# Electrochemical Dechlorination of 4-Chlorophenol to Phenol

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We have hypothesized that hydrogen gas intercalated in a palladium lattice is the powerful reducing agent that reductively dechlorinates chlorinated organic compounds that are adsorbed on the surface of palladized electrodes. We have shown that dechlorination of 4-chlorophenol to phenol occurs rapidly on palladized carbon cloth or palladized graphite electrodes. The reactions on the palladized carbon cloth and graphite depend on the adsorption of the chlorinated organic compound on the carbon surface and the reaction with hydrogen at the palladium/carbon interface. Palladium was much more effective in promoting the dechlorination reaction than platinum, probably because of its ability to intercalate hydrogen in its lattice.

## Introduction

The observation that elemental iron dechlorinates certain toxic volatile organic compounds has led to a revival in the investigation of metals that may be useful for the reductive dechlorination of organic compounds that are considered to be environmental hazards (1, 2). The reactivity of the Fe<sup>0</sup>/  $Fe^{2+}$  system, with a standard potential of -0.42 V, has been attributed to its ability to drive a large number of dechlorination reactions of halo-organic compounds. However, the use of zero-valent iron often results in only partial dechlorination in which the reaction products are sometimes more toxic than the reactants (5). Recently, a method for the rapid aqueous reduction of trichloroethylene and polychlorinated biphenyls to hydrocarbons by palladized iron (Pd/Fe) has been demonstrated (3-5). We have proposed that the high reactivity of the Pd/Fe bimetallic system can be attributed to the following sequence of reactions: (i) the evolution of hydrogen gas by the reduction of water molecules by elemental iron, i.e., the "corrosion" of iron in water; (ii) the adsorption of the evolved hydrogen gas by Pd<sup>0</sup>, and the formation of the powerful reducing species, Pd·H<sub>2</sub>, i.e., hydrogen gas intercalated into the elemental palladium lattice; and (iii) the reduction of the chlorinated organic compound that is adsorbed on the bimetallic Pd/Fe surface.

The principal variables that govern these dechlorination reactions are the surface area of the bimetallic Pd/Fe system and the amount of the species  $Pd \cdot H_2$  that is available for the reduction reactions. We have examined the cathodic reduction of a chlorinated organic compound at electrodes of known surface area in the presence and the absence of evolved hydrogen gas. We have also employed galvanostatic conditions, i.e., we have maintained a constant hydrogen flux at

the electrode surface to assess the role of hydrogen or adsorbed hydrogen (Pd·H<sub>2</sub>) on the reductive dechlorination reactions. This has helped in the evaluation of the role of surface-bound Pd in its role not only as a hydrogen evolution catalyst but also as a facilitator for the reductive dechlorination of organics. The experiments described below were performed as a result of the observation that the Pd/Fe system was able to effect the rapid hydrodehalogenation of TCE as opposed to Fe alone (4). The hydrogen evolution characteristics of platinized iron and palladized iron should be similar, but the rate of hydrodechlorination by Pt/Fe was much slower than that observed with Pd/Fe. This property may be due to the ability of palladium to absorb hydrogen; Pd metal in conjunction with hydrogen gas has been used over the years in hydrogenation schemes (6-9, 16). The organic compound that we have used to follow the course of the dechlorination reaction is 4-chlorophenol (4-CP). This compound was selected for its relative non-volatility and aqueous solubility of both the reactant and the product (phenol). Moreover, 4-CP and phenol can be conveniently determined at parts per million levels in aqueous solutions by HPLC.

Several types of cathodic materials have been studied for the catalytic decomposition of halogenated organics (10-12). Zhang and Rusling utilized either carbon cloth or Pb cathodes for the dechlorination of polychlorinated biphenyls (13). The authors found that Pb cathodes were superior to the former and suggested that this was due to the higher hydrogen overpotential of Pb. Matheson and Tratnyek proposed that it should be possible to rapidly dehalogenate chloro-organics with hydrogen gas if a suitable dechlorination catalyst is used (2). Such a process would take place via the following reaction:

$$H_2 + RX \rightarrow RH + H^+ + X^- \tag{1}$$

Recently, Kulikov and co-workers used Zn-modified carbon cloth for the reductive dechlorination of lindane in aqueous solution (*12*). In their proposed mechanism, lindane was adsorbed on the carbon cloth surface and then reduced by zinc metal. The metallic Zn islands were regenerated by the electrochemical reduction of  $Zn^{2+}$ . No mention was made however of the possibility that lindane may be dechlorinated by hydrogen gas. This route cannot be discounted since zinc metal is a prodigious producer of H<sub>2</sub> in aqueous solutions.

#### **Experimental Section**

**Materials and Chemicals**. Carbon cloth (99.9%) was supplied by Aesar (Ward Hill, MA). Graphite electrode rods, (6.15 mm diameter) designated as ultra-purity "F", were obtained from Ultra Carbon Corporation (Bay City, MI). Iron wire of 0.25 mm (99.9%, Aldrich, Milwaukee, WI), K<sub>2</sub>PdCl<sub>6</sub> (99%, Aldrich), K<sub>2</sub>PtCl<sub>6</sub> (99.99%, Aldrich), sodium acetate (Fisher, Pittsburgh, PA), methanol (HPLC grade, Fisher), and palladium gauze (Aesar) were all used as received. Phenol (99.5%, EM Science, Gibbstown, NJ) and 4-chlorophenol (99%+, Aldrich) were used without purification. All water was of 18.2 MΩ·cm quality obtained from a Millipore-Q system.

Metal Modification of Iron Wire, Carbon Cloth, and Graphite Electrodes. Palladized graphite rods and carbon cloth electrodes were prepared in the following manner. A 2.2 cm<sup>2</sup> (1.0 cm length) area of graphite rod was exposed to a 35.0 mL solution of 1.8 mM  $K_2PdCl_6$  (25.0 mg total) in 0.050 M sodium acetate-acetic acid buffer (pH 5.0) by tightly wrapping Teflon tape to the remainder of the electrode (see Figure 1). Palladium was electrodeposited at a constant current of 5.6 mA until the characteristic yellow color of the

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FIGURE 1. Schematic representation of the cell for both potentiostatic and galvanostatic electrolysis.

K<sub>2</sub>PdCl<sub>6</sub> solution disappeared. This process took about 4 h. During this time, vigorous hydrogen evolution was visually observed from the cathode surface, and large amounts of palladium metal flaked off the cathode surface. The black color of the Pd metal on the electrode indicated that the electrode had a high surface area. The palladized graphite electrode was then removed from the electrolysis solution, dried at room temperature overnight, and weighed to the nearest 0.1 mg. The mass of the graphite rod or the carbon cloth electrodes did not change as a result of palladization; hence, it was assumed that the mass of the Pd on the electrode was less than 0.1 mg. The area of the carbon cloth was 2.0 cm<sup>2</sup>; the true surface area is much larger since this is a threedimensional electrode. Electrical contact to the carbon cloth electrode was made through a copper-plated alligator clip whose surface was isolated from the electrolysis solutions by wrapping it with Teflon tape. Platinization of carbon cloth followed the same procedure and conditions used for palladization. The amount of platinum adhering to the surface of carbon cloth after this procedure was also found to be less than 0.1 mg.

Deposition of Pd onto iron from  $K_2PdCl_6$  is a spontaneous process via the reaction

$$2Fe + PdCl_6^{2-} \rightarrow 2Fe^{2+} + 6Cl^- + Pd \qquad (2)$$

Palladization of iron wire was accomplished by exposing to 20.0 mL of a 0.072 mM solution of  $K_2PdCl_6$  for 30 min. The amount of palladium deposited on the iron surface was assumed to be the result of a 100% completion of reaction 2 (about 1 mg).

Bulk Electrolysis of 4-Chlorophenol Solution. The electrode systems described above were used for the constant current electrolysis of 4-chlorophenol at ambient temperature  $(25 \text{ °C} \pm 3)$ . The cell design, shown in Figure 1, was a threeneck (14/20) round-bottom flask (50 mL). Cathodes were held securely in place with a 14/20 PTFE O-ring adapter. Electrical contact with the carbon cloth and iron wire electrodes was maintained by means of a Cu-plated alligator clip wrapped with Teflon tape. The alligator clip was contacted with a copper wire threaded through 5 mm glass tubing and held in place with a PTFE O-ring adapter. The central 14/20 portal was used for pH measurements or for the measurement of the cathode potential versus saturated calomel electrode (SCE) (Fisher, Pittsburgh, PA). The anode was isolated from the electrolysis solutions by means of a 4% agar salt bridge (0.25 M sodium acetate). The anodic compartment was also vented so that oxygen gas was able to escape. Control experiments indicated that no 4-chlorophenol migrated across the agar salt bridge during the time scale of the experiment. The solutions were unstirred, and therefore, the only means of mechanical mass transport to the cathode surface was a result of hydrogen gas evolution. Constant current and constant potential experiments were conducted on a Princeton Applied Research Corporation Model 173 potentiostat/galvanostat (Princeton, NJ). Cathode potentials were measured versus a saturated calomel electrode (Fisher, Pittsburgh, PA). The pH measurements were made with an Orion Model 91-05 combination electrode and a Perkin-Elmer Metrion III pH meter.

**HPLC Analysis.** Samples of the 4-chlorophenol solution were analyzed by HPLC during the course of the constant current electrolysis. The HPLC apparatus consisted of a Rheodyne Model 7120 injection valve, Milton-Roy Constametric 300 isocratic pump, a 5.0 cm C<sub>18</sub> Zorbex column, Waters Associates Model 440 absorbance detector set at 254 nm, and a Hewlett-Packard Model 3392A integrator. The mobile phase composition was 50/50/2 water/methanol/glacial acetic acid mixture by volume. Phenol ( $t_r = 2.54$  min) and 4-chlorophenol ( $t_r = 4.37$  min) peaks were characterized by using standard solutions. Quantification of phenol production and 4-chlorophenol dechlorination was accomplished by the use of calibration curves. The detection limit of this method for 4-chlorophenol and phenol was 100 ppb.

**Surface Area Measurments.** The surface areas of the electrode materials were determined by nitrogen adsorption and the BET multipoint method with a Gemini 2360 system.

## Results

Carbon Cloth Cathodes. A 25.0 mL solution of 153 ppm 4-chlorophenol in a 0.05 M sodium acetate-acetic acid buffer was electrolyzed at a constant cathodic current of 5.6 mA at a bare carbon cloth cathode. The potential versus saturated calomel electrode was measured throughout the electrolysis and did not vary more than  $\pm 10 \text{ mV}$  of -1.10 V. The pH of the solution increased slowly from 5.0 to 5.6 during the course of electrolysis (16 h), which was carried out under aerobic conditions. During this time period, samples of the electrolysis solution were analyzed for phenol and 4-chlorophenol content by HPLC. The 4-chlorophenol content was found to remain nearly constant throughout the experiment, and minimal amounts of phenol were produced (<10 ppm) at the end of the electrolysis. A vigorous evolution of hydrogen gas was observed at the carbon electrode throughout the experiment. The results of this experiment indicate that the bare carbon cloth surface is not an efficient substrate for the dechlorination of 4-chlorophenol.

The identical carbon cloth electrode was then subjected to palladization by electrodeposition as described in the Experimental Section. Constant current electrolysis of the 4-chlorophenol solution as outlined above with the bare carbon cloth electrode required an initial applied potential of -0.69 V (versus SCE), which increased gradually to -0.85V at the completion of the electrolysis (15 h). Vigorous hydrogen evolution was visually observed throughout the course of the experiment. The solution pH increased from 5.0 to 5.6 during the 15-h period. The dechlorination of 4-chlorophenol to phenol was found to occur much more rapidly at the palladized carbon cloth electrode. The results of the HPLC analyses of the electrolysis solution are shown in Figure 2. Complete dechlorination of the compound occurred after 15 h of constant current electrolysis conducted under aerobic conditions. Elimination of dissolved oxygen by purging with helium gas gave identical results for the bare and palladized carbon cloth electrode systems. Dissolved oxygen was not eliminated in subsequent electrochemical experiments.

Platinized carbon cloth electrodes were able to reduce 4-chlorophenol to phenol, however, to about the same extent



FIGURE 2. Degradation of 4-chlorophenol at palladized carbon cloth electrodes under conditions of constant potential of -0.700 V vs SCE (- $\times$ -), constant current of 5.6 mA (- $\blacktriangle$ -), and constant current of 5.6 mA at a palladized graphite cathode (-+-). Production of phenol at palladized carbon cloth electrodes under conditions of constant potential of -0.700 V vs SCE (- $\blacksquare$ -), constant current of 5.6 mA (- $\blacktriangledown$ -), and constant current of 5.6 mA at a palladized graphite cathode (- $\clubsuit$ -).

as the bare carbon cloth system. Over a 15.7-h period and at a constant current of 5.6 mA, approximately 95% of the 4-chlorophenol remained. Copious amounts of hydrogen were liberated from the electrode during electrolysis.

Constant potential electrolysis (-0.700 V versus SCE) of 4-chlorophenol at the three electrode systems described above gave results that were similar to those obtained with the constant current study. The rate of electrochemically induced dechlorination at 2.0 cm<sup>2</sup> carbon cloth electrodes followed the sequence, palladized  $\gg$  platinized  $\approx$  unmodified electrode. Figure 2 illustrates the results of the constant potential study. The complete dechlorination of 4-chlorophenol at the palladized carbon cloth electrode required 15 h, during which time the current decreased from 2.2 to 0.8 mA. Neither the platinized nor the bare carbon cloth electrodes were able to effect dechlorination of 4-chlorophenol at a constant potential of -0.700 V versus SCE during 15-h time periods.

**Graphite Rod Electrodes.** A similar constant current (5.6 mA) electrolysis of 25.0 mL of the 153 ppm solution of 4-chlorophenol was conducted on both bare and palladized graphite rod electrodes. The geometrical surface area of the electrodes exposed to the solution was  $2.2 \text{ cm}^2$ . As with bare carbon cloth, the unpalladized graphite electrode failed to effect the hydrodechlorination of 4-chlorophenol during a period of 13.5 h. The constant current electrolysis of 5.6 mA required a potential of -1.5 V versus SCE for the bare graphite electrode.

Dechlorination of 4-chlorophenol at the palladized graphite electrode was more facile than at the bare graphite surface, albeit slower than at the palladized carbon cloth cathode. The results of the dechlorination of 4-chlorophenol are presented in Figure 2. Approximately 70% of the 4-chlorophenol was found to dechlorinate to phenol during an electrolysis period of 15 h.

**Iron Wire Electrodes.** A 0.270 g sample of 0.25 mm iron wire (68 cm, 17 cm<sup>2</sup>) was tightly coiled and used for the electrolysis of 153 ppm 4-chlorophenol at 5.6 mA for 16 h. The potential required for this constant current was -0.95 V versus SCE. No detectable phenol was formed at the end of this time period. The 4-chlorophenol concentration remained constant throughout the electrolysis. Palladization of this electrode resulted in only slight increases of phenol production (<10 ppm) during identical electrolysis conditions of 153 ppm 4-chlorophenol. The potential required to maintain a constant 5.6 mA current for the palladized iron wire electrode was -0.95 V versus SCE.

Palladium Gauze Electrodes. A 0.0350 g sample of Pd (area  $\approx$  0.5  $cm^2$ ) gauze cathode was used to electrolyze the

buffered (0.05 M sodium acetate-acetic acid, pH 5.0) 153 ppm solution of 4-chlorophenol for 16 h at both constant current 5.6 mA ( $E_{cathode} = -2.1$  V versus SCE) and constant potential of -0.700 V versus SCE (220  $\mu$ A). The bulk of the palladium gauze electrode was saturated with hydrogen prior to exposure to the 4-chlorophenol solution by applying a constant current of 5 mA overnight in a 0.05 M sodium acetate-acetic acid buffer solution (pH 5.0) (*14*). Neither phenol production nor dechlorination of the 4-chlorophenol was observed during this period of time.

**Pseudo-First-Order Rate Constants.** Table 1 presents the calculated pseudo-first-order rate constants for the disappearance of 4-chlorophenol for each electrode system. The rate constants normalized with respect to BET surface areas indicate that for the palladized electrodes the following trend applies: carbon cloth > graphite rod > iron wire.

## Discussion

**Direct Electroreduction at the Electrode Surfaces.** There are three plausible mechanisms by which electrochemically driven reductive dechlorination may proceed. These routes are shown in Figure 3. All three reaction routes occur at the electrode surfaces. The homogeneous reduction of 4-chlorophenol in solution was ruled out because of the failure of the control experiments on bare metal surfaces. The recent findings regarding the mechanism of reduction by surface-bound 4-aminoazobenzene by zero-valent iron confirms a surface based mechanism (*15*). In the first mechanism (Figure 3A), the reductive dechlorination is a two-electron, one-proton process that takes place at the electrode surface (eq 3):

$$\mathbf{RX} + \mathbf{H}^+ + 2\mathbf{e}^- \to \mathbf{RH} + \mathbf{X}^- \tag{3}$$

Such processes have been mentioned by Matheson and Tratnyek as a possible reaction route for dissolving metal reactions (2). Indeed, corrosion of iron to  $Fe^{2+}$  occurs at a potential of -0.66 V versus SCE, and for this reason metallic iron has been frequently claimed to be a facilitator for the reductive dehalogenation of chloro-organics. In this study, the electrode serves as the reducing agent, either in the potentiostatic (-0.700 V vs SCE) or galvanostatic (5.6 mA) mode. If eq 3 were a plausible reaction route, then palladization of electrode surfaces should be of little relevance since the electrode acts as the thermodynamic equivalent of the corroding iron system. In this role, all the unmodified electrodes including iron failed to electrolyze 4-chlorophenol to phenol during the time scale of the experiment (15 h). This indicates that the route represented by eq 3 is not important for reductive dehalogenation of 4-chlorophenol under the conditions employed in this study.

Dechlorination at Palladium Surfaces. Figure 3B outlines a plausible scheme for the dechlorination of 4-chlorophenol. In this case, palladium islands formed by the electrodeposition of palladium act as catalytic surfaces for the mechanism shown by eq 1. This implies that 4-chlorophenol is adsorbed on the palladium surface. This scheme can be eliminated as a significant route for dechlorination of 4-chlorophenol because the results obtained at the palladium gauze electrode do not support this conclusion. Despite the pretreatment that ensured that the Pd lattice was saturated with hydrogen, the electrode system failed to effect the dechlorination of 4-chlorophenol at a constant current of 5.6 mA. The blockage of 4-chlorophenol adsorption by hydrogen gas evolution cannot be discounted, but it should also be noted that at the applied potential of -0.700 V versus SCE, which resulted in a current of 200  $\mu$ A, hydrogen evolution was much more modest than in the galvanostatic experiment (5.6 mA) and yet there was no evidence of dechlorination at the palladium gauze electrode.

**Dechlorination at the Palladium–Substrate Interface.** Figure 3C illustrates a third reaction route for dehalogenation

### TABLE 1. Pseudo-First-Order Rate Constants for Reduction of 153 ppm of 4-Chlorophenol to Phenol

electrode system	pseudo-first-order rate constant, <i>k</i> 1 (min <sup>-1</sup> )	pseudo-first-order rate constant normalized to BET surface area, k <sub>1</sub> (min <sup>-1</sup> m <sup>-2</sup> )
palladized carbon cloth		
Pd < 0.1 mg, BET area = $0.062 \text{ m}^2$ , $I = 5.6 \text{ mA}$	$5.3  imes 10^{-3}$	$8.5 \times 10^{-2}$
palladized carbon cloth $Pd < 0.1 mm PET Amon = 0.0(2 mm^2) / (2 mm^2) / (2$	$2(10^{-3})$	F 0 10-2
Pd < 0.1  mg, BE1 Area = 0.062 m <sup>2</sup> , $V = -0.700  V$ VS SCE	$3.6 \times 10^{-3}$	$5.8 \times 10^{-2}$
platinized carbon cloth Pt < 0.1  mg RET Area = 0.062 m <sup>2</sup> /= 5.6 mA	$1.6 \times 10^{-4}$	$2.6 \times 10^{-3}$
carbon cloth	1.0 × 10	2:0 × 10
BET Area = $0.062 \text{ m}^2$ . $I = 5.6 \text{ mA}$	$1.5 \times 10^{-4}$	$2.4 \times 10^{-3}$
palladized graphite rod		
Pd < 0.1 mg, BET Area = 0.63 m <sup>2</sup> , $I = 5.6$ mA	$2.0 \times 10^{-3}$	$3.2 \times 10^{-3}$
graphite rod	no reaction	
BET Area = 0.63 m <sup>2</sup> , $I = 5.6$ mA		
palladized iron wire	-	
Pd = 0.57 mg, BET Area = 0.095 m <sup>2</sup> , $I = 5.6 mA$	$7.0 \times 10^{-5}$	$7.4 \times 10^{-4}$
iron wire	no reaction	
BE I Area = $0.095 \text{ m}^2$ , $I = 5.6 \text{ mA}$		
palladium gauze	no reaction	
<i>I</i> = 5.0 IIIA		



FIGURE 3. Proposed mechanisms for the hydrodehalogenation of 4-chlorophenol to phenol. (A) Direct reduction at electrode surface. (B) Hydrogenation at palladium catalyst surface. (C) Adsorption of 4-chlorophenol at electrode substrate followed by hydrogenation at palladium island/electrode surface.

reaction. In this scheme, 4-chlorophenol is adsorbed to the substrate surface and undergoes dechlorination at the Pd island–substrate interface. The results obtained with the palladized iron, graphite, and carbon cloth electrodes support this scheme. In the latter two cases, dechlorination to phenol was relatively successful. Again, as in the Pd gauze system, the interior of the Pd islands (<0.1 mg) is saturated with hydrogen gas during the time scale of our experiments. The amount of charge and the diffusion coefficient of hydrogen in the palladium lattice indicates that less than 20 min is needed for full saturation (14). The hydrodehalogenation

products were detected before this time period was completed.

The palladized graphite and carbon cloth electrodes were both able to dechlorinate 4-chlorophenol (Figure 2). The scheme outlined in Figure 3 C is therefore a plausible reaction route. The ability of carbon surfaces to adsorb organic compounds probably facilitates the dechlorination reaction because it places the compound in the vicinity of hydrogensaturated palladium islands. It is apparent that palladium by itself cannot effect the dechlorination probably because of its inability to adsorb 4-chlorophenol. Negative results for palladized iron wire may also be due to the low concentration of adsorbed 4-chlorophenol in comparison with concentrations adsorbed on carbon surfaces.

Hydrogen Generation and Palladium versus Platinum in Dechlorination Reactions. Our results indicate that hydrogen plays a key role in the dechlorination of 4-chlorophenol to phenol. Therefore, it seems reasonable that the electrochemical evolution of hydrogen gas by the reduction of water will aid in dechlorination. Both platinum and palladium are excellent surfaces for the electrochemical evolution of hydrogen gas. Constant current studies generate the same flux of hydrogen at bare electrodes as well as metalmodified electrodes. In the experiments in which platinum was substituted for palladium, the dechlorination reactions rates decreased under constant potential as well as constant current conditions. Galvanostatic studies on bare and palladized electrode surfaces indicate that only the latter have the ability to reductively dechlorinate 4-chlorophenol. This indicates that, although the fluxes of hydrogen gas generated at these surfaces are approximately equal, palladium has the unique property of promoting dechlorination of organic compounds. This may be due to the ability of palladium to absorb hydrogen into its lattice and to maintain a high surface concentration of hydrogen (14). Both carbon and platinum lack this ability. Carbon and platinum surfaces at which the same flux of hydrogen gas is generated cannot promote dechlorination reactions because hydrogen gas escapes relatively easily from both surfaces.

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### Literature Cited

- Gilham, R. W.; O'Hannesin, S. F. Ground Water **1994**, *32*, 958.
   Matheson, L. J.; Tratnyek, P. G. Environ. Sci. Technol. **1994**, *28*, 2045.
- (3) Schrier, C. G.; Reinhard, M. Chemosphere 1995, 31, 3475.
- (4) Muftikian, R.,; Fernando, Q.; Korte, N. *Water Res.* **1995**, *29*, 2434.
  (5) Grittini, C.; Malcomson, M.; Fernando, Q.; Korte, N. *Environ*.
- *Sci. Tech.* **1995**, *29*, 2898. (6) Marques, C. A.; Selva, M.; Tundo, P. *J. Org. Chem.* **1994**, *59*, 3380.
- (7) Johnstone, R. A.; Wilby, A. H. Chem. Rev. 1985, 85, 129.
- (8) Coq, B.; Hub, S.; Figueras, F.; Tournigant, D. Appl. Catal. A: Gen. 1993, 101, 41.
- (9) Bodnariuk, P.; Coq, B.; Ferrat, G.; Figueras, F. J. Catal. **1989**, *116*, 459.

- (10) Criddle, C. S.; McCarty, P. L. Environ. Sci. Technol. 1991, 25, 973.
- (11) Zhang, S.; Rusling, J. F. Environ. Sci. Technol. 1995, 29, 1195.
- (12) Kulikov, S. M.; Plekhanov, V. P.; Tsyganok, A. I.; Schlimm, C.; Heitz, E. *Electrochim. Acta* **1996**, *41*, 527.
- (13) Zhang, S.; Rusling, J. F. Environ. Sci. Technol. 1993, 27, 1375.
- (14) Lawson, D. R.; Teirney, M. J.; Cheng, I. F.; Van Dyke, L. S.; Espenscheid, M. W.; Martin, C. R. *Electrochim. Acta* **1991**, *36*, 1515.
- (15) Weber, E. J. Environ. Sci. Technol. 1996, 30, 716.
- (16) Carturan, G.; Facchin, G.; Cocco, G.; Enzo, S.; Navazio, G. J. Catal. **1982**, *76*, 405.

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