Ligand-Enhanced Reduction of Perchlorate in Water with Heterogeneous Re−Pd/C Catalysts

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Ongoing concerns over the ingestion of perchlorate from water and food, especially for infants,[1,2] have prompted the EPA to issue a health advisory target of 15 ppb for drinking water sources;[3] two states, California and Massachusetts, have mandated even lower limits.[4,5] Removal of perchlorate from a water supply can be accomplished by selective ion exchange or reverse osmosis, but complete destruction of the contaminant requires pyrolysis or reduction by biological or chemical means.[6−8] Perchlorate reduction by dihydrogen with heterogeneous metal catalysts is extremely clean, producing only chloride and water, but the systems currently available have various limitations in terms of activity, longevity, and operating conditions.[9−11] Here we describe how one of these systems, derived from the combination of a Pd/C hydrogenation catalyst with the perrhenate ion,[10] can be improved dramatically in activity and stability by the presence of simple pyridine compounds as ligands. Furthermore, the observed ligand effects provide key mechanistic insight into the operation of the system and also open an avenue for further development toward sustainable operation.

Two approaches were adopted for the preparation and handling of the catalytic materials, one largely aerobic for convenience and the other strictly anaerobic. Full experimental details are provided in the Supporting Information. In the first approach, activated carbon powder with 5 wt % Pd was impregnated to "incipient wetness" with an ethanol solution of one of the Re(V) complexes *trans*-$[ReO_2(py\text{-}X)_4]^+$ (py-X = 4-substituted pyridine; X = H, Me, OMe, NMe$_2$),[12] after which each sample was dried in vacuo at 70 °C. These bimetallic materials were quite effective (in a batch reactor under flowing hydrogen) in promoting the reduction of perchlorate to chloride within a few hours at room temperature. Figure 1 illustrates the dramatic improvement for the case X = NMe$_2$ compared with the previous system.[10] Moreover, the observed reduction rate constants depended markedly on the pyridine ligand substituent, as shown by the linear free-energy plot in the inset, with increasing donor character (basicity) leading to higher rates (H < Me < OMe < NMe$_2$).

Characterization of these materials indicated variable formation of perrhenate from exposure to ambient conditions (see the Supporting Information). For example, Re 4f high-resolution X-ray photoelectron spectroscopy (XPS) scans of the pure reference compound $[ReO_2(py)_4][ReO_4]$[13] clearly showed both Re(V) and Re(VII) oxidation states,[14] but XPS of the impregnated materials showed evidence of Re(VII) only (see Figure S-5 in the Supporting Information). Facile generation of perrhenate from exposure of lower-oxidation-state Re complexes to air and moisture, especially under acidic conditions, has been documented rather frequently.[15]
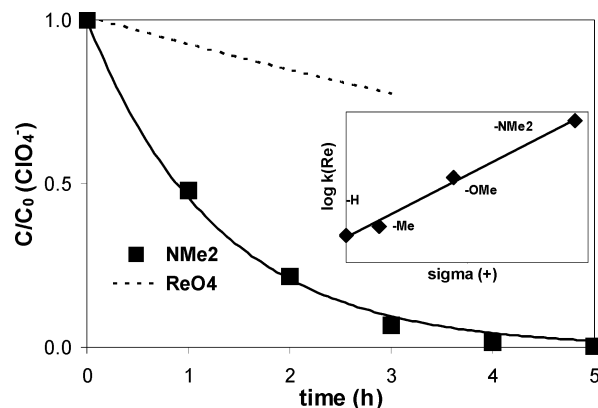

Figure 1. Perchlorate reduction profile (as 2 mM HClO$_4$ or 2 mM each NH$_4$ClO$_4$ + HCl; pH 2.7) for a Re−Pd/C catalyst prepared from *trans*-$[ReO_2(py\text{-}NMe_2)_4]Cl$ compared with a calculated curve at a similar Re loading (∼3.7 wt %) for a catalyst prepared from ReO$_4^-$ alone, based on reported data.[10] The inset shows plot of log k(Re) vs substituent $\sigma+$ parameter for catalysts from complexes with X = H, Me, OMe, and NMe$_2$, where k(Re) is k(obs) normalized by the Re content of the catalyst material.

Our second approach involved maintaining a constant hydrogen atmosphere for all operations. The ligand, NH$_4$ReO$_4$, and HCl were mixed with the Pd/C powder suspended in water, and adsorption of perrhenate was followed until completion. Each of the added pyridine ligands promoted adsorption (see Figure S-6), and the resulting materials proved effective in reduction of added perchlorate, with normalized k(Re) values consistently better than those seen with the impregnated catalysts. The rate order with respect to X was H < Me < OMe < NMe$_2$, as before. Figure 2 illustrates aspects of extended studies with dimethylaminopyridine (DMAP; X = NMe$_2$) and ReO$_4^-$ under various conditions. At pH 3, the observed reduction rate increased by ∼10-fold as the DMAP/Re ratio was increased from 0.25:1 to 1:1, but it then remained essentially constant up to a ratio of 10:1. The relatively sharp break in this curve suggests the predominant formation of a surface complex with a specific DMAP−Re stoichiometry. This surface complexation substantially stabilizes Re on the catalyst for operation at higher pH values. As shown in the inset, consistent reduction of perchlorate occurred (with DMAP/Re = 2) even as the pH was raised from 3 to 4.5. The previous ReO$_4^-$ + Pd/C catalyst, with no added ligand, was unstable above pH 3.5, and reduction was not only slow but incomplete.[10] Extrapolating the data in Figure 2 (inset plot slope of −0.5) to pH 7 predicts a pseudo-first-order rate constant of ∼9 × 10^{-3} h^{-1}, which is comparable with the best value claimed for heterogeneous reduction by nano-ZVI at 25 °C[16] but multifold faster when normalized by weight [2.0 × 10^{-2} L h^{-1} (g of catalyst)$^{-1}$ vs 6.7 × 10^{-3} L h^{-1} (g of Fe)$^{-1}$]. However, the corresponding Re-normalized rate [45 L h^{-1} (mol of Re)$^{-1}$] is over

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30 times slower than the analogous perchlorate reduction rate [1620 L h^{-1} (mol of Re)$^{-1}$] observed for the *homogeneous* Re complex catalyst [ReO(hoz)$_2$]$^+$ operating in aqueous acetonitrile.[17] This latter comparison suggests the degree of improvement in the heterogeneous system that might be achieved by optimizing the coordination environment of the Re centers in the catalyst.
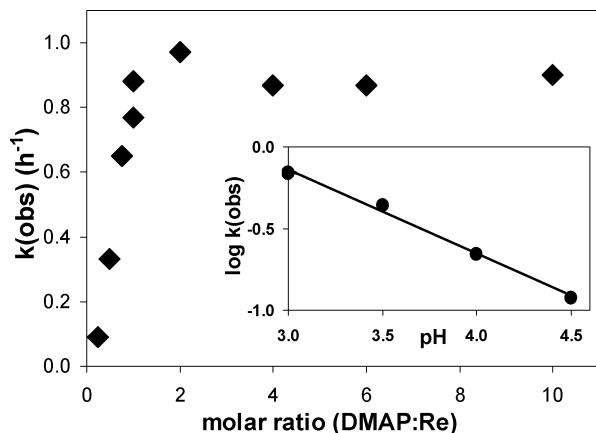

Figure 2. Perchlorate reduction rate constants vs equiv of DMAP (py-NMe$_2$) added to the HCl + NH$_4$ReO$_4$ + Pd/C system under hydrogen (pH 3, 0.2 mM NH$_4$ClO$_4$, 0.45 g of catalyst/L, 7 wt % Re). The inset shows the variation in rate with pH (DMAP/Re = 2).

The current results clearly show that an added pyridine ligand coordinates to the reaction center involved in the rate-determining step for perchlorate reduction. Scheme 1 illustrates this step as an oxygen atom transfer (OAT)[17,18] from perchlorate coordinated to a Re(V) center, oxidizing it to Re(VII) and releasing chlorate and a proton. The OAT results in a decrease in electron density at the Re center as the rhenium to oxygen double bond is formed, and a resonant ligand interaction donating electron density to the Re center stabilizes the developing positive character and increases the reaction rate. Other aspects of the catalytic cycle, i.e., coordination of perchlorate facilitated by an ancillary hydrogen-bonding interaction (not available for chloride) and spillover of H equivalents from the Pd nanoparticles to reduce the O═Re(VII) centers, are as previously proposed for the ReO$_4^-$ + Pd/C system.[10]

Scheme 1. Catalytic Cycle for Perchlorate Reduction at a Ligand-Modified Oxo—Re Site Supported on Pd/C
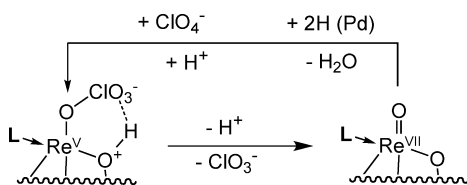
In summary, we have found that the presence of substituted pyridine ligands (added either as a Re complex precursor or separately with ReO$_4^-$) leads to a Re—Pd/C catalyst for perchlorate reduction that exhibits dramatically improved properties in terms of activity and stability toward increased pH. The dependence of activity on donor capability of the ligand supports a rate-determining step involving oxidation of the Re center, consistent with OAT from perchlorate coordinated to Re(V) to form O═Re(VII) and chlorate. More generally, observation of a significant ligand effect for this heterogeneous catalytic system suggests that opportunities exist to "fine-tune" the coordination environment of the active Re centers, not only to maximize the electronic influence on the OAT reaction but also to minimize the prospect of deactivating release of perrhenate into solution upon oxidation. Such improvements would continue to relax the limitations on practical use recognized previously for the Re—Pd/C system,[10] which could allow an engineered catalyst to be given serious consideration for perchlorate remediation applications.

Supporting Information Available: Experimental details for preparation, characterization, and use of impregnated [ReO$_2$(py-X)$_4$]Cl-derived catalysts; procedures and results for adsorbed catalysts. This material is available free of charge via the Internet at http://pubs.acs.org.

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