Exploring beyond palladium: Catalytic reduction of aqueous oxyanion pollutants with alternative platinum group metals and new mechanistic implications

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Abstract

For over two decades, Pd has been the primary hydrogenation metal studied for reductive catalytic water treatment applications. Herein, we report that alternative platinum group metals (Rh, Ru, Pt and Ir) can exhibit substantially higher activity, wider substrate selectivity and variable pH dependence in comparison to Pd. Cross comparison of multiple metals and oxyanion substrates provides new mechanistic insights into the heterogeneous reactions. Activity differences and pH effects mainly originate from the chemical nature of individual metals. Considering the advantages in performance and cost, results support renewed investigation of alternative hydrogenation metals to advance catalytic technologies for water purification and other environmental applications.

Keywords: rhodium, ruthenium, bromate, chlorate, water treatment, reductive catalysis

1. INTRODUCTION

Toxic oxyanions, such as BrO_3^- , ClO_3^- , NO_3^- and ClO_4^- , are ubiquitous drinking water contaminants originating from both anthropogenic and natural sources [1-4], or are generated during water treatment processes (e.g., chlorination, ozonation, desalination, and electrochemical treatment) [5-9]. These ions target multiple organs, and can have carcinogenic, mutagenic, and/or endocrine disrupting properties [10-12]. Ion exchange is the primary technology used to treat oxyanion-contaminated water; reverse osmosis is also used when salt removal is required. These technologies effectively serve to either trap the contaminants in a resin matrix, or to concentrate the contaminants in a waste brine. Thus, it would be preferable to apply destructive treatment technologies to convert oxyanions into less toxic or innocuous end products (e.g., Br^- , Cl^- and N_2), contributing to more sustainable drinking water treatment processes [13-16].

Pd-based heterogeneous catalysis has garnered significant attention as a potential strategy for reduction of oxyanions and other highly oxidized contaminants (e.g., halogenated and nitro organics) [17]. Ever since 1993 when Pd was identified as the “optimum” hydrogenation metal for water treatment applications (based on the screening of hydrogenation metals for nitrite reduction [18]), research efforts have reported on many aspects of Pd-based catalysis, including the effects of Pd nanoparticle size and morphology [19], catalyst supports [20-23], bimetallic formulations for treating recalcitrant substrates [14, 24, 25], water matrix effects [26, 27], and pilot-scale field testing [28-30]. We argue here that the narrow focus on Pd has limited advancement of reductive water treatment catalyst technologies. Little effort has been devoted to investigating water treatment applications with periodically related hydrogenation metals, e.g., Rh, Ru, Pt and Ir, which have seen many advances in other areas of catalytic science, including organic synthesis [31], biomass valorization [32], and vehicle exhaust gas conversion [33].

In recent screening studies by the Pereira and Neves team [34-38], several hydrogenation metals were evaluated for BrO_3^- and NO_3^- reduction, and Pd-based catalysts were still reported as having the highest activity. However, our group recently found that a Rh/C catalyst exhibited substantially higher activity than Pd/C for ClO_3^- reduction in acidic solution [39]. In literature, Rh/ Al_2O_3 [40-42] and Pt/C [43] also exhibit unique activities, such as hydrodefluorination, that the corresponding Pd-based catalysts do not. These findings suggest that other hydrogenation metals besides Pd may have unique catalyst attributes that could benefit individual water treatment applications and therefore deserve renewed attention.

Herein we report results of a series of catalytic water treatment experiments comparing the activities of alternative platinum group metals (supported on activated carbon or alumina) for reduction of four oxyanion contaminants with a broad range of chemical reactivity ($\text{BrO}_3^- \gg \text{ClO}_3^- > \text{NO}_3^- \gg \text{ClO}_4^-$). Rh exhibits substantially higher activity than Pd during reduction of BrO_3^- , ClO_3^- and NO_3^- . Ru, with a substantially lower cost compared to the other four metals (Pd, Rh, Pt and Ir), shows unique pH insensitivity and the highest activity for ClO_3^- and NO_3^- reduction at circumneutral pH conditions. All five metals are also able to reduce ClO_4^- when combined with Re species as bimetallic Re-M/C catalysts. Cross comparison of multiple oxyanion substrates and metals reveals new mechanistic insights and suggest new directions to develop novel catalysts for challenging water contaminants.

2. EXPERIMENTAL SECTION

2.1 Chemicals and Materials

Unless otherwise specified, all chemicals and metal catalysts (nominal 5 wt% or 1 wt% hydrogenation metal nanoparticles dispersed on activated carbon and alumina supports) were purchased from Sigma–Aldrich or Alfa–Aesar. Detailed catalyst information and characterization data are shown in **Table 1**. The Ru/Al₂O₃ catalyst required a pretreatment (1 atm H₂ flow in a tube furnace under 350 °C for 2 h) for metal reduction and activation of oxyanion reduction activity [44]. Aqueous solutions were prepared using deionized (DI) water (resistivity 18.2 MΩ·cm). H₂ gas (99.9999% UHP, Matheson) was used for catalytic reactions.

2.2 Catalytic reduction of oxyanion contaminants

2.2.1 Bromate (BrO₃[−]). In a 50-mL pear-shaped flask (round bottom, 24/40 joint), a magnetic stir bar, 5 mg of catalyst (dry weight basis), and 50 mL of DI water were added and sonicated for 1 min to make a 0.1 g L^{−1} catalyst suspension. A rubber stopper loaded with two 16 gauge stainless needles capped the flask. H₂ was sparged through one needle below the liquid surface, and the head space was open to the atmosphere through another needle above the liquid surface. All batch reactions were conducted under 1 atm H₂ at room temperature (20–22°C). The solution pH was adjusted by 1 mM HCl (pH 3.0), 0.5 mM Na₂HPO₄ plus 0.5 mM NaH₂PO₄ (pH 7.2), or 0.5 mM NaHCO₃ plus 0.5 mM Na₂CO₃ (pH 10.3). Tests showed that these buffers were sufficient to maintain the pH for BrO₃[−] and ClO₃[−] reductions. After the suspension was pre-sparged for 1 h to pre-reduce any surface oxides present on the immobilized metal nanoparticles, the reaction was initiated by adding 1 mL of the 50 mM NaBrO₃ stock solution (C₀ = 1 mM). For the rapid BrO₃[−] reduction reactions, a high H₂ flow rate (~100 mL min^{−1}) was necessary to

observe pseudo-first-order kinetics in the batch experiments. Samples were collected at periodic time intervals using a 3-mL syringe introduced through the H₂ outlet needle, and the collected aliquot was immediately filtered (0.45-μm nylon membrane) to quench the reaction before subsequent analysis of the filtrate sample.

2.2.2 Chlorate (ClO₃⁻). The reaction setup was the same as for BrO₃⁻ reduction, except that the catalyst loading in the suspension was increased to 0.5 g L⁻¹ because initial tests showed this oxyanion to generally exhibit lower reactivity with the catalysts. H₂ gas flow rates higher than ~20 mL min⁻¹ did not increase reaction rates. An aliquot of KClO₃ stock solution (50 mM, 1 mL) was added to the reactor to initiate individual batch reactions with C₀ = 1 mM.

2.2.3 Nitrate (NO₃⁻). The reaction setup was the same as for ClO₃⁻ reduction, and a NaNO₃ stock solution (50 mM) was added to initiate batch reactions with C₀ = 1 mM. The pH was stabilized using higher buffer concentrations [1 mM HCl plus 10 mM H₃PO₄ (pH pre-adjusted with NaOH to 3.0), 5 mM Na₂HPO₄ plus 5 mM NaH₂PO₄ (pH 7.2), or 5 mM NaHCO₃ plus 5 mM Na₂CO₃ (pH 10.3)] because NO₃⁻ reduction consumes one [N₂ product, Eq. (1)] or up to two equivalents of H⁺ [NH₄⁺ product, Eq. (2)] [14].

2.2.4 Preparation of Re-M/C and reduction of perchlorate (ClO₄⁻). In a 50-mL pear shape flask, a magnetic stir bar, 50 mg of M/C catalyst and 25 mL of DI water (pH pre-adjusted to 3.0 using 1 mM HCl) were added and sonicated for 1 min to yield a 2.0 g L⁻¹ catalyst suspension. A NH₄ReO₄ stock solution (5000 ppm as Re, 0.5 mL) was added to the M/C catalyst suspension to reductively immobilize Re (C_T = 100 ppm) into the porous carbon support matrix under H₂

sparging (flow rate $\sim 10 \text{ mL min}^{-1}$). The immobilization process was monitored by measuring dissolved ReO_4^- in filtered water samples with ion chromatography until concentrations were below detection [14]. Overnight sparging with H_2 led to complete immobilization of Re and yielded bimetallic catalysts containing 5 wt% Re. Reactions with ClO_4^- were then initiated by adding an aliquot of NaClO_4 stock solution (200 mM, 0.625 mL) to the suspension ($C_0 = 5 \text{ mM}$). Samples were collected and filtered using the same procedures described above.

2.3 Water sample analysis

The concentrations of BrO_3^- , Br^- , ClO_3^- , Cl^- , and NO_3^- were determined by a Dionex ICS-3000 ion chromatography system (25- μL injection loop and a suppressed conductivity detector). An IonPac AS19 column maintained at 30°C was used as the stationary phase and 10 mM KOH at 1.0 mL min^{-1} was the eluent. The concentrations of ClO_4^- and ReO_4^- were analyzed by a Dionex ICS-2000 ion chromatography system (25- μL injection loop and a suppressed conductivity detector). An IonPac AS16 column maintained at 30°C was used as the stationary phase and 65 mM KOH at 1.2 mL min^{-1} was the eluent.

2.4 Catalyst characterization

Specific surface area (BET method) and average pore size (BJH method) of the catalyst support materials were measured by N_2 physisorption with a Micromeritics ASAP 2020 analyzer. Dispersion of the hydrogenation metals was determined by chemisorption based on literature methods [45-47] with a Micromeritics AutoChem II analyzer equipped with a thermal conductivity detector. Results of physisorption and chemisorption measurements are summarized in **Table 1**. To determine surface zeta potentials of selected catalysts under varied pH and the H_2 atmosphere, catalyst suspensions (0.5 g L^{-1}) containing different pH buffers (as described in

2.2.1) were sparged with 1 atm H₂ for 30 min, and immediately transferred into an anaerobic glovebox (97% N₂, 3% H₂; Coy Laboratories). An aliquot of suspension was then transferred into a cuvette and sealed with the plastic cap before analyzing for zeta potential (Malvern Zetasizer Nano ZS).

2.5 Kinetic data analysis

Under the reaction conditions described above, reduction of all oxyanion contaminants generally followed a pseudo-first-order rate law for at least two half-lives (i.e., 75% decay). The initial turnover frequency (TOF₀, min⁻¹), which represents the number of oxyanion molecules reduced per surface metal site per minute, was calculated by Eq. (3) [19]:

$$TOF_0 = \frac{kC_0}{C_{\text{surface metal}}} = \frac{kC_0M_{\text{metal}}}{C_{\text{total metal}}D_{\text{metal}}} \quad \text{Eq. (3)}$$

where k is the measured pseudo-first-order rate constant (min⁻¹) for oxyanion reduction in the batch reaction, C_0 is the initial oxyanion concentration (mol L⁻¹), $C_{\text{surface metal}}$ is the concentration of surface metal in the catalyst suspension (mol L⁻¹), M_{metal} is the molar mass of metal element (g mol⁻¹), $C_{\text{total metal}}$ is the total concentration of metal loaded in the catalyst suspension (g L⁻¹), and D_{metal} is the metal dispersion on the catalyst support material (**Table 1**), representing the fraction of metal atoms exposed on the surface of the dispersed metal nanoparticles.

3. RESULTS AND DISCUSSION

3.1 Catalytic reduction of bromate

Figure 1a shows catalytic reduction of bromate (BrO_3^-) at pH 7.2 by the five activated carbon supported metal catalysts [M/C, 0.1 g L⁻¹ catalyst loading with nominal 5 wt% (Pd, Pt, Rh, Ru) or 1 wt% (Ir) of each metal]. A good mass balance between BrO_3^- and Br^- is obtained for each catalyst (**Figure S1**), demonstrating complete BrO_3^- reduction with negligible accumulation of BrO_x^- ($x < 3$) intermediates [Eq. (4)].

Comparing the observed BrO_3^- reduction profiles shows that Rh/C is substantially more active than the other four M/C catalysts. At the catalyst loading of 0.1 g L⁻¹, the reduction of 1 mM BrO_3^- is complete within 5 min. The activity of Rh/C is much higher than most supported hydrogenation metal catalysts reported to date when compared on a metal mass-normalized basis [34, 36-38, 48, 49]. Since the metal dispersion of individual catalysts differ (**Table 1**), the activities of hydrogenation metals are further compared using initial turnover frequency values [TOF_0 , Eq. (3)]. As shown in **Table 2**, Rh/C exhibited significantly higher TOF_0 than other catalysts at pH 7.2. Although the apparent reactivity of Ir/C with BrO_3^- is slightly lower than that of Pd/C (**Figure 1a**), Ir/C exhibited the second highest TOF_0 . Thus, the catalysts incorporating the two Group 9 metals, Rh and Ir, show the highest activity for BrO_3^- reduction at neutral pH conditions that are highly relevant for water treatment systems.

Acidic pH conditions have been previously reported to accelerate BrO_3^- reduction by Pd catalysts [20, 48]. To examine if this trend extends to other hydrogenation metals, BrO_3^- reduction by all five M/C catalysts was also measured at pH 3.0. Results from these experiments

(**Table 2**, **Figure S2a**) show that catalysts incorporating the two Group 10 metals, Pd and Pt, exhibit significant pH dependence, with TOF_0 increasing by more than an order of magnitude when pH is lowered from 7.2 to 3.0. In comparison, the catalysts incorporating Group 9 (Rh and Ir) and Group 8 (Ru) metals show less activity change when pH is lowered. TOF_0 for Rh/C and Ru/C decrease by 35-40%, and Ir/C increases 3-fold when the pH is lowered from 7.2 to 3.0.

3.2 Catalytic reduction of chlorate

Results for catalytic reduction of chlorate (ClO_3^-) by M/C at pH 7.2 are shown in **Figure 1b**. In comparison to BrO_3^- , ClO_3^- is much more inert to reduction (note that the suspension catalyst loading used in the experiments was increased to 0.5 g L^{-1}). Like BrO_3^- , a good mass balance with ClO_3^- and Cl^- (**Figure S3**) is observed during reactions, consistent with the following reaction [Eq. (5)] and confirming negligible accumulation of ClO_x^- ($x < 3$) intermediates.

The highest apparent reactivity with ClO_3^- is observed with Ru/C, a Group 8 metal, and the resulting TOF_0 (6.0 min^{-1}) is substantially higher than catalysts incorporating the other four Group 9 and 10 metals (**Table 2**), due, in part, to the low dispersion of Ru nanoparticles on the carbon support. TOF_0 values measured for the two Group 9 metals (0.17 min^{-1} for Rh and 0.061 min^{-1} for Ir) are higher than those observed for the two Group 10 metals ($< 0.01 \text{ min}^{-1}$ for Pd and Pt). Thus, for neutral pH conditions, periodic trends suggest that ClO_3^- reactivity follows Group 8 >> Group 9 >> Group 10 metals.

Comparing pH dependences for ClO_3^- reactions with the different M/C reveals some other interesting trends. Catalysts incorporating the Group 9 and 10 metals show significantly

enhanced reactivity with ClO_3^- under acidic pH conditions compared to pH 7.2 (**Figure S2b** and **Table 2**), whereas reactions are inhibited under these conditions for Ru, the Group 8 metal. At pH 3.0, Rh/C is the most active catalyst for ClO_3^- reduction (TOF_0 increases from 0.17 min^{-1} at pH 7.2 to 6.7 min^{-1}). A mirror trend is observed for Ru/C, where TOF_0 decreases from 6.0 min^{-1} at pH 7.2 to 0.11 min^{-1} at pH 3.0. The unique pH dependence observed for Ru/C suggests different rate-controlling surface reaction mechanisms for this catalyst compared to those incorporating Group 9 and 10 metals.

3.3 Catalytic reduction of nitrate

Of the catalysts examined, only Rh/C and Ru/C show meaningful reactivity with the more recalcitrant nitrate ion (NO_3^-) in 0.5 g L^{-1} catalyst suspensions monitored for 4 h. As shown in **Table 2** (and **Figure S4**), Ru shows much higher activity than Rh, and both metals exhibit enhanced activities when pH is reduced from 7.2 to 3.0. The observed product of NO_3^- reduction by these two metals under the test conditions is mostly $\text{NH}_3/\text{NH}_4^+$ [Eq. (2)] rather than the desired N_2 [Eq. (1)]. Nevertheless, results show that monometallic Rh and Ru catalysts are capable of reducing NO_3^- without the need for secondary promoter metals (e.g., In, Cu, Sn, and Re) used to activate Pd catalysts towards NO_3^- reduction [14, 18, 25]. Motivated by the low market price of Ru ($\$1.4 \text{ g}^{-1}$) in comparison to the other metals ($\$17$ to $\$38 \text{ g}^{-1}$) (**Table S1**), an in-depth study of Ru-catalyzed NO_3^- and NO_2^- reduction by our team was undertaken and reported separately [44].

3.4 Effect of metal catalyst support materials

We also examined reactions of the three tri-oxy anions with Pd, Pt, Rh, and Ru supported on porous alumina ($\text{M}/\text{Al}_2\text{O}_3$), another common catalyst support material, and found generally the

same reactivity trends observed for the M/C catalysts. Alumina is unstable under acidic pH conditions, so reactivity was only compared with M/C at pH 7.2. Compared to activated carbon support materials, the alumina supports generally have an order of magnitude lower specific surface areas and two times larger pore average size (**Table 1**). As shown in **Figure 2** and **Table 2**, M/Al₂O₃ catalysts generally exhibit similar activity compared to the corresponding M/C. Still, the highest activity for BrO₃[−] reduction at pH 7.2 is observed with both Rh/C and Rh/Al₂O₃, and the highest activity for ClO₃[−] and NO₃[−] reduction is observed with both Ru/C and Ru/Al₂O₃. These similar trends suggest that activity differences among the catalysts primarily originate from the chemical nature of the immobilized metal nanoparticles, and the effects of the support materials may be minor.

3.5 Catalytic reduction of perchlorate

For the tetra-oxyanion perchlorate (ClO₄[−]), the most inert of the target oxyanions examined, no reaction is observed using any of the monometallic catalysts (**Table S2**). We previously reported on preparation of bimetallic Re–Pd/C catalysts that are able to reduce aqueous ClO₄[−] because the immobilized surface oxorhenium(V) species [from the catalytic reduction of oxorhenium(VII) with Pd/C, Eq. (6)] are able to abstract the most challenging oxygen atom, via oxygen atom transfer (OAT) reaction, converting ClO₄[−] to ClO₃[−] [Eq. (7)], which is further reduced to Cl[−] [Eq. (8)] by OAT with Re^V or directly by reaction with hydrogenation nanoparticles (**Figure 3a**) [39, 50, 51].

And thus the overall reaction is

In order to assess the dependence of ClO_4^- reduction on the other four hydrogenation metals, we followed the same approach for bimetallic catalyst synthesis [14, 52] to prepare Re–M/C catalysts using each of the M/C catalysts discussed already. **Figure 3b** shows the reactivity of 5 mM ClO_4^- with 2 g L⁻¹ of each Re–M/C catalyst. The apparent reactivity of the bimetallic catalysts follows Re–Pd/C > Re–Ru/C > Re–Rh/C > Re–Ir/C > Re–Pt/C. Mechanistic interpretation of this trend is unclear at this time. This is complicated by the fact that previous work shows that the rate of ClO_4^- reduction by OAT reactions is more heavily influenced by the speciation of the immobilized Re species than the identity of the hydrogenation metal [53, 54]. Nevertheless, these results demonstrate that all five hydrogenation metals are capable of sustaining the redox turnover of surface Re species [Eqs. (6) and (7)] required to catalyze the OAT reaction with ClO_4^- (turn over number, TON = 38 for each Re atom to fully reduce 5 mM ClO_4^- to Cl^- with the catalyst loadings used in the experiment).

3.6 Mechanistic insights from metal and AO_3^- reactivity cross comparisons

Comparison of observed reactivity trends among the platinum group metals and trioxyanion substrates (AO_3^-) reveals new insights on the controlling reaction mechanisms. First, since the optimum metals for the reduction of BrO_3^- (Rh at pH 7.2) and ClO_3^- (Ru at pH 7.2) differ, the oxyanion substrates should have direct interactions with metal nanoparticle surfaces to undergo reduction (**Figure 4a**). If the oxyanions mainly react with dissociated atomic hydrogen that is

“spilled” away from the metal nanoparticles (**Figure 4b**) [55, 56], the order of catalytic activity for the five metals toward the three oxyanions may be expected to be more similar. However, the measured activity order is $\text{Rh} > \text{Ir} > \text{Pt} \sim \text{Pd} \sim \text{Ru}$ for BrO_3^- reduction at pH 7.2, and $\text{Ru} \gg \text{Rh} > \text{Ir} > \text{Pt} > \text{Pd}$ for ClO_3^- reduction at pH 7.2 (**Table 2**). In addition, we note that the observed activity trends are different from those previously report by Restivo *et al.* [34], where the M/C catalysts were prepared in the researchers’ own laboratory and exhibited much lower BrO_3^- reduction activity (e.g., > 15 min was required to completely reduce 0.078 mM BrO_3^- by 2 g L⁻¹ of 1 wt% M/C catalysts) than our experimental results (e.g., 5 min to completely reduce 1.0 mM BrO_3^- by 0.1 g L⁻¹ 5 wt% Rh/C). We note that the differences of BrO_3^- concentration and catalyst loading have outweighed the effect of metal loading. Explanation of the discrepancies of catalyst activity in different reports, if necessary, would require substantial amount of catalyst characterization and comparison. It is probable that critical catalytic properties of individual metals might have not be revealed when using a uniform catalyst preparation recipe for all metals (i.e., the recipes were not optimized for individual metal) by the Pereira and Neves team.

Nevertheless, results suggest that the mechanistic interpretation, which might be used as design rationale for future catalyst development work, should be considered with caution. Restivo *et al.* observed Pt and Ru to be the most active metals for BrO_3^- reduction, and this observation was correlated with the hydrogen chemisorption energy on each metal using the Sabatier principle [34]. However, based on the activity of Rh and Ir in the current study, we propose that hydrogen chemisorption energy might not necessarily be the key parameter controlling reactivity of different metals with BrO_3^- , and that the interaction between oxyanion substrates and different metal surfaces should also be considered.

Second, the pH responses of the five metals are also different. For BrO_3^- reduction, the pH responses of Rh and Ru contrast those of Pd, Pt and Ir (**Table 2**). Also, the same Rh/C catalyst exhibits differing pH dependence for BrO_3^- reduction compared to ClO_3^- and NO_3^- reduction (**Figure 5**, activity presented in apparent rate constants normalized by the mass of M/C catalysts), even though the three oxyanions carry the same -1 charge in solutions between pH 3.0 and 10.3. In comparison, Ru/C catalyst did not show a simple trend of pH dependence. Zeta potentials of Rh/C and Ru/C under variable pH (with a H_2 atmosphere [20, 52]) were measured and results are shown in **Figure 6**. Although the zeta potentials of both catalysts are significantly increased when the pH decreases from 7.2 to 3.0, the BrO_3^- reduction by Rh/C and Ru/C (**Figure 6a**) as well as the ClO_3^- reduction by Ru/C (**Figure 6b**) are not accelerated. Previous reports attribute slower rates of BrO_3^- reduction by Pd catalysts at higher pH to increased negative surface charge and the resulting unfavorable electrostatic interactions between the surface and the negatively charged oxyanions [20, 57]. Here, results demonstrate that a more positively charged support at lower pH does not necessarily increase rates of oxyanion reduction for all M/C. Hence, the intrinsic reactivity of metals may outweigh the effects of catalyst surface charge. Therefore, the priority of designing an oxyanion reduction catalyst should consider the selection of active metal according to the characteristics of oxyanion substrates and reaction conditions (e.g., solution pH).

3.7 Outlook in catalyst development and application

In this study, four platinum group metals, which have been largely overlooked during the development of Pd-based water treatment catalysts, exhibit much higher or at least similar performance in comparison to Pd, in terms of catalytic turnover frequency, pH dependence, and oxyanion substrate scope. Specifically, Ru shows outstanding activity for ClO_3^- and NO_3^- reduction over a wide pH range, and the price of Ru is more than an order of magnitude lower

than the other four metals (**Table S1**). Thus, lower cost and more sustainable reductive catalytic technologies [15, 16] may be achieved by developing Ru-based multi-functional materials. Moreover, our research group has developed highly stable ClO_4^- reduction catalysts based on Rh rather than Pd, because the former could rapidly scavenge ClO_x^- intermediates that can deactivate Re complex reaction sites [39, 54]. Results from this study are expected to initiate the development of new catalysts for a variety of water treatment scenarios.

Various factors such as size and morphology of both the metal nanoparticles and the support materials can also influence the reactivity of platinum group metals [19, 57], but the effects are generally less pronounced compared to the effects of metal identity (e.g., Pd versus Rh in ClO_3^- reduction, or Pd versus Ru in NO_3^- reduction) as demonstrated in this study. Computational studies [19, 58] are also needed to provide detailed theoretical insights into these metal-specific effects and metal-substrate interactions. We emphasize that research priority should be given to further examining novel activity of these previously overlooked metals in water treatment applications, such as (1) exploring multi-functional activities in treating various emerging and challenging contaminants (e.g., nitro [59], fluoro [40-43] and polychloro [60, 61] compounds), and (2) rational development of catalyst formulation and engineering processes to apply these metals for practical water treatment.

4. CONCLUSION

Four platinum group metals (Ru, Rh, Ir, and Pt), largely overlooked in the development of water treatment catalysts compared to Pd, are shown here to exhibit favorable reactivity with aqueous bromate, chlorate, nitrate and perchlorate at ambient conditions. Specifically, Rh and Ru show significant advantages over Pd in terms of catalytic turnover frequency, pH dependence, oxyanion substrate scope, or cost. Cross comparison of multiple metals and tri-oxyanion substrates suggest that some previous interpretations of the pH influence on catalyst reactivity should be revisited. The chemical nature of each metal element is a key factor determining the catalyst activity and adaptability to different water treatment conditions. We recommend that rational selection of metals could be one of the current priorities in the development of water treatment catalysts.

SUPPLEMENTARY INFORMATION

Additional materials as noted in the text.

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Figure captions

Table 1. Catalyst information and characterization data.

Table 2. Initial turnover frequencies for the reaction of 1 mM oxyanions with M/C and M/Al₂O₃.

Figure 1. Timecourse profiles with for reduction of **(a)** 1 mM BrO₃[−] by 0.1 g L^{−1} M/C catalysts and **(b)** 1 mM ClO₃[−] by 0.5 g L^{−1} M/C catalysts with 1 atm H₂ at pH 7.2 and 22°C (nominal 5 wt% metal for Pd, Rh, Ru, and Pt; 1 wt% metal for Ir).

Figure 2. Timecourse profiles with for reduction of **(a)** 1 mM BrO₃[−] by 0.1 g L^{−1} M/Al₂O₃ catalysts and **(b)** 1 mM ClO₃[−] by 0.5 g L^{−1} M/Al₂O₃ catalysts with 1 atm H₂ at pH 7.2 and 22°C (nominal 5 wt% metal for all catalysts).

Figure 3. **(a)** Mechanisms for Re–M/C catalyst reactions with ClO₄[−] and ClO_x[−] intermediates (x = 4, 3, 2, or 1); adapted from Refs [50, 51]. **(b)** Reduction of 5 mM ClO₄[−] with 2 g L^{−1} Re–M/C (5 wt% Re, 5 wt% M) bimetallic catalysts.

Figure 4. Mechanism illustrations of **(a)** the reduction of oxyanion substrates (AO_x[−]) requiring direct interaction with the hydrogenation metal nanoparticles; **(b)** the reaction between AO_x[−] and spilled over atomic hydrogen at the catalyst support surface away from the hydrogenation metal nanoparticles.

Figure 5. Catalyst loading normalized rate constants at different pH for the reduction of 1 mM **(a)** BrO₃[−], **(b)** ClO₃[−] and **(c)** NO₃[−] with Rh/C and Ru/C catalysts. Error bars represent replicate-averaged 95% confidence intervals. “NR” indicates no reaction observed within the reaction period monitored.

Figure 6. Influence of pH on the zeta potential of 0.5 g L^{−1} Rh/C and Ru/C catalysts in H₂-saturated aqueous suspension at 22 °C.

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Table 1. Catalyst information and characterization data.

Entry	Metal	Supplier and catalog number	Surface area (m ² g ⁻¹)	Average pore size (nm)	Metal dispersion	Metal particle diameter (nm)
<i>Activated Carbon Support</i>						
1	5 wt% Pd	Sigma-Aldrich #205680	958	3.1	30.3%	3.7
2	5 wt% Rh	Sigma-Aldrich #206164	870	3.6	31.3%	3.5
3	5 wt% Ru	Alfa-Aesar #44338	704	3.4	11.2%	11.8
4	5 wt% Pt	Sigma-Aldrich #205931	1370	3.4	23.9%	4.7
5	1 wt% Ir	Alfa-Aesar #38330	839	3.3	31.8%	3.7
<i>Alumina Support</i>						
6	5 wt% Pd	Sigma-Aldrich #205710	106	8.9	66.3%	1.7
7	5 wt% Rh	Sigma-Aldrich #212857	168	10.0	64.1%	1.7
8	5 wt% Ru	Sigma-Aldrich #381152	93	15.3	9.8%	13.5
9	5 wt% Pt	Sigma-Aldrich #205974	94	9.2	23.4%	4.8

Table 2. Intial turnover frequencies for the reaction of 1 mM oxyanions with M/C and M/Al₂O₃.

Entry	Catalyst	Catalytic oxyanion reduction turnover frequency (TOF ₀ , min ⁻¹) ^a					
		BrO ₃ ⁻		ClO ₃ ⁻		NO ₃ ⁻	
		pH 7.2	pH 3.0	pH7.2	pH 3.0	pH 7.2	pH 3.0
1	Pd/C (10) ^b	2.7 ± 0.1 ^c	33.4 ± 2.7	0.0012 ± 0.0005	0.070 ± 0.002	ND ^d	ND
2	Rh/C (9)	54.4 ± 5.5	32.3 ± 0.6	0.17 ± 0.01	6.7 ± 0.5	0.0019 ± 0.0001	0.046 ± 0.004
3	Ru/C (8)	2.0 ± 0.1	1.3 ± 0.5	6.0 ± 1.1	0.11 ± 0.01	0.33 ± 0.01	0.71 ± 0.01
4	Pt/C (10)	3.7 ± 0.1	42.9 ± 0.4	0.0076 ± 0.0010	0.090 ± 0.006	ND	ND
5	Ir/C (9)	15.5 ± 0.5	47.0 ± 1.9	0.061 ± 0.003	1.2 ± 0.1	ND	ND
6	Pd/Al ₂ O ₃	0.83 ± 0.01		ND		ND	
7	Rh/Al ₂ O ₃	5.9 ± 0.6		0.014 ± 0.001		0.0025 ± 0.0001	
8	Ru/Al ₂ O ₃	7.0 ± 0.4		1.1 ± 0.1		0.30 ± 0.02	
9	Pt/Al ₂ O ₃	6.5 ± 0.3		0.0058 ± 0.0001		ND	

^aDetermined for catalyst reactions with 1 mM oxyanions, 22°C, continuous mixing and sparging with 1 atm H₂. 0.1 g L⁻¹ catalyst suspensions used for reactions with BrO₃⁻, 0.5 g L⁻¹ used for ClO₃⁻ and NO₃⁻.

^bNumber in parenthesis indicate the Periodic Table group number of the hydrogenation metal.

^cErrors represent 95% confidence intervals.

^dMeaningful catalytic activity not detected within the 4 h of reaction at the 0.5 g L⁻¹ catalyst loading.

Figure 1. Timecourse profiles with for reduction of (a) 1 mM BrO_3^- by 0.1 g L^{-1} M/C catalysts and (b) 1 mM ClO_3^- by 0.5 g L^{-1} M/C catalysts with 1 atm H_2 at pH 7.2 and 22°C (nominal 5 wt% metal for Pd, Rh, Ru, and Pt; 1 wt% metal for Ir).

Figure 2. Timecourse profiles with for reduction of (a) 1 mM BrO_3^- by 0.1 g L^{-1} $\text{M}/\text{Al}_2\text{O}_3$ catalysts and (b) 1 mM ClO_3^- by 0.5 g L^{-1} $\text{M}/\text{Al}_2\text{O}_3$ catalysts with 1 atm H_2 at pH 7.2 and 22°C (nominal 5 wt% metal for all catalysts).

Figure 3. (a) Mechanisms for Re-M/C catalyst reactions with ClO_4^- and ClO_x^- intermediates ($x = 3, 2, \text{ or } 1$); adapted from Refs [50, 51]. (b) Reduction of 5 mM ClO_4^- with 2 g L⁻¹ Re-M/C (5 wt% Re, 5 wt% M) bimetallic catalysts.

Figure 4. Mechanism illustrations of **(a)** the reduction of oxoanion substrates (AO_x^-) requiring direct interaction with the hydrogenation metal nanoparticles; **(b)** the reaction between AO_x^- and spilled over atomic hydrogen at the catalyst support surface away from the hydrogenation metal nanoparticles.

Figure 5. Catalyst loading normalized rate constants at different pH for the reduction of 1 mM (a) BrO_3^- , (b) ClO_3^- and (c) NO_3^- with Rh/C and Ru/C catalysts. Error bars represent replicate-averaged 95% confidence intervals. "NR" indicates no reaction observed within the reaction period monitored.

Figure 6. Influence of pH on the zeta potential of 0.5 g L^{-1} Rh/C and Ru/C catalysts in H_2 -saturated aqueous suspension at 22°C .