

## Heterogeneous Catalytic Reduction of Perchlorate in Water with Re–Pd/C Catalysts Derived from an Oxorhenium(V) Molecular Precursor

Yunxia Zhang,<sup>†,‡</sup> Keith D. Hurley,<sup>‡,§</sup> and John R. Shapley<sup>\*,‡</sup>

<sup>†</sup>Key Laboratory of Pollution Processes and Environmental Criteria, Ministry of Education, College of Environmental Science and Engineering, Nankai University, Tianjin 300071, P. R. China, and

<sup>‡</sup>Department of Chemistry and Center of Advanced Materials for the Purification of Water with Systems, University of Illinois at Urbana–Champaign, Urbana, Illinois 61801, United States.

<sup>§</sup>Current address: Department of Chemical and Biochemical Engineering, University of Maine, 5737 Jenness Hall, Orono, Maine 04469

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The molecular Re(V) complex, chlorobis(2-(2'-hydroxyphenyl)-2-oxazoline)-oxorhenium(V),  $\text{Re}(\text{O})(\text{hoz})_2\text{Cl}$ , has been investigated as a suitable precursor, when combined with activated carbon powder containing 5 wt % Pd, to provide a heterogeneous catalyst for the reduction of aqueous perchlorate by hydrogen. Two general methods for catalyst preparation have been adopted: first, by a standard "incipient wetness" impregnation of the carbon powder with handling under largely aerobic conditions for convenience and, second, by a completely anaerobic procedure maintaining a hydrogen atmosphere during adsorption of the complex in water onto the powder. Both types of catalyst were efficient for the complete reduction of perchlorate to chloride within a few hours at room temperature over a range of initial concentrations (2–200 ppm) under 1 atm of  $\text{H}_2$  and acidic conditions (pH 2.7–3.7). The perchlorate reduction profiles displayed pseudo-first-order kinetics, and the rates were insensitive to excess chloride. Complete reduction of perchlorate was observed even at pH 5.9 in a phosphate buffer over the course of two weeks. Under comparable conditions, chlorate reduction proceeded ca. 10 times more quickly than perchlorate reduction. The impregnated catalyst was examined by STEM/EDS, which revealed a wide distribution in Pd nanoparticle sizes and also suggested that the Re complex did not aggregate preferentially on or near the Pd particles. XPS of this material provided evidence for reduced Pd after the reaction, but only a +7 oxidation state was seen for the Re sites both pre- and postreduction. Elemental analyses of the catalyst materials taken pre- and postreduction showed variable amounts of Re loss (0–50%) but relatively unchanged amounts of nitrogen. These results show the need to maintain a reducing atmosphere during the preparation and operation of the catalyst in order to achieve optimum activity and stability.

### Introduction

The perchlorate ion,  $\text{ClO}_4^-$ , is established as a widespread contaminant of ground and surface waters, as well as soil, throughout the United States, with corresponding carryover into some foodstuffs.<sup>1–3</sup> The aqueous chemistry of perchlorate is dominated by its high kinetic barrier to reduction, which makes it essentially inert to reaction with typical nucleophilic reducing agents, and by its low basicity, which leads to weak surface adsorption and ease of transport in

environmental systems.<sup>4–6</sup> The public health concerns surrounding perchlorate contamination are based on its known interference with the uptake of iodide by the thyroid, which is especially significant due to the enhanced role played by this gland in regulating neural development in the early stages of human life.<sup>7–9</sup> The U.S. EPA is currently conducting an intensive assessment of the environmental risk posed by perchlorate in advance of a decision whether to issue a national regulation for drinking water.<sup>8,9</sup> The interim advisory level is

\*To whom correspondence should be addressed. E-mail: shapley@illinois.edu.

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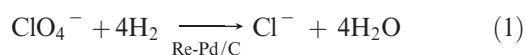
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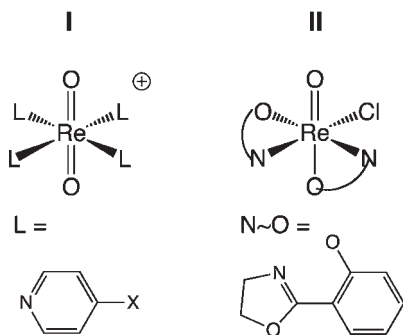
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15 ppm,<sup>8</sup> but in the absence of a federal mandate, some states have set lower legal limits, e.g., California at 6 ppm.<sup>10</sup> Effective remediation strategies for perchlorate are limited currently to selective ion exchange or bioremediation.<sup>11,12</sup> The biological approach completely destroys perchlorate, but doubts remain about public acceptance of its direct application to drinking water. Ion exchange effectively separates perchlorate from drinking water, but postseparation treatment (e.g., incineration) of the loaded resin or of a concentrated regeneration brine is necessary for complete destruction.

The chemical or electrochemical reduction of perchlorate by a heterogeneous catalyst is an alternative approach, but typical cases are slow and inefficient under ambient conditions.<sup>13–16</sup> Nevertheless, in previous work, we showed that efficient reduction of aqueous perchlorate to chloride can be achieved with a *bimetallic* heterogeneous catalyst prepared by dispersing a Re(VII) complex precursor, e.g., ammonium perrhenate, onto a commercial 5 wt % Pd/activated carbon powder.<sup>17</sup> Hydrogen provides the reducing equivalents, and no intermediates or products other than chloride are observed (see eq 1).



More recently, we reported that adding a substituted pyridine ligand with the perrhenate or starting with a preformed Re(V) complex, e.g.,  $[\text{ReO}_2(\text{py-X})_4]^+$  (see I), generates a catalyst with significantly improved activity as well as greater stability toward pH changes.<sup>18</sup>



Our initial work was inspired by seminal observations published in 1995 by Abu-Omar and Espenson,<sup>19</sup> who showed that the compound methyltrioxorhenium(VII) in strongly acidic aqueous solution could catalyze the reduction of perchlorate with hypophosphorous acid ( $\text{H}_3\text{PO}_2$ ) through

an oxygen atom transfer (OAT) cycle.<sup>20</sup> In succeeding investigations, Abu-Omar and co-workers demonstrated that the complex chlorobis(2-(2'-hydroxyphenyl)-2-oxazoline)-oxorhenium(V),  $\text{Re}(\text{O})(\text{hoz})_2\text{Cl}$  (see II), was an effective perchlorate reduction catalyst in aqueous acetonitrile, by using organic sulfides as oxygen acceptors from an intermediate Re(VII) dioxo complex.<sup>21–23</sup> Oxazoline ligands are found in naturally occurring metalloenzymes, and they are attractive as ligands for metal catalysts in water, since they are typically less sensitive to hydrolysis than more commonly used chelating imine ligands.<sup>24</sup> We have found that using compound II as a precursor provides an active and robust catalyst system for perchlorate (and chlorate) reduction. Significant aspects of the preparation, characterization, and use of this new Re–Pd/C heterogeneous catalyst are reported here.

## Experimental Section

**Chemicals and Compounds.** Catalytic reduction experiments used 18.2  $\text{M}\Omega\cdot\text{cm}$  of water (TOC < 10 ppb) obtained from a Barnstead E-pure four-cartidge 240 V deionization system, Model D4642-33. Tanks of hydrogen (> 99.9%) were supplied by Linde Gas. All other chemicals and solvents were reagent grade or better and were supplied by Sigma Aldrich or Fisher Scientific. The complex  $\text{Re}(\text{O})(\text{hoz})_2\text{Cl}$ , the precursor compound  $\text{Re}(\text{O})\text{Cl}_3(\text{OPPh}_3)(\text{SMe}_2)$ , and the ligand Hhoz were prepared according to literature methods.<sup>25</sup>

Palladium, as 5 wt % Pd on activated carbon (wet, Degussa-type E101 NO/W), was a damp powder as received from Sigma Aldrich. It was first calcined at 110 °C for 1 h under flowing air, then reduced at 250 °C for 1 h under flowing hydrogen. The material was allowed to cool to room temperature under the hydrogen atmosphere, then exposed to air until the highly exothermic formation of surface oxide was complete. Since this surface oxide of palladium is easily reduced by hydrogen,<sup>26,27</sup> the material was stored in the air until needed. The 5 wt % Pd on  $\gamma$ -alumina (Sigma Aldrich) and 5 wt % Pd on silica (Strem) materials were received as dry powders, and no pretreatment was applied.

**Analytical Methods.** Measurements of pH were conducted with a ThermoOrion Model 420 m and a standard Ag/AgCl pH electrode. Elemental analyses were performed in the Microanalysis Laboratory of the School of Chemical Sciences (UTUC); analysis for metal content was conducted by ICP-MS. Perchlorate, chlorate, chloride, and perrhenate concentrations were determined by ion chromatography with a Dionex ICS-1000 system (AS 40 autosampler, 25  $\mu\text{L}$  injection loop, 35 mM NaOH eluent, 1 mL/min flow rate, 4 mm AS-16 analytical and guard columns, 30 °C). The hydroxide eluent was maintained under an argon atmosphere to limit carbonate formation.

X-ray photoelectron spectra were obtained on a Kratos Axis ULTRA spectrometer by using monochromatized Al  $K\alpha$  radiation with a hemispherical mirror analyzer. For the survey scans,

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a 15 keV accelerating voltage was used with an emission current of 8 mA and a pass energy of 160 eV. For the high resolution scans, the pass energy was lowered to 40 eV. The spectra were referenced to the C 1s binding energy peak at 284.5 eV and were fit by using the curve-fitting function in CasaXPS.

Dark-field scanning transmission electron microscopy (STEM) and energy-dispersive X-ray spectroscopy (EDS) were performed on a JEOL 2010F field emission TEM with an accelerating voltage of 200 keV and an emission current of 150  $\mu$ A. The HREM resolution was 0.24 nm, and the probe size for spot analysis by EDS was ca. 1 nm.

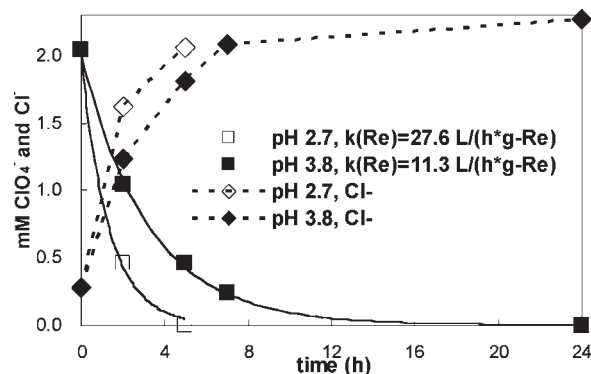
The BET surface area of the activated carbon powder was determined on a Quantachrome Nova 2200e analyzer. Palladium metal surface areas were determined by CO pulse chemisorption on a Micromeritics Pulse ChemiSorb 2705 system. The specific quantities of CO adsorbed (mmol CO/g catalyst) were 0.077 for 5 wt % Pd/C, 0.119 for 5 wt % Pd/alumina, and 0.054 for 5 wt % Pd/silica.

**Effect of Hydrogen on pH of Pd/C Powder Suspended in Water.** A set of two experiments were performed with the dry Pd/C powder in the absence of any added acid, base, or Re complex. Two samples of equal mass were dispersed into two flasks, each filled with an equal volume of deionized water (loading = 0.5 g/L). One of the flasks was exposed to a flowing H<sub>2</sub> atmosphere, whereas the other was exposed to flowing N<sub>2</sub>. The pH was measured prior to introducing the gas, again after 1 h of gas flow, and finally after 5 h of gas flow. The solution in the flask under nitrogen displayed a pH of 6.4, which was unchanged after either 1 h or 5 h. In contrast, the solution in the flask under hydrogen had dropped to a pH of 3.7 after 1 h and remained at this value at 5 h.

**Catalyst Preparation by Incipient Wetness Impregnation.** The Re(O)(hoz)<sub>2</sub>Cl complex was dissolved in a minimum of dichloromethane, and the solution was added in several small portions to the dry Pd/C powder, taking care not to exceed the pore volume and wet the surface. Once the incipient wetness point was reached, the damp material was dried *in vacuo* at 70–80 °C for 10–15 min. This process was repeated, if necessary, until the desired Re loading was reached. Finally, the fully loaded material was dried *in vacuo* at 70–80 °C for 1 h. The same procedure was used to prepare catalysts with 5 wt % Pd/ $\gamma$ -alumina and 5 wt % Pd/silica.

**Reactor System and Sampling.** Catalytic reduction experiments were performed in a batch reactor situated in a water bath at 23  $\pm$  1 °C on top of a magnetic stirrer. The reactor consisted of a three-neck round-bottom flask containing 200 mL of aqueous solution, the powdered catalyst (typically 100 mg), and a Teflon-coated magnetic stir bar. With continuous stirring of the suspension, hydrogen was introduced via the submerged tip of a glass pipet seated in a rubber O-ring sealed adapter in one neck of the flask. A second neck was sealed with a rubber septum and fit with a 25 gauge needle to allow for gas outflow. The final neck was sealed with a glass stopper or a rubber septum. Samples were withdrawn periodically by syringe, filtered through a 0.2  $\mu$ m nylon syringe filter, diluted if necessary, and stored in glass vials for later analysis by ion chromatography. Measurements of pH and/or temperature were conducted periodically. The used catalyst was recovered by filtration in the air and was dried at ca. 110 °C before subsequent microanalysis.

**Catalyst Preparation by *in Situ* Adsorption of Re(O)(hoz)<sub>2</sub>Cl.** A weighed amount of Pd/C powder was dispersed into nanopure water with stirring, and the flask was purged with hydrogen for ca. 2 h until the pH was steady (*vide supra*). Then, solid Re(O)(hoz)<sub>2</sub>Cl (an amount sufficient to achieve ca. 7–8 wt % Re in the final Re–Pd/C catalyst) was added to the flask against the hydrogen flow, and the mixture was maintained under a hydrogen atmosphere for 6 h. Deoxygenated concentrated ammonium perchlorate solution was added at the end of the adsorption period in order to begin the reaction.



**Figure 1.** Perchlorate reduction and chloride release profiles at two different pH values. Solid lines for perchlorate are data fits; dotted lines for chloride are added for clarity. Conditions: 2 mM HClO<sub>4</sub>, 0.5 g/L catalyst, 5.5 wt % Re; pH 3.8 obtained by adding NaOH.

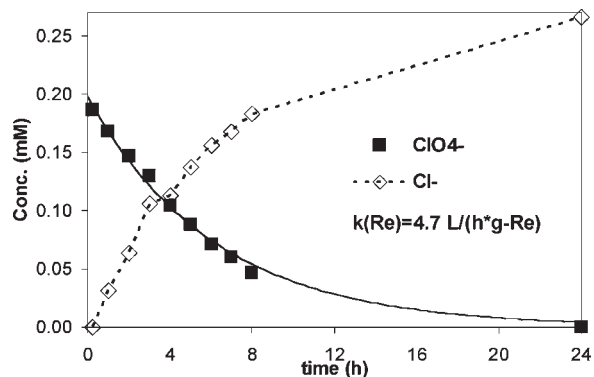
**Catalyst Preparation from Perrhenate and Hhoz.** A 100 mM Hhoz stock solution was prepared with HCl at a pH of ca. 3. The Hhoz solution and a perrhenate solution were mixed to form a 2:1 molar ratio (Hhoz/Re) solution with [Re] = 0.2 mM, and the pH was readjusted to 3 with HCl. A weighed amount of Pd/C powder (loading 0.35 g/L) was dispersed into this solution with stirring, and the flask was purged with hydrogen for 6 h. At this point, perrhenate was no longer detected in solution (see Figure 9). In the absence of added Hhoz, more than 12 h was required for complete adsorption of perrhenate. At the end of the adsorption period, a concentrated, deoxygenated perchlorate solution was added, and sampling for IC analysis began immediately.

**Buffer Systems.** A NaH<sub>2</sub>PO<sub>4</sub>·H<sub>2</sub>O (0.01 M)/H<sub>3</sub>PO<sub>4</sub> (x M) buffer system was employed for the pH range of 2.6–4.5. A pH of 5.9, buffer was prepared by combining 10 mM NaH<sub>2</sub>PO<sub>4</sub> and 1.1 mM Na<sub>2</sub>HPO<sub>4</sub>. The catalyst was stirred in the buffer solution overnight under flowing hydrogen to establish a stable pH value before ammonium perchlorate (2 mM) was added.

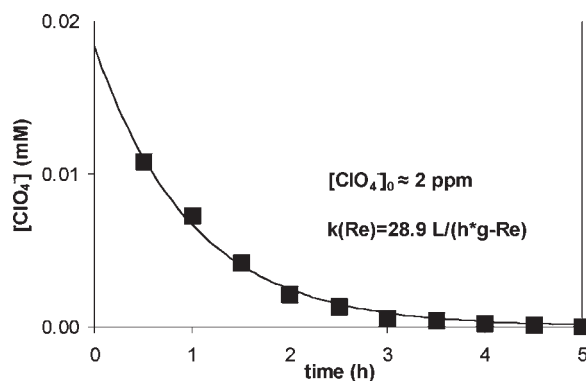
## Results

**Perchlorate Reduction by Impregnated Re–Pd/C Catalysts.** The material prepared from Re(O)(hoz)<sub>2</sub>Cl by standard incipient wetness impregnation of Pd/C powder showed significant catalytic activity for perchlorate reduction under conditions analogous to those used in our previous studies.<sup>17,18</sup> As shown in Figure 1, a reaction conducted with an initial concentration of 2 mM HClO<sub>4</sub> (200 ppm ClO<sub>4</sub><sup>-</sup>, pH 2.70) proceeded to completion in a few hours under a hydrogen atmosphere. Only chloride was observed as a product, with good overall material balance. The perchlorate concentration profile was fit well by a pseudo-first-order kinetic model with  $k(\text{obs}) = 0.76 \text{ h}^{-1}$ . As also shown in Figure 1, raising the solution pH to 3.8 caused the reaction rate to decrease ( $k(\text{obs}) = 0.31 \text{ h}^{-1}$ ), but the reduction continued nevertheless to below detection limits (< 1 ppm). At pH 2.7, our previous perrhenate-based system showed a reduction rate approximately an order of magnitude smaller, and at pH 3.7 the reduction was not only slower in initial rate but also incomplete overall due to catalyst instability.<sup>17</sup> However, the properties of this catalyst compare well with the best performance observed for perrhenate catalysts promoted by pyridine ligands.<sup>18</sup>

A higher pH for this system was also produced by starting with a lower concentration of perchloric acid. Thus, 20 ppm HClO<sub>4</sub> provided a reaction pH of 3.5, and



**Figure 2.** Reduction of 0.2 mM  $\text{ClO}_4^-$  (added as  $\text{HClO}_4$ ), pH 3.5, 0.5 g/L catalyst. Solid line for perchlorate is data fit; dotted line for chloride connects successive points.



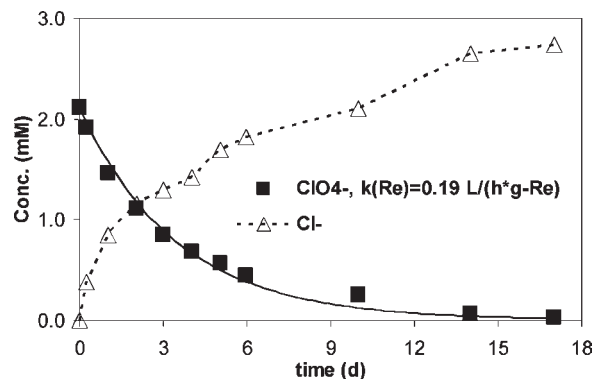
**Figure 3.** Reduction of 0.02 mM  $\text{ClO}_4^-$  ( $\text{NH}_4\text{ClO}_4$ ), pH 2.7 (HCl), 0.5 g/L catalyst. Solid line is data fit for perchlorate.

reduction proceeded to completion, as shown in Figure 2, with  $k(\text{obs}) = 0.15 \text{ h}^{-1}$ . At this concentration level, the excess chloride released from the catalyst material (*vide infra*) became visible.

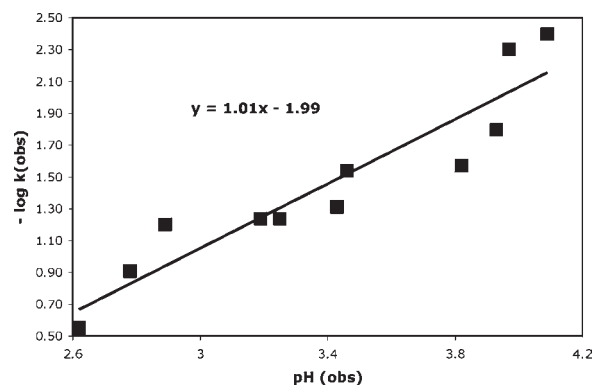
The catalyst was also effective at a much lower concentration of perchlorate ( $\sim 2$  ppm) added as ammonium perchlorate with HCl added to achieve a pH of 2.7. This resulted in a 100-fold excess of chloride over perchlorate. As shown in Figure 3, perchlorate reduction nevertheless proceeded to completion in a matter of hours, with  $k(\text{obs}) = 0.83 \text{ h}^{-1}$ . This value is quite comparable with the reduction rate observed at pH 2.7 with 200 ppm  $\text{HClO}_4$  when excess chloride was not present.

An attempt was made to reduce 200 ppm perchlorate (2 mM) at an initial reaction pH of 5.6, created by adding NaOH to the standard mixture. The reaction proceeded to completion, but the pH at the end of the reaction was determined to be 3.6, apparently due to acid produced by the Pd/C material under hydrogen. Separate experiments verified that the Pd/C material alone in water produced acid when exposed to hydrogen (ca. pH 3.7 at 0.5 g/L). However, a phosphate buffer could be used to maintain consistent pH values in contact with the Pd/C material under a hydrogen atmosphere. As shown in Figure 4, perchlorate could be completely reduced to chloride at a pH of 5.9 over several days. The observed reduction rate constant was  $0.28 \text{ d}^{-1}$ .

A plot of log reduction rate versus different (buffered) reaction pH values is shown in Figure 5. The slope was



**Figure 4.** Reduction of perchlorate and release of chloride in pH 5.9 phosphate buffer solution. Solid line for perchlorate is data fit; dotted line for chloride connects successive points.

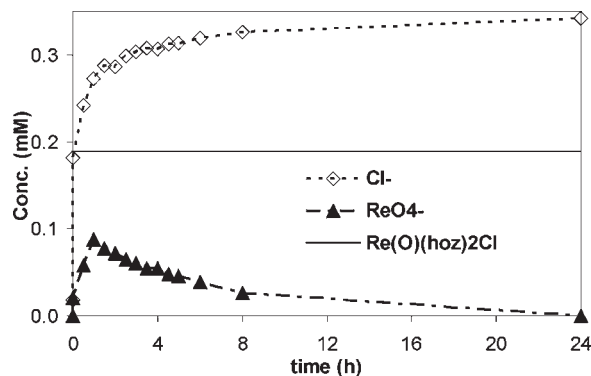


**Figure 5.** Correlation of observed reduction rate constant with buffered reaction pH.

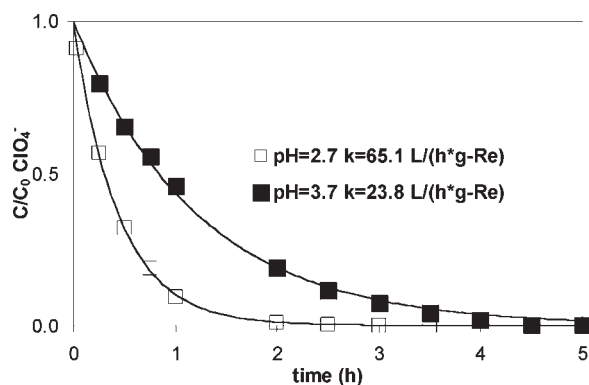
found to be  $-1.0(0.1)$ . It should be noted that the Re normalized rate at a pH of 2.7 was smaller in the phosphate buffered system, suggesting that competitive inhibition by (dihydrogen) phosphate was occurring.

**Desorption Studies of Impregnated Catalyst.** A sample of impregnated catalyst was suspended in water under a hydrogen atmosphere (no perchlorate added). Under these conditions, the pH of the solution was ca. 3.6 due to acid released from the Pd/C support material under  $\text{H}_2$  (see the Experimental Section). As shown in Figure 6, significant amounts of both chloride and perrhenate were released. For chloride, an initial amount of 0.18 mM rose slowly to a value of 0.34 mM after 24 h. From the amount of  $\text{Re}(\text{O})(\text{hoz})_2\text{Cl}$  complex delivered with the powdered support, ca. 0.19 mM would have been expected. Therefore, it appears that the Pd/C powder contained the equivalent of ca. 0.15 mM chloride and the remaining 0.19 mM was released from the complex. For perrhenate, the amount in solution rose rapidly to ca. 0.09 mM and then slowly declined to zero after 24 h. The maximum amount of perrhenate released corresponded to almost half of the Re present on the support from the preparation.

**Perchlorate Reduction with *in Situ* Catalyst Using  $\text{Re}(\text{O})(\text{hoz})_2\text{Cl}$  As Precursor.** The Re-Pd/C catalyst prepared from  $\text{Re}(\text{O})(\text{hoz})_2\text{Cl}$  by adsorption onto Pd/C powder under the protection of hydrogen showed high activity for perchlorate reduction. As shown in Figure 7, reductions run at initial pH values of 2.7 or 3.7 proceeded



**Figure 6.** Perrhenate and chloride desorption from incipient wetness catalyst (0.5 g/L). The dotted and dashed lines are added to aid the eye. The solid middle line represents the concentration of  $\text{Re(O)(hoz)}_2\text{Cl}$  as added with the catalyst sample.

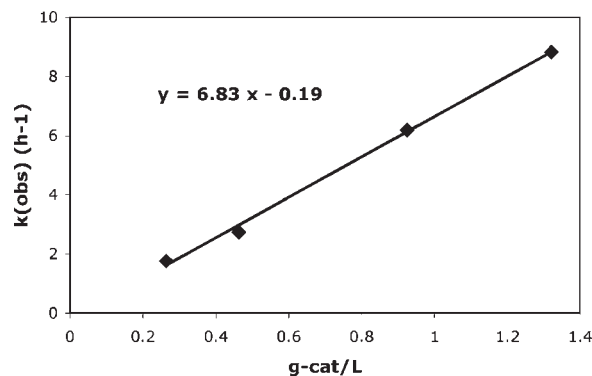


**Figure 7.** *In situ* catalyst (0.5 g/L) for perchlorate reduction: pH 2.7 (HCl), 0.2 mM  $\text{ClO}_4^-$  ( $\text{NH}_4\text{ClO}_4$ ); pH 3.7, 0.1 mM  $\text{ClO}_4^-$  ( $\text{HClO}_4$ ). Solid lines are data fits.

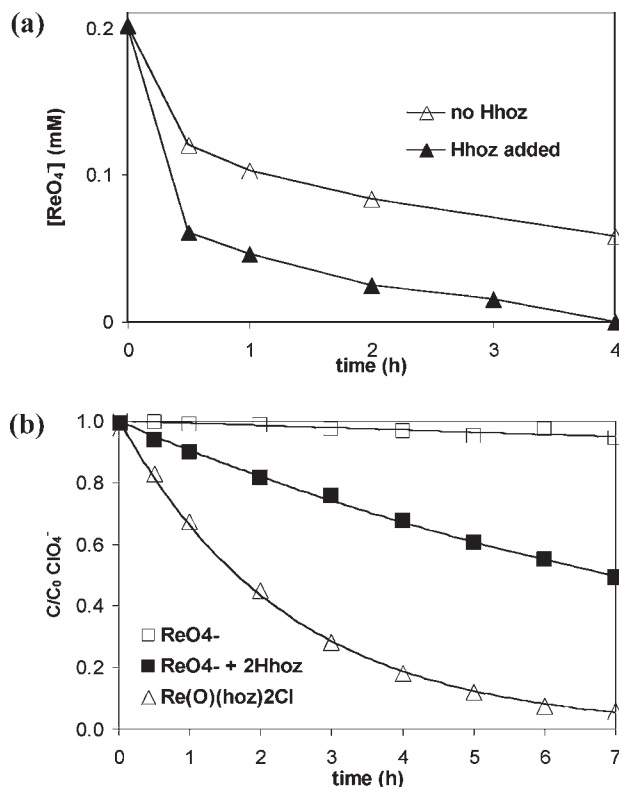
to completion in a few hours, and the profiles were well fit by a pseudo-first-order kinetic model. Little or no perrhenate was detected in solution during these reactions, in contrast to the significant amounts of perrhenate observed during reactions conducted with the impregnated catalyst. Note that the reduction rates depicted in Figure 7 are effectively double those shown for the impregnated catalyst in Figure 1.

A set of experiments conducted with different amounts of catalyst prepared by adsorption directly in the reactor demonstrated a good linear correlation of observed reduction rate with catalyst concentration, as shown in Figure 8. The slope of this plot can be normalized by the amount of rhenium in the reactor to give  $84.8 \text{ h}^{-1} (\text{g Re/L})^{-1}$ , the value of which is ca. 20 times greater than that derived from a similar plot reported for the first generation catalyst with 9.4 wt % Re at a pH of 2.7.<sup>17</sup> This linear plot also suggests that mass transfer of hydrogen to the surface of the powdered catalyst is not a limiting factor affecting the reaction rate.

***In Situ* Preparation of a Re–Pd/C Catalyst from  $\text{ReO}_4^-$  and the Hhoz Ligand.** The effects of added Hhoz on the adsorption of perrhenate under hydrogen as well as on the activity of the resulting catalysts were briefly examined. As shown in Figure 9, adding two equivalents of Hhoz caused a significantly faster and more complete loss of perrhenate from the solution, and the resulting material



**Figure 8.** Perchlorate reduction rate constants observed for different concentrations of catalyst prepared by adsorption: pH 3 (HCl), 0.2 mM  $\text{ClO}_4^-$ , 8.05 wt % Re.



**Figure 9.** (a) Top: Effect of Hhoz on perrhenate adsorption, pH 3 (HCl), 0.35 g/L Pd/C; lines shown connect successive points. (b) Bottom: comparison of perchlorate reduction profiles; solid lines show data fits. Perchlorate was added following complete precursor adsorption.

displayed a significantly better capability for reducing perchlorate.

**Physical Characterization of the Impregnated Re–Pd/C Catalyst.** Since the impregnated Re–Pd/C catalyst material was prepared and handled in the air, no special precautions were taken before it was examined by several physical techniques. The total (BET) surface area of the 5 wt % Pd on activated carbon material employed in this work was found to be  $744 \text{ m}^2/\text{g}$  by  $\text{N}_2$  physisorption. This result compares well with literature values for other activated carbon catalysts.<sup>28</sup> From CO chemisorption data, the active metal surface area and dispersion were

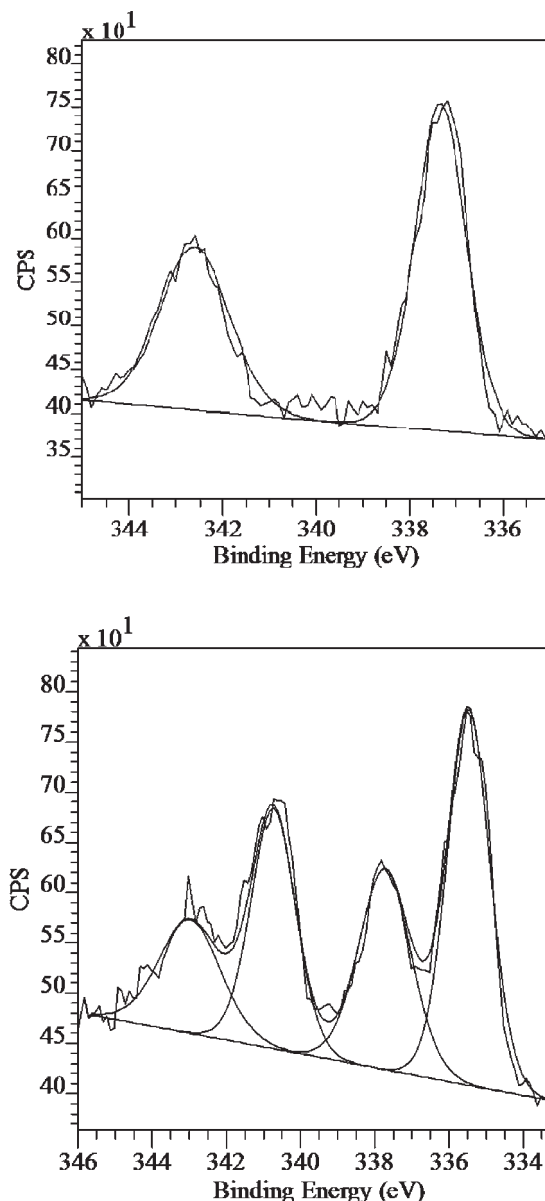
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calculated, by assuming a Pd/CO binding ratio of 2:1,<sup>29,30</sup> as 7.54 m<sup>2</sup>/g Pd, corresponding to a dispersion (% surface Pd) of 28%. Following the addition of the Re(O)(hoz)<sub>2</sub>Cl complex to the Pd/C powder, a lowered CO chemisorption was measured, corresponding to an active palladium surface area of 3.8 m<sup>2</sup>/g Pd and a dispersion of 18%. Elemental analyses were obtained for a variety of catalyst samples both before and after use for perchlorate reduction. Postreduction values for catalysts filtered in the air showed an amount of Re lost that corresponded with ca. 30–50% of that initially present, but the observed wt % N was relatively constant and close to that expected from the initial impregnation. Thus, Re was lost to solution from the catalytic material without a corresponding loss of N-containing ligand or ligand fragment.

Scanning transmission electron microscopy (STEM) provided images of the catalyst material that showed carbon particles with diameters of tens of micrometers decorated with Pd nanoparticles (see Figure S-1, Supporting Information). There was a wide variation in the size of the metal particles with the average Pd particle size calculated to be ca. 4 nm, on the basis of the analysis of 111 nanoparticles. This value is consistent with the CO chemisorption data. The addition of the Re(O)(hoz)<sub>2</sub>Cl complex to the carbon material had no apparent effect on the Pd nanoparticle size distribution by visual examination of STEM images. Energy dispersive X-ray spectroscopy (EDX) spot analysis of a bright palladium particle showed the expected large Pd peak as well as small Re peaks. When the X-ray beam was aimed away from any Pd particles, there was the expected reduction in Pd peak height, but small Re peaks remained and Cu appeared from the carbon-coated TEM grid (see Figure S-2, Supporting Information). These results suggest that the Re species were distributed rather evenly across the entire surface of the material and that they did not aggregate preferentially near the Pd particles.

X-ray photoelectron spectroscopy (XPS) data were obtained on a sample of Re(O)(hoz)<sub>2</sub>Cl/Pd/C both before and after its use as a catalyst. Scans of the Pd 3d<sub>5/2</sub> region (see Figure 10) for the as-prepared catalyst were consistent with only one Pd oxidation state, with a binding energy of 337.3 eV indicating PdO.<sup>31</sup> Following exposure to the reducing environment, but re-exposure to air with handling, the material exhibited two distinct binding energies of 335.5 and 337.7 eV, due to Pd(0) and Pd(II) oxidation states, respectively,<sup>31</sup> in the ratio of ca. 1.5:1.

Figure 11 shows high resolution XPS scans over the Re 4f<sub>7/2</sub> region. The binding energy for both the pre- and postreaction sample was 45.6 eV, which is consistent with a +7 oxidation state for rhenium.<sup>31,32</sup> Since XPS has a relatively shallow sampling depth, these results indicate that facile oxidation of the Re(V) complex took place on



**Figure 10.** High-resolution XPS scans (and fit curves) of Pd 3d<sub>5/2</sub> region for Re(O)Cl(hoz)<sub>2</sub>/Pd/C catalysts handled in the air: (top) prereduction, (bottom) postreduction.

the surface of the carbon support as the material was handled under ambient conditions.

**Silica and Alumina as Supports.** We briefly examined catalysts prepared by the addition of a comparable amount of Re(O)(hoz)<sub>2</sub>Cl to both 5 wt % Pd/silica and 5 wt % Pd/ $\gamma$ -alumina. These two oxide support materials do yield catalysts for perchlorate reduction (see Figure S-3, Supporting Information), but the rate constants are more than an order of magnitude slower at pH 2.7 than the value found for the activated carbon system. The catalyst stability toward a unit increase in pH is significantly poorer. The characteristics of the Re–Pd based catalyst system are strongly tied to the nature of the support surface, and activated carbon is currently the support of choice.

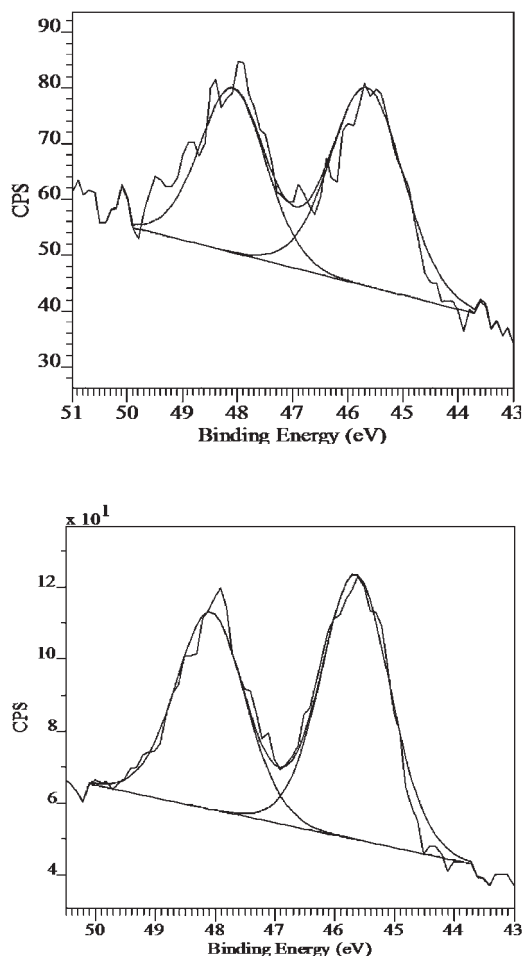
**Chlorate Reduction.** Chlorate is reduced by metal complexes typically much more rapidly than perchlorate.<sup>19,23</sup> Figure 12 provides representative concentration profiles

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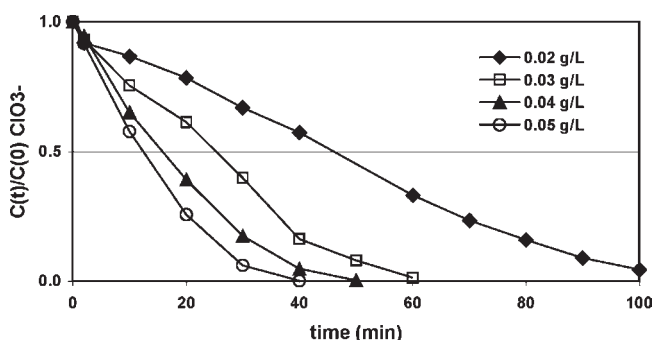
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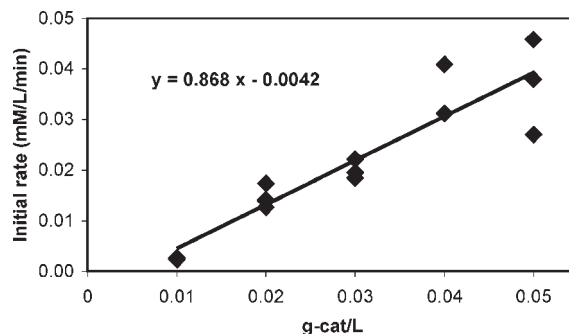


**Figure 11.** High-resolution XPS scans (and fit curves) of Re  $4f_{7/2}$  region for  $\text{Re}(\text{O})\text{Cl}(\text{hoz})_2/\text{Pd}/\text{C}$  catalysts handled in the air: (top) prereduction, (bottom) postreduction.



**Figure 12.** Representative profiles for the reduction of chlorate by  $\text{Re}(\text{O})\text{Cl}(\text{hoz})_2/\text{Pd}/\text{C}$  with different catalyst loadings: 5.95 wt % Re, 1.2 mM  $\text{ClO}_3^-$ , pH 2.7 (HCl). Lines shown connect successive points to aid the eye.

for chlorate reduction with the Re–Pd/C catalyst. The reaction proceeded to completion in minutes rather than hours, and it did so with 10% or less of the catalyst loading used for perchlorate. Under comparable conditions, the Pd/C powder alone also catalyzed chlorate reduction, but the rates were 10–20 times slower in the absence of added rhenium. No evidence for perchlorate reduction by Pd/C alone was observed, even under more severe conditions.



**Figure 13.** Dependence of chlorate initial reduction rate on catalyst loading: 5.95% Re;  $[\text{ClO}_3^-] = 1.2 \text{ mM}$ ; pH 2.7 (HCl).

The concentration profiles for chlorate were not fit well by an exponential function, since they typically were nearly linear for more than half the reaction, with curvature appearing only near the end. Attempts were made to fit the entire profile with a two-parameter pre-equilibrium kinetic model (see Discussion); however, the two fitting parameters were highly correlated and not individually statistically reliable. Therefore, initial rates, determined from the first 50% or less of the reaction, were adopted as a means of comparison among different experiments.

As shown in Figure 13, a plot of the initial chlorate reduction rate vs catalyst loading is reasonably linear within the scatter of the data. This confirms that delivery of hydrogen to the catalysts particles is not a limiting factor in the reduction of chlorate over the loading range examined. The slope of this plot provides a normalized initial rate of  $0.868 \text{ mM ClO}_3^-/\text{min}\cdot\text{g cat}$ , which is  $14.59 \text{ mM ClO}_3^-/\text{min}\cdot\text{g Re}$  or  $875 \text{ mM ClO}_3^-/\text{h}\cdot\text{g Re}$ . From the slope of the similar plot for perchlorate shown in Figure 8, an initial reduction rate for 100 ppm perchlorate (1.0 mM/L) would be  $85 \text{ mM ClO}_4^-/\text{h}\cdot\text{g Re}$ . Thus, at comparable concentrations of chlorate and perchlorate, the turnover rate at each active rhenium center is ca. 10 times faster for chlorate than for perchlorate under these conditions.

## Discussion

**Characteristics of the  $\text{Re}(\text{O})(\text{hoz})_2\text{Cl}$ -Derived Re–Pd/C System.** The process of “heterogenizing” a molecular complex by interacting it with a solid support necessarily raises the question of what changes ensue at the molecular center after the adsorption process is complete. The Pd/C “support” used in this work is a typical commercial high surface area activated carbon material, consisting of micrometer-sized carbon particles decorated with nanosized Pd particles. The latter have a distribution of sizes centered at 4 nm, with CO chemisorption measurements indicating ca. 28% of the total Pd atoms accessible before adsorption of  $\text{ReO}(\text{hoz})_2\text{Cl}$  and 18% thereafter. Although the decrease in metal surface area might indicate substantial selective adsorption onto Pd nanoparticles, this conclusion is not supported by the EDS data, which show no preferential linkage between Pd and Re concentrations in the material. The measured loss of metal surface area was more likely due to blockage of micropores containing some Pd nanoparticles by the adsorbed molecular complex.

The specific ligand set surrounding the Re center during and after catalysis is subject to some uncertainty. The release of an equivalent of chloride to solution was clearly observed for the impregnated material (see Figure 6). This result is consistent with the facile formation of the cationic complex  $[\text{ReO}(\text{hoz})_2(\text{S})]^+$  ( $\text{S} = \text{H}_2\text{O}, \text{CH}_3\text{CN}$ ) in aqueous acetonitrile solution that has been described by Abu-Omar and co-workers.<sup>21,22</sup> For the complex adsorbed onto Pd/C, the chloride release may be promoted by coordination of a surface functional group (e.g., hydroxide, phenoxide, or carboxylate) to the Re center. Pre- and postreduction elemental analyses of the catalytic material showed relatively constant %N values, suggesting that free Hhoz was not released to solution. In contrast, the %Re values of catalyst material recovered by filtration frequently showed significant decreases, consistent with the significant amounts of perrhenate observed in solution for the air-handled catalysts.

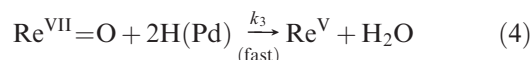
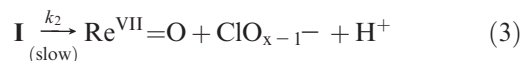
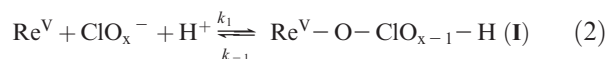
The dominant presence of one or more compounds with rhenium in a Re(VII) oxidation state on the surface of the impregnated material was revealed by XPS analysis. However, these data do not distinguish among various possible Re(VII) compounds that might be present. Of foremost interest is the dioxo Re(VII) species  $[\text{ReO}_2(\text{hoz})_2]^+$  that has been observed in solution as an intermediate stage in OAT reactions.<sup>21–23</sup> This type of species might well exhibit a longer lifetime and higher stability when dispersed on the support surface in the absence of easily oxidizable acceptors. Recently, the direct formation of oxorhenium(VII) complexes from rhenium(V) complexes reacting with dioxygen has been reported.<sup>33</sup> Second, partial hydrolysis of  $[\text{ReO}_2(\text{hoz})_2]^+$  has been reported to form the mono-hoz complex  $\text{ReO}_3(\text{hoz})$ .<sup>21</sup> This Re(VII) complex would very likely form  $\text{ReO}_4^-$  upon further contact with water, especially in the presence of acid, so that it might represent an intermediate stage in the formation of the perrhenate ion actually observed to be released into solution from the air-handled catalyst.

Reductive adsorption of perrhenate onto Pd/C powder under  $\text{H}_2$  is relatively slow,<sup>34</sup> and we observed that adding two equivalents of Hhoz not only enhanced the rate and extent of perrhenate adsorption but also significantly improved the catalytic activity of the resulting material for perchlorate reduction (see Figure 9). However, the observed catalytic activity was still markedly less than that achieved by starting with the preformed  $\text{ReO}(\text{hoz})_2\text{Cl}$  complex. Overall, maximal activity was obtained when the catalyst preparation was conducted by *in situ* adsorption of the  $\text{Re}(\text{O})(\text{hoz})_2\text{Cl}$  precursor under the protection of hydrogen, in which case no perrhenate was detected in solution during the reduction reaction. This result presumably indicates that for the Re center two hoz ligands are better than one, although it does not establish that the hoz ligands are bound to Re in exactly the same manner (chelating, O-deprotonated) as in the precursor  $\text{ReO}(\text{hoz})_2\text{Cl}$  complex.<sup>21–23</sup> A strong indication that two N-donor ligands per rhenium center are

required for maximum activity was found in our previous report on promotion of the perrhenate-based Re–Pd/C catalyst by adding N,N-dimethylaminopyridine.<sup>18</sup>

**Mechanism for the  $\text{ReO}(\text{hoz})_2\text{Cl}$ -Derived Re–Pd/C System.** The specific properties displayed by this new Re–Pd/C catalyst are as follows: (i) There is a pseudo-first-order reduction of perchlorate; separate experiments showed that chlorate, presumably the first intermediate, is reduced ca. 10 times faster than perchlorate. (ii) Chloride is the only observed product, but a 100-fold excess of chloride does not affect the reduction rate of perchlorate. (iii) The reduction rate is significantly dependent on pH, decreasing as the pH rises. These are the same basic features exhibited by our original Re–Pd/C system using perrhenate as a precursor<sup>17</sup> as well as by our more recently developed system in which perrhenate is enhanced by substituted pyridine ligands.<sup>18</sup>

These properties are embodied in the following set of eqs 2–4 that describe the catalytic cycle for the reduction of perchlorate ( $x = 4$ ) or chlorate ( $x = 3$ ).



Equation 4 indicates that the role of Pd is to activate  $\text{H}_2$  and thereby provide the two hydrogen atom equivalents needed to reduce  $\text{Re}(\text{VII})=\text{O}$  to  $\text{Re}(\text{V})(\text{OH})_2$  for a complete catalytic cycle. Hydrogen spillover is a well-documented phenomenon for supported metal particles,<sup>35–40</sup> and it has been observed directly at room temperature for Pd/C.<sup>39,40</sup> In the present case, we observed  $\text{H}^+$  production when the aqueous suspension of Pd/C was exposed to  $\text{H}_2$ . This is very likely due to hydrogen spillover that results in partial hydrogenation of oxygenated functional groups on the activated carbon<sup>41</sup> (e.g., aldehyde/ketone to alcohol or quinone to hydroquinone) to produce more acidic groups. Activation of dihydrogen on a Pd surface is known to be very fast at room temperature,<sup>42,43</sup> and limiting the rates of hydrogen transfer reactions on Pd nanoparticle sites requires very low  $\text{H}_2$  partial pressures.<sup>44</sup> We suggest that overall hydrogen transport (Pd activation + spillover) is not rate limiting in our system for perchlorate (or chlorate) reduction. Varying the loading of the catalyst in the reactor gave a linear response in observed reduction rate. These data expressed in terms of

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the concentration of Re in the reactor are shown in Figure 10 (and Figure 13). The linear plot and its intersection at the origin strongly suggest that the observed rates are directly determined by the availability and activity of the Re sites in the catalyst and that the hydrogen reducing equivalents originating at Pd are provided in a continuous flux completely sufficient to meet the needs of the perchlorate (or chlorate) reduction reaction. We note reports of oxo-rhenium compounds activating hydrogen directly in reactions with epoxides<sup>45</sup> and alkynes;<sup>46</sup> however, the conditions used (80–150 °C, 5–40 atm) were much more severe than those needed for perchlorate reduction, which further supports the idea of separate roles for Pd and Re in the Re–Pd/C catalyst system.

Equation 3 depicts the rate-determining step as the OAT reaction occurring within the (protonated) perchlorate–Re(V) complex (I) to generate an oxo-rhenium(VII) species with release of chlorate and a proton. Since this step involves oxidation of the rhenium center, its rate should depend on the electron-releasing capability of ligands attached to rhenium. Our results with substituted pyridine ligands showed a direct correlation between the donor ability of the ligand and the rate of perchlorate reduction.<sup>18</sup>

Finally, eq 2 explicitly includes the role of a proton, which is to promote a secondary hydrogen bonding interaction between one of the perchlorate oxygens and the surface in order facilitate perchlorate coordination. This interaction is not available for chloride, which therefore does not compete strongly with perchlorate for coordination to rhenium and does not act to inhibit the OAT reaction, at least at the levels we have examined.

**Kinetics Model.** Applying the steady-state assumption for the intermediate complex (I) shown in eqs 2 and 3 leads to the following rate expression (eq 5):

$$\text{Rate} = d/dt[\text{ClO}_x^-] = \frac{k_2(\text{Re})_T[\text{ClO}_x^-]}{\frac{k_{-1} + k_2}{k_1[\text{H}^+]} + [\text{ClO}_x^-]} \quad (5)$$

where  $(\text{Re})_T = [\text{Re}^V] + [\text{Re}^V\text{--O--ClO}_{x-1}\text{--H}]$  and  $[\text{Re}^{\text{VII}} = \text{O}]$  is assumed negligible at the steady state. Since we assume  $k_2 \ll k_{-1}$ , the former parameter can be neglected in the denominator, and if we define a pre-equilibrium “constant”  $K' = k_1[\text{H}^+]/k_{-1}$ , the result is expressed in eq 6:

$$d/dt[\text{ClO}_x^-] = \frac{k_2(\text{Re})_T[\text{ClO}_x^-]}{1/K' + [\text{ClO}_x^-]} \quad (6)$$

From this rate expression, two limiting cases can be considered. In the first,  $1/K' \gg [\text{ClO}_x^-]$ , and the rate expression collapses to a pseudo-first-order dependence on  $[\text{ClO}_x^-]$  (eq 7):

$$\begin{aligned} d/dt[\text{ClO}_x^-] &= k_2K'(\text{Re})_T[\text{ClO}_x^-] \\ &= k_{\text{obs}}[\text{ClO}_x^-] \end{aligned} \quad (7)$$

where the observed rate constant  $k_{\text{obs}} = k_2K'(\text{Re})_T$ . In the second case,  $[\text{ClO}_x^-] \gg 1/K'$ , and a pseudo-zero-order

**Table 1.** Composite Rate Parameters for Perchlorate Reduction with Various Re Catalysts

catalyst	$k_2K'$ (L/M s)	aqueous medium	ref
ReO <sub>2</sub> CH <sub>3</sub>	7.3	1.0 M CF <sub>3</sub> SO <sub>3</sub> H	19
ReO(hoz) <sub>2</sub> Cl	0.45	90% CH <sub>3</sub> CN	21
[NH <sub>4</sub> ][ReO <sub>4</sub> ] + Pd/C	0.21	2.0 mM HCl	17
[NH <sub>4</sub> ][ReO <sub>4</sub> ] + 2 DMAP + Pd/C	1.6	1.0 mM HCl	18
ReO(hoz) <sub>2</sub> Cl + Pd/C	4.4	1.0 mM HCl	This work

rate expression emerges (eq 8).

$$d/dt[\text{ClO}_x^-] = k_2(\text{Re})_T \quad (8)$$

The kinetic behavior observed for chlorate reduction appears to approach the second case, in that an initially linear concentration profile was typical (see Figure 12). However, the onset of curvature late in the reaction suggested that the strict condition for case 2 was not true throughout the reaction. We examined using the more complete eq 6 for numerical fits to the entire reduction profiles. Unfortunately, the two fitting parameters were found to be highly correlated. A value of ca. 3.4 L/mM for  $K'$  allowed a reasonable fit in nearly all cases, but the values for “best” fit (minimizing RMS deviations) in each case varied from ca. 1 to 10 L/mM, with a corresponding large variation in values of  $k_2$ . Nevertheless, with a value of  $K'$  in this range, the denominator in eq 6 will have values of  $[\text{ClO}_3^-]$  greater than  $1/K'$  through at least the early part of the reaction. Thus, the observed initial rate for chlorate reduction will approximate  $k_2(\text{Re})_T$ , and an estimate of  $k_2$  is provided from the slope of a plot of initial rates against total Re as shown in Figure 13.

Our observed perchlorate reduction profiles were pseudo-first-order, which conforms to the first case. This is understandable, since  $K'$  is expected to be very small for this weakly binding oxyanion, so  $[\text{ClO}_4^-]$  will always be  $\ll 1/K'$ . As shown in eq 7, the observed pseudo-first-order rate parameter is the product of  $k_2$ , the intrinsic rate for the OAT reaction;  $K'$ , the “complexation constant” for coordination of perchlorate to the Re center under the reaction conditions; and  $(\text{Re})_T$ , the total amount of Re available in the reaction system. A plot of  $k_{\text{obs}}$  vs catalyst loading is indeed linear, as shown in Figure 8, and the slope provides, after normalizing for Re content in the catalyst, a value of the product  $k_2K' = 4.4 \text{ s}^{-1} \text{ L/M Re}$ . Furthermore, since  $K'$  as defined is proportional to  $[\text{H}^+]$ ,  $k_{\text{obs}}$  is predicted to decrease significantly as the pH increases. This is qualitatively consistent with the observed effect of a unit increase in pH on the reduction rate, as shown in Figures 1 and 7. In an attempt to overcome the buffering effect of the Pd/C catalyst material in water when exposed to H<sub>2</sub>, we used a phosphate buffer to access a larger range of pH values under relatively consistent conditions. As shown by the data plotted in Figure 5, the dependence of  $\log k_{\text{obs}}$  on pH under these conditions has the predicted slope of  $-1$ , although confidence in the precise value of this result must be tempered by the expectation of competition by H<sub>2</sub>PO<sub>4</sub><sup>−</sup> with ClO<sub>4</sub><sup>−</sup> for binding to the Re centers.

As is apparent from examination of eq 7, the product is effectively a second-order rate coefficient for the direct

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interaction of a Re center with the oxyanion substrate. This composite parameter provides a measure of the catalytic efficiency for OAT from perchlorate to the Re centers in various catalysts. A similar pre-equilibrium kinetics model was developed by Espenson and Abu-Omar in the previous studies of the homogeneous MDO<sup>19</sup> and Re(O)(hoz)<sub>2</sub>Cl<sup>21</sup> systems reacting with perchlorate. Values of the “second-order” rate parameter for these systems are compared with analogous values derived for the heterogeneous Pd/C-supported systems in Table 1. It should be noted that the solution media were quite varied, ranging from aqueous triflic acid at pH 1 for MDO to 10% H<sub>2</sub>O/90% NCCH<sub>3</sub> with no added acid for the homogeneous ReO(hoz)<sub>2</sub>Cl system. Nevertheless, it is interesting that the “heterogenized” ReO(hoz)<sub>2</sub>Cl catalyst reported here is an order of magnitude more efficient for perchlorate reduction than the homogeneous system, under the specific conditions used in each case.

### Conclusion and Prospects

The ReO(hoz)<sub>2</sub>Cl–Pd/C catalyst, when prepared and maintained under a hydrogen atmosphere, exhibited a Re normalized composite rate constant,  $k_2K'$ , that was over 20 times faster than that observed for the perrhenate-based catalyst.<sup>17</sup> The activity improvement of the new system toward perchlorate reduction is clearly due to the presence of the hoz ligands around the Re center. This ligand promotion effect has also been demonstrated with a series of substituted pyridine ligands, most dramatically with N-dimethylamino-pyridine (DMAP).<sup>18</sup> The effect on rate enhancement is attributed to promotion of the rate-determining OAT step in the catalytic cycle, since this step results in a decrease in electron density at the Re center as the rhenium to oxygen double bond is formed (Re(V) oxidized to Re(VII)=O), and the donating ligand interaction with the Re center stabilizes the developing positive character. Furthermore, in both cases, the ligand-modified Re reaction site is stabilized toward increases in pH relative to the perrhenate-only system. In particular, we showed here that the ReO(hoz)<sub>2</sub>Cl-derived catalyst is sufficiently stable in a pH 5.9 phosphate buffer

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that complete reduction of perchlorate to chloride could be achieved after a reaction period of ca. 15 days.

The most likely use of a Re–Pd/C catalyst for perchlorate remediation would be in a two-stage system involving direct removal from drinking water by ion exchange followed by batch purification of the brine solution used for regeneration of the ion exchange column.<sup>17,34,47</sup> Any needed adjustment of pH in the regenerant brine for optimal activity in perchlorate reduction would not be prohibitive for this relatively modest volume of water. The significantly higher normalized activity for the catalyst derived from ReO(hoz)<sub>2</sub>Cl compared with that from ReO<sub>4</sub><sup>–</sup> would allow much shorter treatment times or much lower catalyst loadings. However, in both cases, leaching of ReO<sub>4</sub><sup>–</sup> from the catalyst into solution due to oxygen exposure serves to limit the catalyst activity, to reduce its capacity for reuse, and also to release a new contaminant into solution. Thus, careful and continuous maintenance of a reducing atmosphere for both the preparation and the use of a ReO(hoz)<sub>2</sub>Cl-derived catalyst would be necessary in order to take advantage of its superior properties.

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**Supporting Information Available:** STEM images of 5 wt % Pd on activated carbon powder, histogram of Pd nanoparticle size, EDS spot analyses of Re(O)(hoz)<sub>2</sub>Cl–Pd/C catalyst, and perchlorate reduction profiles for catalysts with 5 wt % Pd on silica and  $\gamma$ -alumina. This material is available free of charge via the Internet at <http://pubs.acs.org>.