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

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HIGHLIGHTS

- Rh, Ru, Pt and Ir are shown to be alternatives to Pd for aqueous oxyanion reduction.
- Individual metals exhibit specific advantages when compared to Pd.
- Cross comparison of metals and oxyanions yield new mechanistic insights.
- Activity differences and pH effects originate from the chemical nature of metals.

GRAPHICAL ABSTRACT
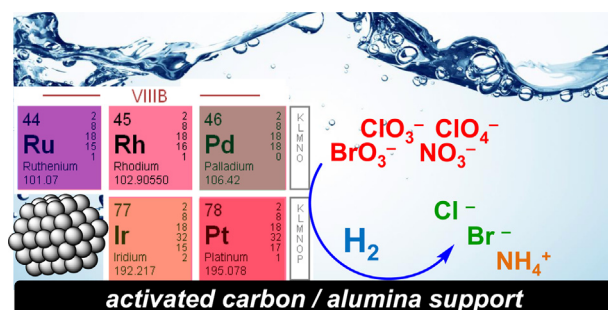
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ABSTRACT

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.

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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 ($BrO_3^- \gg ClO_3^- > NO_3^- \gg ClO_4^-$). 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/Al_2O_3

catalyst required a pretreatment (1 atm H_2 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). H_2 gas (99.9999% UHP, Matheson) was used for catalytic reactions.

2.2. Catalytic reduction of oxyanion contaminants

2.2.1. Bromate (BrO_3^-)

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. H_2 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 H_2 at room temperature (20–22 °C). The solution pH was adjusted by 1 mM HCl (pH 3.0), 0.5 mM Na_2HPO_4 plus 0.5 mM NaH_2PO_4 (pH 7.2), or 0.5 mM $NaHCO_3$ plus 0.5 mM Na_2CO_3 (pH 10.3). Tests showed that these buffers were sufficient to maintain the pH for BrO_3^- and ClO_3^- 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 $NaBrO_3$ stock solution ($C_0 = 1$ mM). For the rapid BrO_3^- reduction reactions, a high H_2 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 H_2 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 (ClO_3^-)

The reaction setup was the same as for BrO_3^- 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. H_2 gas flow rates higher than ~20 mL min^{-1} did not increase reaction rates. An aliquot of $KClO_3$ stock solution (50 mM, 1 mL) was added to the reactor to initiate individual batch reactions with $C_0 = 1$ mM.

2.2.3. Nitrate (NO_3^-)

The reaction setup was the same as for ClO_3^- reduction, and a $NaNO_3$ stock solution (50 mM) was added to initiate batch reactions with $C_0 = 1$ mM. The pH was stabilized using higher buffer concentrations [1 mM HCl plus 10 mM H_3PO_4 (pH pre-adjusted with NaOH to 3.0), 5 mM Na_2HPO_4 plus 5 mM NaH_2PO_4 (pH 7.2), or 5 mM $NaHCO_3$ plus 5 mM Na_2CO_3 (pH 10.3)] because NO_3^- reduction consumes one [N_2 product, Eq. (1)] or up to two equivalents of H^+ [NH_4^+ product, Eq. (2)] [14].

$$NO_3^- + 2.5H_2 + H^+ \rightarrow 0.5N_2 + 3H_2O \tag{1}$$

$$NO_3^- + 4H_2 + 2H^+ \rightarrow NH_4^+ + 3H_2O \tag{2}$$
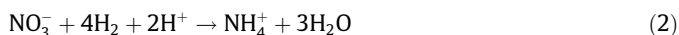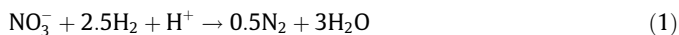
2.2.4. Preparation of Re–M/C and reduction of perchlorate (ClO_4^-)

In a 50-mL pear-shaped 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 NH_4ReO_4 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 H_2 sparging (flow rate ~10 mL min^{-1}). The