$−Pd/C and $ReO_x$−Pd/C showed opposite trends for monodentate N versus bidentate N−N ligands. Currently, the selection of organic ligands for $ClO_4^-$ reduction catalysts is still empirical rather than rational. Notably, most research resources have been spent on other directions, such as the synthesis of nanostructured metal particles and support materials (Chaplin et al., 2012; Yin et al., 2018; Heck et al., 2019), rather than the molecular design of coordinated metals.

The $[(NH_2)_2$*bpy*]$MoO_x$−Pd/C catalyst was further evaluated under a series of harsh conditions (Fig. 5) that simulated real waste brine treatment applications, where (1) concentrated salts (e.g., $Cl^-$, $SO_4^{2-}$, $NO_3^-$) and natural organic matters (NOM) are present, (2) the catalyst is under extended exposure to $H_2$, (3) the catalyst is under excessive oxidative stress by concentrated $ClO_4^-$ in brine and $O_2$ during the handling in air (Ren et al., 2022). Similar to the $ReO_x$−Pd/C catalyst, the $[(NH_2)_2$*bpy*]$MoO_x$−Pd/C was deactivated by $NO_3^-$ but the use of In−Pd/$Al_2O_3$ to reduce $NO_3^-$ could solve the issue. This phenomenon broke our initial expectation because (1) nitrate was considered more labile than perchlorate to reduce, and (2) common nitrogen products such as NO, $N_2O$, or $NH_3$ were not expected to inhibit either Re or Mo catalysts. Such an interesting issue in selectivity and inhibition indicated our shallow understanding of coordination chemistry and great scientific promise for future studies. The $[(NH_2)_2$*bpy*]$MoO_x$−Pd/C showed high stability against multiple spikes of 100 mmol/L $ClO_4^-$ (Fig. 5(a)), air exposure, and up to 50 mg/L of humic acid. Although the prolonged ligand hydrogenation lowered the activity by 90 % after three weeks (Fig. 5(b)), a simple pH adjustment to 12.0 could remove all Mo species. The Pd/C could thus be reused with a new batch of Mo and $(NH_2)_2$*bpy* ligand (Fig. 5(c)). The $[(NH_2)_2$*bpy*]$MoO_x$−Pd/C appears to be competent for practical applications.

In short, coordinating selected organic ligands with the OAT metal (e.g., Mo and Re) substantially enhanced activity, more than three orders of magnitude, for reducing the most recalcitrant $ClO_4^-$. The above examples showcase the importance of (1) utilizing alternative reaction mechanisms by new metal elements and (2) harnessing the power of coordination chemistry to advance environmental catalysis. These two directions are much less explored compared to the tuning of nanostructured particles and supports of Pd-only catalysts.

A typical reservation about adding organic ligands to accelerate the reaction is that the catalyst becomes more complicated than the ligand-free (or "totally inorganic") system. To address such concerns, we can compare the catalysts with natural systems, which rely on various organic-metal complexes in enzymes to degrade pollutants. However, it is also worth comparing the usually neglected but substantial "organic footprint" from

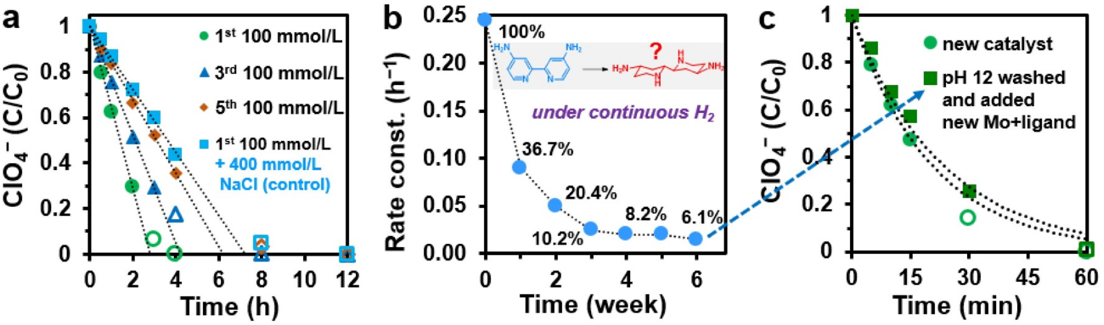

**Fig. 5** Examples of robustness tests of the $[(NH_2)_2$*bpy*]$MoO_x$−Pd/C catalyst: continuous treatment of highly concentrated $ClO_4^-$; long-term exposure to $H_2$; and Pd/C reuse after the deactivation of Mo species. The data have been reported by Ren et al. (2022) and shown here with modified displays.

the preparation of “inorganic” nanostructures. For example, the synthesis of PGM nanocrystals and nanostructured supports consumed organic polymers (e.g., polyvinylpyrrolidone and poloxamers) and organic solvents (e.g., ethanol and tetrahydrofuran). The nitrogen doping on the support material uses urea, melamine, etc. The functionalization of inorganic oxides used 3-aminopropyltriethoxysilane and so on. The formation of ordered pore structures required surfactant templates such as cetyltrimethylammonium bromide, which was later burnt in oven or washed away by organic solvents. The synthesis of inorganic oxides started from organic reagents such as tetraethyl silicate and tetrabutyl titanate. Even the single-atom catalytic sites could use organometallic complexes as the precursor. While citations are not included here, the readers can readily find a handful of reports with detailed information. After comparison, the advantage of the ligand-enhanced catalysis would be overwhelming in terms of simplicity and performance, all attributed to the amazing power of coordination chemistry.

### 2.5 Lowering technical barriers for catalyst development

Despite the evolution of catalyst formulations and functionalities, a frequently encountered challenge is the cost of PGM. In a majority of reports, the Pd content was 5 wt%. While 5 wt% Pd on carbon, alumina, and silica supports are commercially available, the reason for this specific value and the suitability for water pollutant treatment is unknown. However, as most supported Pd catalysts were prepared by multi-step protocols that usually involve drying, calcination, and reduction with heated $H_2$ flow in specialized ovens and furnaces, the effect of Pd content was not investigated in fine detail. We recently developed an “instant” all-*in-situ* preparation method to prepare supported Pd catalysts with any metal content (Gao et al., 2021). The working principle was the high reactivity of $Pd^{II}$ species with $H_2$. In both the aqueous phase and pure solid, $Na_2Pd^{II}Cl_4$ can be rapidly reduced to $Pd^0$ by 1 atm $H_2$. Therefore, after near-complete adsorption of $Pd^{II}$ from water onto the porous carbon support within 5 min, the following exposure to 1 atm $H_2$ at room temperature for another 5 min yielded $Pd^0$/C (Fig. 6a).

Microscopic characterization and kinetic testing using $BrO_3^-$, $ClO_3^-$ (by Pd/C and $MoO_x$–Pd/C) and $ClO_4^-$ (by $ReO_x$–Pd/C) found no significant difference between the prepared Pd/C and commercial Pd/C. This new and convenient approach allowed extensive screening of Pd contents from 0.1 wt% to 10 wt% on the same support material. The result was surprising because the optimal Pd content on the carbon support seemed to be around 0.5 wt%, just 1/10 of the prevalently used 5 wt%. Although the reaction rate by 0.5 wt% Pd/C was lower than 5 wt% Pd/C, the decrease in reaction rate was not in proportion to the decrease in Pd content. In other words, at higher Pd contents, more Pd atoms are inside bigger particles and thus do not participate in the catalysis (Fig. 6(b)). With the same solid catalyst loading, the activity of 0.5 wt% Pd/C was about half of that of 5 wt% Pd/C. Therefore, by doubling the catalyst loading, the catalytic activity remained the same while saving 80% of Pd. This simple optimization of Pd content is equivalent to increasing the catalyst activity by four times (Gao et al., 2021). Our ongoing studies have found that multiple catalyst formulations (for both PGM and OAT metals) can be further lowered from the arbitrary 5 wt%.

It is worth mentioning again that $MoO_x$–Pd/C, $ReO_x$–Pd/C, and $[(NH_2)_2bpy]MoO_x$–Pd/C were all prepared by directly adding the components ($Na_2MoO_4$, $KReO_4$, and free $(NH_2)_2bpy$ ligand) into Pd/C suspension (Fig. 7) (Choe et al., 2010; Ren et al., 2020; Ren et al., 2021a). Under 1 atm $H_2$ and room temperature, the catalytic species were assembled spontaneously from these precursors. In other words, one can rapidly prepare the catalysts from scratch− a porous material (e.g., carbon, alumina, silica, etc.), a PGM precursor (e.g., $Na_2PdCl_4$), an OAT metal precursor (e.g., $Na_2MoO_4$, $KReO_4$), and an organic ligand enhancer, without any heating equipment or specialized synthesis technique. The simplicity and reproducibility are based on the use of

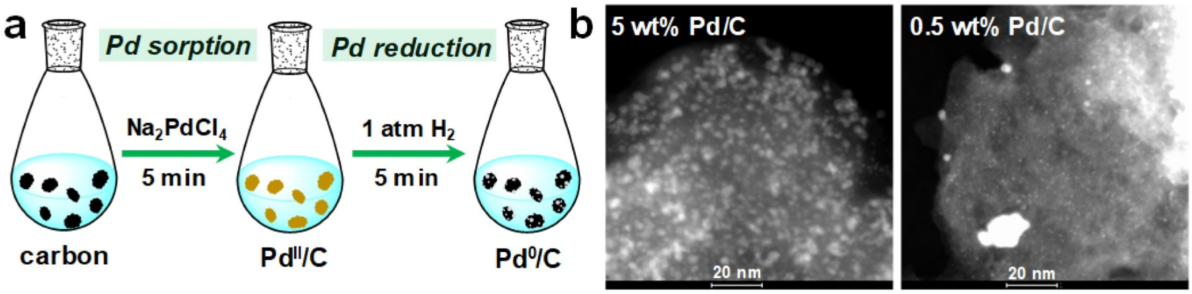

**Fig. 6** Facile preparation of Pd/C catalysts and the scanning transmission electron microscopy (STEM) imagings of 5 wt% Pd/C and 0.5 wt% Pd/C. The two images are reproduced from Gao et al. (2021) with permission. Note that some large Pd particles are present with the expected small ones. This is a common phenomenon (but often not shown in literature for a “good size control”) and similar to the commercial Pd/C catalyst (Fig. 7).

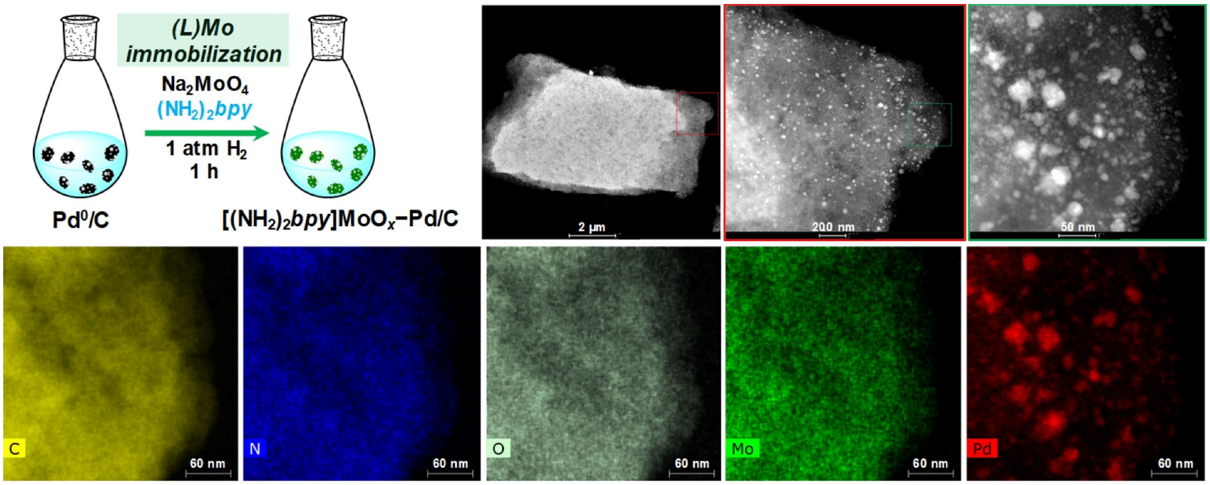

**Fig. 7** Facile preparation of the $[(NH_2)_2$*bpy*$]MoO_x$–Pd/C catalyst and STEM–energy dispersive X-ray (EDX) elemental mapping of a ~10 μm sized catalyst particle. Note that the Pd particles shown here in a commercial 5 wt% Pd/C have a wide size distribution. But this Pd/C showed very similar catalytic performance as the 5 wt% Pd/C prepared by the all-*in-situ* method in Fig. 6.

dissolved molecular components, while the variance of performance would be primarily attributed to the heterogeneous support material.

## 3 Perspectives for catalyst development research

### 3.1 Lessons learned from early efforts

While the five case studies above illustrate the core missions of catalyst development–new functionality, high activity, high stability, and low cost, there have been many other constructive efforts of catalyst development. This perspective cannot summarize all such works, but it is essential to also discuss some directions that we feel are not the priority of catalyst development. To be accurate and fair, we use our own studies as examples:

1) *Systematic study of performance loss of a catalyst that is still under development.* Evaluating the loss of performance is crucial for applications. However, this downstream effort is meaningful only when the catalyst has been adequately developed and researchers are confident to move forward to the application aspects. Suppose a catalyst in the initial development phase holds various intrinsic limitations. In that case, priority should be given to better catalyst design that can overcome such limitations rather than a comprehensive measurement of how the original catalyst fails. For example, the first Re(O)(*hoz*)$_2$–Pd/C catalyst tended to irreversibly decompose into $ReO_4^-$ and two free *hoz* ligands (Liu et al., 2015b). After the general decomposition mechanism was found, a viable solution was to modify the ligand structure to improve stability (Liu et al., 2016a; Ren and Liu, 2021) rather than meticulously measure the effects of water matrices (e.g., 10 mmol/L of $Cl^-$, $Br^-$, $I^-$, $SO_4^{2-}$, $H_2PO_4^-$; $Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$, $Mn^{2+}$, $Fe^{2+}$; pH 2,3,4,5,6; $[ClO_4^-]_0$ = 0.01, 0.1, 1, 10 mmol/L) to the original catalyst (Liu et al., 2015a). For comparison, after the $[(NH_2)_2$*bpy*$]MoO_x$–Pd/C was developed, our evaluation of its application potential used a much more challenging and realistic set of metrics (concentrated salts, five spikes of 100 mmol/L $ClO_4^-$, air exposure, etc.) in greater motivation and confidence (Fig. 5) (Ren et al., 2022). After we became more encouraged to challenge the catalysts with extreme conditions, we also found that the Pd/C catalyst was not inhibited by 2 mol/L $Cl^-$ or 1 mol/L $SO_4^{2-}$ for $BrO_3^-$ reduction at pH 7 (Gao et al., 2021).

2) *Anti-fouling catalyst designs.* Although sulfide and NOM are known fouling species to PGM catalysts (Chaplin et al., 2012), there are instant methods to remove them. Sulfide can be rapidly oxidized into inert $SO_4^{2-}$ using hydrogen peroxide, sodium/calcium hypochlorite, and ferrous/ferric salts (Gao et al., 2021). NOM can be readily removed by coagulation. It is important to point out that the catalytic process is less likely to be integrated into the drinking water treatment process. Hence, a long exposure to trace sulfide and NOM in flowing drinking water seems not a realistic scenario. Instead, treating the concentrated oxyanions after ion-exchange resin regeneration would be important. Therefore, using common oxidants or coagulants to prevent catalyst fouling, rather than cleaning fouled catalysts with oxidants or alkaline chemicals, is a more realistic strategy for the application. The use of reverse osmosis membranes requires various pre- and post-treatment modules (e.g., microfiltration, chlorination, dechlorination, pH adjustments). Therefore, additional treatment steps to protect the central process is a well-established approach. The PGM catalyst is not designed as an independent technology to stand all water matrix challenges. Even if the catalyst is severely fouled by

unexpected species, the PGM can be recycled by established chemical extraction protocols (Fontana et al., 2018; Nogueira et al., 2020; Fotouhi-Far et al., 2021).

3) *Use of novel support materials for known metal species.* There have been numerous studies on using various novel materials to support Pd nanoparticles for the reduction of $BrO_3^-$ and chlorinated organics. In particular, novel electronic properties demonstrated in other disciplines (e.g., graphene for electronic devices) were hypothesized to enhance the supported Pd catalysts. However, there has been no significant activity improvement by such effort yet. This is not surprising because the interaction between PGM particles and the support material is not well understood. A systematic comparison of conventional support materials (e.g., carbon and alumina for different Pd precursors) has been conducted very recently (Cerrillo et al., 2021). How the support can impact the interaction between the PGM particles and pollutant molecules is not well elucidated, either. Although no arbitrary recommendation could be made for this direction, most published data have suggested that the benefits of changing the support material are far less pronounced than altering the metal speciation and reaction pathway. We prepared a "hierarchal" nanostructure, where Pd nanocrystals were immobilized outside an amino-functionalized silica sphere and then encapsulated by a mesoporous silica ($mSiO_2$) layer (Wang et al., 2014). Surprisingly, the $BrO_3^-$ reduction activity of the $mSiO_2$-coated catalyst was > 10x higher than the exposed Pd catalyst. The substantial enhancement was explained by Langmuir-Hinshelwood kinetic model. Probably, this finding may also be attributed to the recently introduced "nanoconfinement" effect. However, even with the $mSiO_2$ coating, the $BrO_3^-$ reduction activity was only 1/40 of a commercial Pd/C (Chen et al., 2017). The explorations of novel support materials may reveal novel insights, but they are not closely relevant to practical application. The further point is that if the practical application is not the goal, the research should focus on the structure-activity relationship. Under such circumstances, the "application evaluation" under hypothesized scenarios (i.e., water matrix effects as requested by most environmental technology journals) is unnecessary.

In short, the three aspects above are not the technical priority of catalyst development. Similar thinking logic may be applied to other research topics beyond this paper.

### 3.2 Clarifications of some misconceptions

There have been a series of technical points that may need clarification to enhance the researcher's interest or confidence in developing catalytic treatment systems. Representative ones are addressed below:

1) *Hydrogen gas consumption.* In many research reports, a rapid $H_2$ flow rate of 0.1 or 0.2 L/min was used in a $\leqslant$ 200 mL solution containing $\leqslant$ 1 mmol/L pollutant. However, such a vigorous $H_2$ supply was not required by the reaction kinetics. In many cases, this value was adapted simply because the lowest reading on the standard gas flowmeter is 0.1 L/min. This setting not only wasted $H_2$ gas but also blew away the water. The solution volume might be reduced to a significant extent, adversely concentrating the pollutant. Although the $H_2$ mass transfer is a limiting factor in high-volume systems, for batch reactions less than 200 mL, it is only needed to maintain a positive pressure of $H_2$ to prevent air backflow. This condition is achieved by allowing one $H_2$ bubble from the gas supply needle tip every 1−2 s. An $H_2$ balloon attached to the reactor is also a common approach to maintain the positive reactor pressure (Wu et al., 2012). In short, for small-volume reactions, a vigorous $H_2$ flow is not necessary. The concern about using an $H_2$ gas cylinder may be addressed by using an $H_2$ generator. Nevertheless, $H_2$ and other flammable hydrocarbon gases have been commonly used in microbial reactors for reductive pollutant degradation (Chung et al., 2007; Zhao et al., 2011; Lai et al., 2021), whereas the heterogeneous catalysis design has been frequently challenged by $H_2$ safety concerns. While ventilation is essential, using $N_2$-$H_2$ mixed gas can be an additional measure to reduce the safety risk further.

2) *PGM loss from the catalyst.* There have seldom been bench-scale studies reporting Pd leaching at room temperature. In most reports, the dissolved Pd was below the detection limit. Although significant PGM leaching may be possible from long-term applications, the lack of leaching during the short-term tests indicates the promise of short-term application (i.e., hours to days). Such a scenario is possible because the treatment of ion-exchange regeneration waste is an intermittent operation. However, it is essential to note that concentrated ligands (organics, chloride anion, etc.) can promote the dissolution of $Pd^{II}$ upon oxidation of $Pd^0$ particles. Pd leaching from heterogeneous catalysts during organic catalysis has been well documented (Webb et al., 2007), but those applications typically involve concentrated organics, oxidative mechanisms, and elevated temperatures. Because the application of PGM catalysts for water treatment is still far from mature, the knowledge regarding metal leaching under practical applications is still lacking. Nevertheless, the use of oxidants to clean the "sulfide-fouled" Pd catalyst is not recommended due to the potential oxidative dissolution of metal nanoparticles (Howe and Mercer, 1925; Clem and Huffman, 1968).

3) *High cost of PGM.* A very common criticism for applying PGM catalysts is the high price of metals. This viewpoint must be addressed by the reality that most chemical treatment processes are not for integration into large-scale drinking water treatment trains. Thus, exposing PGM catalysts to giant volumes of drinking water flow is not a realistic scenario. Modern ion-

exchange resins have high selectivity toward $ClO_4^-$. After several months, the resins can be regenerated by as small as one bed volume of the regeneration solution (Gu et al., 2007). Therefore, the waste brines with concentrated $ClO_4^-$ have a minimized volume and may not even need continuous treatment operations. As discussed above, chemical innovations in catalyst formulation can significantly improve cost-effectiveness. If the optimized $[(NH_2)_2bpy]MoO_x$−Pd/C (0.5 wt% Pd and 3 wt% Mo) (Ren et al., 2022) is applied to treat 1 $m^3$ of the waste brine (after the ion-exchange purification of > 50,000 $m^3$ of drinking water), a quick estimation of Pd and Mo needed for a typical 1 g/L (or 1 kg/$m^3$) catalyst loading would be 5 g Pd and 30 g Mo. Moreover, the catalyst is to be reused many times. For comparison, the catalyst converter in a typical gasoline vehicle contains 2−5 g of Pd. Hence, there is no unique economic barrier to applying PGM catalysts for water treatment applications.

### 3.3 New research opportunities

Based on the discussions above, the field of reductive catalysis for pollutant degradation has not been adequately developed for multiple reasons. The innovation of catalyst formulation, including the rational choice of metal elements, metal speciation, and reaction pathway, is far from mature. To date, limited successes include the use of (i) Cu, Sn, and In to allow $NO_3^-$ reduction, (ii) Ru and Rh to achieve novel functions that Pd does not have, and (iii) OAT metals (e.g., Re and Mo oxides and complexes) to enable the reduction of highly recalcitrant $ClO_4^-$. Due to the limit of our research experience and the length of this paper, we have not discussed PGM-catalyzed dehalogenation. Here we just briefly note that the switch from Pd (highly active in dechlorination) (Grittini et al., 1995; Lowry and Reinhard, 2000; 2001; Zhuang et al., 2011) to Rh enabled hydrodefluorination from fluoroarenes (Baumgartner and McNeill, 2012; Baumgartner et al., 2013; Yuan et al., 2021), vinyl fluoride (Yu and Chiu, 2014), and fluorinated pharmaceutical pollutants (Fig. 1) (Park et al., 2020). As the majority of previous catalyst development have been focusing on novel support materials and nanostructure controls, we envision that the re-allocation of the research effort will substantially expand the scope of the catalyst formula and discover various functionalities toward pollutant degradation.

We also hope that the examples, lessons, and clarifications in this paper can largely remove the concerns and misconceptions regarding reductive catalysis research. The high activity can be achieved through both rational design and extensive screening. The experimental approach is not necessarily "advanced" or "complicated". At least, most examples shown in this paper do not involve the multiple-step construction of hierarchical nanostructures. Instead, the one-pot and *in-situ* preparation methods (Figs. 6 and 7) are ideal for engineering applications. The conceived inhibition by water matrix components is not necessarily true for all catalysts. Even if some are identified as strong fouling species, they can be removed before using the catalyst.

Below are three "fundamental" questions we consider valuable for future research efforts:

1) What new functions can the single-metal (beyond Pd) or multi-metal formulations (beyond the reported ones) provide for water pollutant degradation?

2) With the existing metal selections, how to further improve the activity through simple design (e.g., using additives) rather than complicated and costly procedures?

3) How to improve the robustness and stability of catalysts by tuning the intrinsic properties of catalyst components?

Below are five "applied" questions we consider worth doing for future research efforts:

1) What is the performance of the sufficiently developed catalyst formulation (i.e., after adequate optimization) under the most challenging conditions relevant to the real applications?

2) For the final catalyst, how to maintain the activity and minimize the fouling issues through process design?

3) How to apply the powder catalyst in the pilot-scale process?

4) How to capture the leached metals and recycle the catalyst materials?

5) Where to use these catalysts beyond the drinking water treatment contexts? One emerging need is the degradation of oxyanion co-contaminants during the treatment of per- and polyfluoroalkyl substances (PFAS). For example, $NO_3^-$ is a confirmed inhibiting species for UV-sulfite degradation of PFAS (Ren et al., 2021b). $ClO_4^-$ is a common byproduct from electrochemical degradation of PFAS (Schaefer et al., 2015). A comprehensive treatment of waste streams will need to address the toxic oxyanions and other organic halides. Therefore, reductive catalysis may become a key component of the treatment train system.

### 3.4 Extended recommendations

Because the prior goals of this research direction are still achieving more active, stable, and realistic catalysts and reactors for engineering application, we also recommend reducing some efforts that may adversely exhaust the researchers' interest, patience, and belief:

1) Avoid excessive morphology control, instrument characterization, and theoretical calculation/simulation during the initial stage of catalyst development. Serious mechanistic studies are undoubtedly imperative for both fundamental understanding of conventional catalyst structures (Cerrillo et al., 2021) and technology advancement of new catalyst structures with novel functions (Choe et al., 2014; Chu et al., 2021; Ren et al.,

2021a). However, one could not deny that the core mission of water treatment technology research is still methodology development. How much earlier efforts in the advanced mechanistic investigation have contributed to the improvement of catalyst performance remains a question. Whether those efforts primarily played a decorative role is an open topic for debate. In practice, the aggravating trend of mixing methodology development and mechanistic elucidation in every single work on heterogeneous catalyst development has become a heavy burden for researchers. Many publications seem comprehensive but insufficient in either aspect. Furthermore, the obsession with complicating theoretical explanations has triggered warnings from top-tier journals of both nanotechnology (Nature Nanotechnology Editorial Board, 2022) and physics (Mazin, 2022). For a stark comparison, the field of homogeneous Pd catalysis for organic synthesis prioritizes the rate, yield, condition, and scope of reactions for applications (e.g., pharmaceuticals, organic materials, etc.) without too much burden on mechanistic elucidation. Systematic mechanistic understandings are often achieved on the most promising catalyst families at a later time (Singh et al., 2002; Shekhar et al., 2006; Strieter and Buchwald, 2006; Barder and Buchwald, 2007a; 2007b). Readers can check these references to find how many previous methodology studies supported an adequate mechanistic investigation. We (and many peer researchers) believe that reducing unnecessary effort is the key to efficiently advancing catalyst research.

2) Avoid simply immobilizing known metal species on various "popular" supporting materials, especially when the materials are not commercially available but require laborious steps to synthesize or have no clear rationale to enhance the catalyst performance. If one has the resource to conduct such experiments, this paper has shown many alternative efforts that can be more rewarding in terms of advancing environmental technology.

3) Avoid conducting "symbolic engineering testings" that only include one "representative" concentration of $Cl^-$, $SO_4^{2-}$, and NOM, or running 3–5 quick recycles when the catalyst has not been fully developed for real application. For instance, the result of 20 % inhibition by 10 mM $Cl^-$ cannot help evaluate the catalyst when 100 mM or more concentrated $Cl^-$ is present. The premature recycling/reuse demonstration has been disputed by the catalysis community (Scott, 2018), although such a trend still continues for unknown reasons. As such demonstrations have been primarily decorations in most publications, there is no need to keep following them. Because not all catalysts are developed for direct application in real water, any scientific advance made by proof-of-concept is highly valuable for the research community. For catalysts developed for practical application, we have provided an example of systematic engineering evaluations and technical solutions to all the identified challenges (Ren et al., 2022). Such work can be separated from the proof-of-concept studies.

4) Avoid comparing the cost and sustainability while the catalyst has not been adequately developed and optimized. The premature conclusions, especially negative ones, would not hold long after better (and probably significantly better) catalysts are developed.

## 4 Conclusions

Toxic oxyanions, organic halides, and other oxidized pollutants remain realistic challenges in various environmental protection scenarios. While reductive catalysis for water pollutant degradation is not a very hot topic at this moment, we have discussed the history, analyzed the current status, summarized examples of advances in the catalyst functionality and preparation method, and pointed out the knowledge gaps, lessons, misunderstandings, and pitfalls of catalyst development research. The facts and reasoning suggest that this research field is far from mature but has great promise for innovation and application. New design rationale, re-allocated research effort, and the necessary escape from the decorative experimental frameworks are three key factors for the continued success of this research direction.

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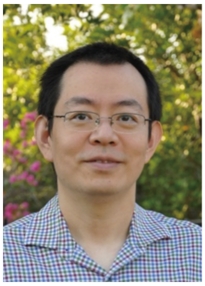
## Author Biography



Dr. Jinyong Liu is currently an Associate Professor at the Department of Chemical and Environmental Engineering, University of California, Riverside (UCR), USA. He received his Bachelor's degree in Chemistry and Master's degree in Environmental Science & Engineering from Tsinghua University, China and his Ph.D. degree in Environmental Engineering from the University of Illinois at Urbana-Champaign, USA. After the postdoctoral training at Colorado School of Mines, he joined UCR in 2016. The ongoing research topics in his lab include (i) degradation of per- and polyfluoroalkyl substances (PFAS), (ii) catalytic reduction of oxyanions, and (iii) transition metal chemistry for environmental applications.

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