Heterogeneous Catalytic Reduction of Perchlorate in Water

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The perchlorate ion, ClO_4^-, is today widely regarded as a contaminant of ground and surface waters, as well as soil, throughout the United States, with over 400 recognized contaminated sites in 35 states [1]. The chemistry of perchlorate is dominated entirely by kinetics, and its high kinetic barrier to reduction makes it effectively inert to reduction by typical nucleophilic reducing agents or to complexation [2-4]. The argument for perchlorate remediation is based on its known interference with normal thyroid function [5]. The cause of this interference is the preferential uptake of perchlorate over iodide by the thyroid [6]. It is well established that the thyroid regulates neural development in fetuses and infants [7]. Current perchlorate remediation strategies are largely limited to ion exchange (IX) or bioremediation [8, 9].

In 1995 Abu-Omar and Espenson [10] showed that a rhenium(V) complex in aqueous solution, formulated as methylrhenium dioxide (MDO), can react relatively rapidly with perchlorate by an oxygen atom transfer (OAT) reaction to form an rhenium(VII) complex (methylrhenium trioxide, MTO) and chlorate. The cycle could be closed by reducing the Re(VII) complex back to the Re(V) complex with hypophosphorous acid (H_3PO_2) [11]. Such a *homogeneous* catalyst with a soluble phosphorus or sulfur reducing agent is not readily compatible with water purification systems.

In an effort to make a catalytic system more compatible with water treatment a heterogeneous catalyst has been developed that promotes the reduction by hydrogen of perchlorate ion in water under mild conditions. The catalyst is prepared by adsorption of an rhenium(VII) precursor (either ammonium perrhenate or methylrhenium trioxide) onto carbon powder containing 5% palladium by weight. Under standard batch conditions of room temperature, 1 atm hydrogen, and 200 ppm perchlorate (as $HClO_4$) reduction proceeded to less than 1 ppm in as little as five hours. Extended reaction times led to residual perchlorate at low ppb levels. Chloride was the only observed product, with good material balance. Catalytic materials ranging from ca. 1-13% Re showed (pseudo) first order rates linearly dependent on Re content. Representative normalized rate constants for catalysts with 5% Re were on the order of 2.9 L h^{-1} $(g\text{-}Re)^{-1}$. Inhibition by chloride was not significant, with little change in perchlorate reduction rate in the presence of excess chloride to 1000 ppm. However, optimal activity occurred in acidic solutions (pH ca. 3), and both the rate and extent of reaction decreased at higher values of pH.

We suggest that this catalyst has a bifunctional mode of operation as shown in Scheme I. The Pd component is known to 'activate' H_2, forming adsorbed surface H, which can then 'spill over' to the Re-O species dispersed on the support [12]. The reaction of $Re^{(VII)}=O$ with 2H will reduce it to $Re^{(V)}(OH_2)$. Dissociation of the water ligand then provides a coordinatively unsaturated rhenium(V) center for perchlorate complexation. Oxygen atom transfer, as discussed thoroughly for the soluble cases [10, 11], regenerates the original $Re^{(VII)}=O$ center and releases chlorate. Subsequent reactions with chlorate, chlorite, and hypochlorite will complete the stepwise reduction to chloride and water.

The pH dependence of the reduction rate suggests that the complexation and activation of perchlorate is assisted by a proton. Since perrhenic acid ($pK_a \sim$ -1.25) is a weaker acid than perchloric acid ($pK_a \sim$ -7) [13], an extra proton incorporated into a rhenium-perchlorate surface complex should be attached primarily to a more basic rhenium-bound oxygen atom. However, a hydrogen-bonding interaction with one of the ancillary perchlorate oxygen atoms would serve to stabilize the intermediate by providing a specialized (enzyme-like) binding site. This idea is consistent with the observed lack of inhibition by chloride, since although chloride is a much better anionic ligand than perchlorate, it would not be nearly as capable of entering into a secondary hydrogen bonding interaction with the catalytic reaction center.
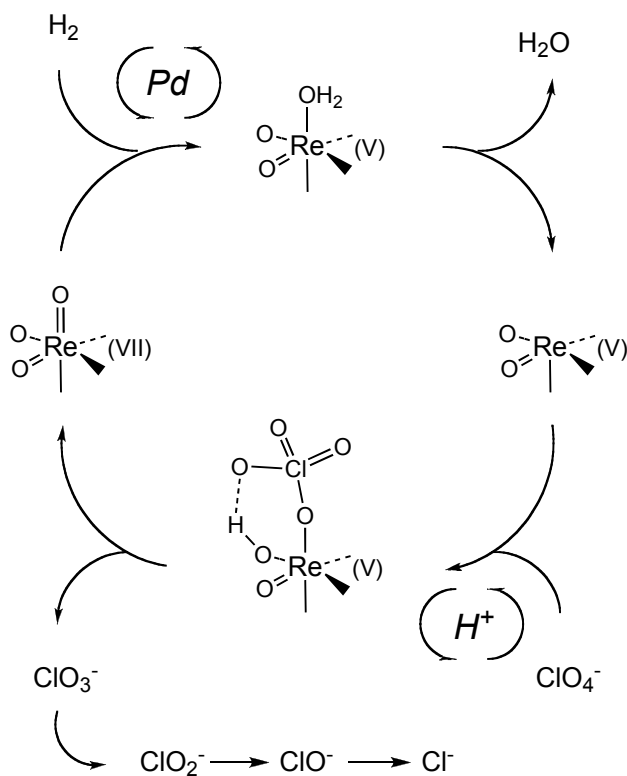
Scheme I. Proposed mechanism for catalytic reduction of ClO_4^- by Re(VII)/Pd/C.

Based on the proposed Re(VII)-Re(V) couple, a Re(V) complex, chlorobis(2-(2'-hydroxyphenyl)-2-oxazoline)-oxorhenium(V) ($Re(O)_2Cl(hoz)_2$), was adapted for use as a heterogeneous catalyst. Like MTO, $Re(O)_2Cl(hoz)_2$ had been shown to be an active homogeneous catalyst for perchlorate reduction, using phosphines or organic sulfides as oxygen acceptors in 95:5 (v/v) acetonitrile/water [14]. The normalized rate constant for reduction of 200ppm ClO_4^- by 0.5 g/L of the carbon supported catalyst is 27.56 L/(h*g-Re). CO chemisorption measurements yielded a Pd dispersion of 18.2 % with an active Pd surface area of 80.8 m^2/g-Pd. XPS spectroscopy provided evidence of a +7, rather than the expected +5, oxidation state for the supported catalyst. STEM/EDS experiments revealed a wide distribution in Pd nanoparticle size and a random distribution of Re sites over the entire surface of the support material. An examination of the dependence of the observed reduction rate on pH revealed the involvement of one proton in the rate determining step of the catalytic cycle. The

reduction of perchlorate by $Re(O)_2Cl(hoz)_2/Pd/C$ follows pseudo-first order kinetics with chloride being the only product observed. Lack of buildup of any intermediates, along with the observed pH dependence, suggest oxygen atom transfer from perchlorate to the active form of the catalyst is the rate determining step in the reduction. Chlorate is rapidly reduced by the catalyst and can be modeled with Langmuir-Hinshelwood kinetics.

The catalytic reduction of perchlorate was also achieved by supporting *trans*-$[Re(O)_2L_4]^+$ X, (L = pyridine, 4-methylpyridine, 4-methoxypyridine, or 4-dimethylaminopyridine, X = Cl^- or $[ReO_4]^-$) or *trans*-$[ReO_2(L-L)_2]I$ (L-L =ethylenediamine) on nominally 5 wt.% Pd on activated carbon. Unlike previous materials, these complexes had never been demonstrated as oxygen atom transfer catalysts. All materials completely reduced perchlorate to chloride in the presence of 2mM excess Cl^- while exhibiting pseudo-first order kinetics. The most active catalyst proved to be derived from $[Re(O)_2(DMAP)_4]Cl$ (DMAP = dimethylaminopyridine), with a normalized rate constant of k(Re) = 13.37 L/(h*g-Re). The *bis*-ethylenediamine exhibited the slowest kinetics, with k(Re) = 2.66 L/(h*g-Re). XPS spectra of all the supported complexes exhibited Re binding energies consistent with only one oxidation state, +7, present. XPS analysis of an unsupported $[Re(O)_2(L)_4][ReO_4]$ complex clearly showed both the +5 and +7 oxidation states, indicating that all of the Re complexes are oxidized to Re(VII) on the surface. Figure 1 shows the XPS spectra for a supported and unsupported Re complex along with curve fitting.
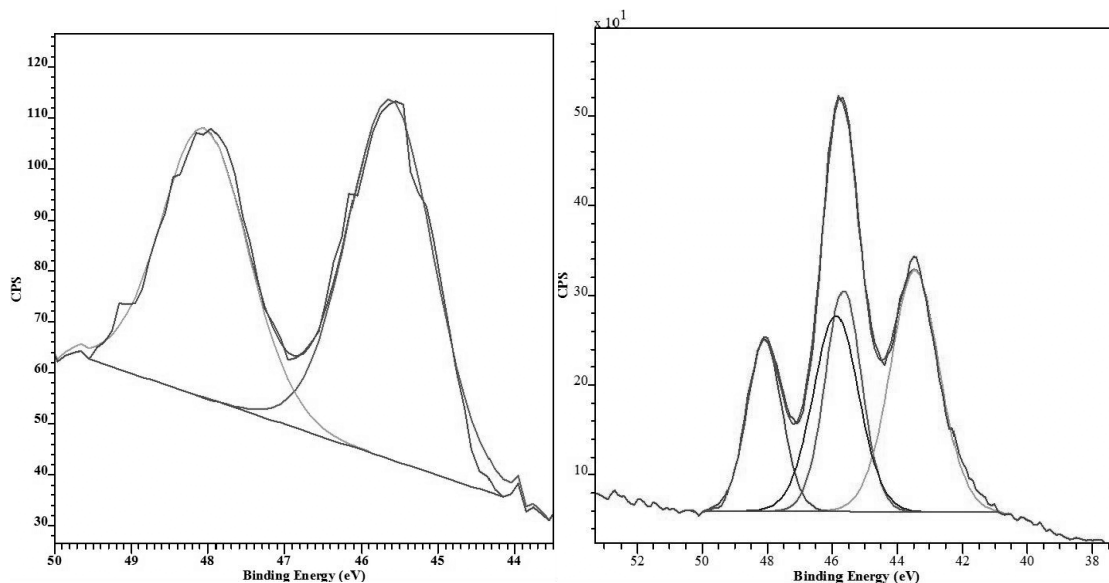

Figure 1. XPS high resolution scans of Re 4f region of (left) $[Re(O)_2(py)_4][ReO_4]/Pd/C$ and (right) $[Re(O)_2(py)_4][ReO_4]$.

A free energy relationship was found between the electron donating ability of the substituted pyridine ligands and the reduction rate constant. The use of a Hammett-Brown plot yielded a consistent negative slope for both washed and unwashed chloride salt based catalysts. The negative value is consistent with the buildup of positive charge at the Re(V) center during oxidation to Re(VII).

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