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## Electrocatalysis and Charge-Transfer Reactions at Redox-Modified Zeolites

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### ABSTRACT

When aluminosilicate zeolites, which are microporous crystalline scaffolds, intersect with electrochemistry, new opportunities arise for control of ion- and electron-transfer reactions. In this Account, we describe how zeolites modified with either redox solutes or nanocrystalline particles (which when electrified behave as nanoelectrodes) give rise to new reaction products for old catalytic schemes, improve catalytic turnovers relative to the zeolite-free electrocatalyst, and generate practical amounts of electrosynthesized product at nanoelectrode-modified zeolites. The electrochemical reactions driven at redox-modified zeolites demonstrate the ability of the truncated topography of the zeolite boundary to affect charge-transfer reactions.

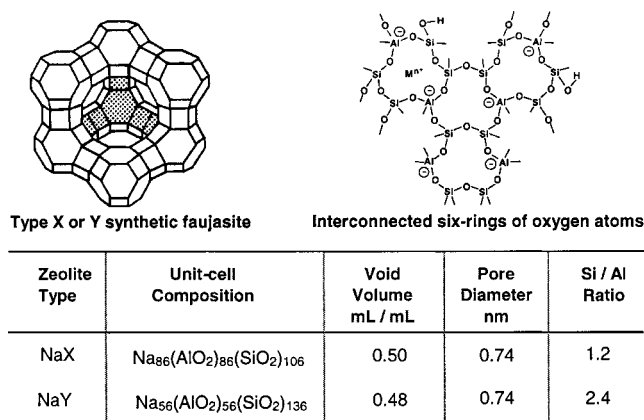
### Introduction

Why should one couple electrochemistry and zeolites?

Debra Rolison received her B.S. from Florida Atlantic University in 1975 and her Ph.D. with Royce Murray from the University of North Carolina in 1980. She joined the Naval Research Laboratory as a staff scientist in 1980 and currently heads Advanced Electrochemical Materials. Her research interests include electrochemistry, surface chemistry, microheterogeneous reactions at zeolites, and nanoscale mesoporous materials, such as aerogels.

Carol Bessel received her B.S. (1988) and Ph.D. (1993) from the State University of New York at Buffalo. She joined Debra Rolison at the Naval Research Laboratory as a National Research Council Postdoctoral Fellow from 1993 to 1995. Since 1995, she has been an Assistant Professor at Villanova University with interests in heterogeneous catalysis in supercritical fluids, trans-spanning phosphine ligands, and novel carbon materials.

Scheme 1. Physical Characteristics and Properties of Synthetic Zeolites X and Y<sup>†</sup>



Electrochemical reactions rely on the smallest and most energetically flexible of reactants: the electron. As a reagent, the electron may be added to a reaction in any quantity (measured in coulombs, the number of electrons flowing per second) and at any potential energy (thus controlling the free energy ( $\Delta G$ ) of the reaction).

Zeolites are crystalline microporous solids that provide molecular-sized cages and passageways for excellent steric control of reaction paths. The pore windows and cage or channel structures of zeolites result in physical exclusion or inclusion; i.e., molecules or ions that are too large cannot sorb into the interior of the zeolite crystal, just as molecules constructed within the crystal can be too large to leave. Aluminosilicate zeolites also offer a fixed negative charge for every aluminum atom in the lattice, which is balanced by mobile cations. The extraframework nature of these cations creates the cation-exchange capacity of zeolites and affords a simple synthetic means to diversify the chemical complexity of the crystal, including modifying zeolites with redox-active guests. These physical characteristics are summarized in Scheme 1.

An attractive goal of recent research has been to join electrochemical methods (which require motion of charge)

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with sterically controlling materials in order to control both the electronic and steric properties of chemical pathways. Although zeolites are electronic insulators, the extraframework cations provide the ionic carriers required to maintain charge balance when any intrazeolitic species undergoes electron transfer. The intersection of zeolite science and electrochemistry encompasses important commonalities: reactions in both realms are innately heterogeneous and occur in the presence of large local electrostatic fields; reactants and products diffuse; and mobile ions maintain overall charge neutrality.

The most recent intersection of electrochemistry and zeolite science<sup>1–9</sup> has explored (1) the effect of zeolite overlayers at electrode surfaces on electron transfer to redox solutes (electroactive molecules or ions); (2) the effect of a structured environment on electron transfer to zeolite-associated redox solutes; and (3) the use of electrocatalyst-modified zeolites to perform redox chemistry in microheterogeneous media.

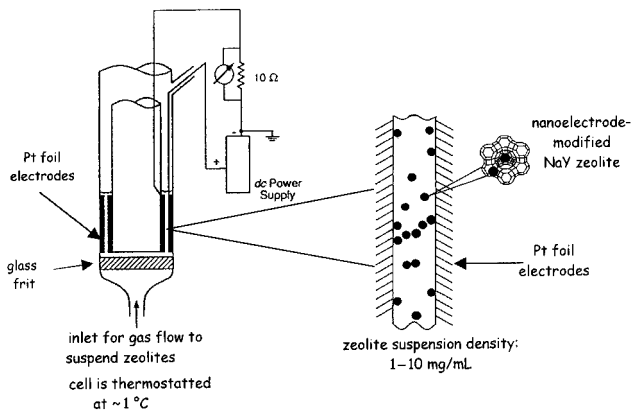
## Breaking Commandments

In electrochemistry, one long-standing “thou-shalt” specifies that electron-transfer reactions to/from electrode surfaces should be performed in media of high ionic strength. Typically, electrolyte concentrations  $\geq 0.1$  M are preferred so that ions of sufficient number and mobility are present to minimize electric-field effects and to balance positive/negative charge as interfaces are electrified and electrons are exchanged. In size-selective organic catalysis with zeolites, a long-standing “thou-shalt” dictates that reactions be run in anhydrous fluids using dehydrated zeolites. Anhydrous conditions are desired because the preferred neutral adsorbate for the charged interior of aluminosilicate zeolites is a polar molecule, such as water, rather than a less polar organic substrate.<sup>10–12</sup>

Much of our electrochemical research with zeolites has involved a deliberate choice to break both of these customary commandments. This approach enables us to explore the opportunities possible when one works with zeolites in water-rich media that contain no (or submillimolar concentrations of) deliberately added electrolyte ions. Three areas have evolved from this choice: (1) electrified microheterogeneous catalysis (EMC); (2) electrochemical reactions using nanoelectrode-modified zeolites; and (3) electrocatalyzed syntheses using microheterogeneous dispersions of zeolite-associated, redox-active coordination complexes.

Breaking the zeolitic commandment—no water!—moves the primary reaction zone to the external boundary of the zeolite crystal, because the organic substrate does not displace sorbed intrazeolitic water.<sup>13</sup> The three-dimensional control of nanoscale space that the zeolite interior imposes on a diffusing and reacting molecule is sacrificed. In its stead, the truncated topology of the zeolitic boundary is left to influence—or not—the ionic and steric environment of the reaction. This interface between intrazeolite/external boundary is exactly where one needs

Scheme 2. Dispersion Electrolysis Cell Showing the Electrode Particles Contained between Feeder Electrodes with an Exploded View of Intra/Extracrystalline Pt Supported on Zeolite Y



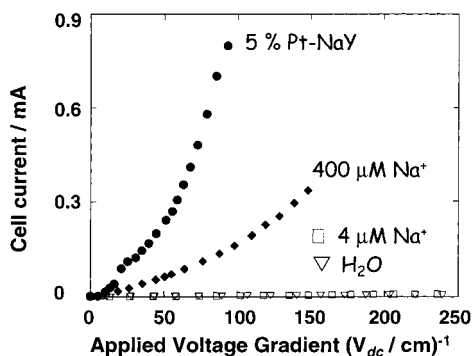
to be for any reasonable access to electrons, because the electrons must come from or go to an extrazeolitic electrode.<sup>14</sup>

A pragmatic question thus becomes, how many degrees of nanoscopic space must be controlled to influence a reaction pathway? Can the truncated topology of a zeolite boundary orient the necessary dimensional coordinate sufficiently to control the yields and selectivity of a chemical reaction? Certain zeolite-catalyzed isomerizations have recently been deemed to be surface-dominated and topology-driven.<sup>15,16</sup> The boundary-only reactions at zeolites can be further examined using electrochemical reactions at redox-modified zeolites in aqueous media, as we discuss below.

## Electrified Microheterogeneous Catalysis

Unlike most chemical reactions driven by temperature or pressure, electrochemical reactions can be achieved by exactly controlling the energy and number of electrons delivered to reacting species, thereby controlling the pathways and extent of reaction. The high ionic strength media of typical electrochemical reactions minimizes resistive losses in the electrolyte so that voltage drops [ $\Delta V = i$  (current)  $\times R$  (solution resistance)] do not detract from the controlled, thermodynamically known potential that is applied at the electrode. High electrolyte concentrations present practical disadvantages for electrosynthesis because separating the product from the electrolyte is time-consuming and difficult and the potential window of reaction (i.e., the maximum positive or negative voltage that can be applied in the electrochemical cell) is limited by the electrochemical reactivity of the electrolyte.

Electrochemistry in low-ionic-strength media ( $\mu \leq 1$  mM) can be performed at a microelectrode (with a characteristic dimension of  $\sim 1$ – $10$   $\mu\text{m}$ <sup>17,18</sup>) because the magnitude of charging or faradaic current that flows at a single microelectrode is very small (picoamperes to nanoamperes) and can be carried by the few ions in solution. Individual microelectrodes, although important analytically, are not useful synthetically because only a minute quantity of product is made. At 1 nA of constant faradaic



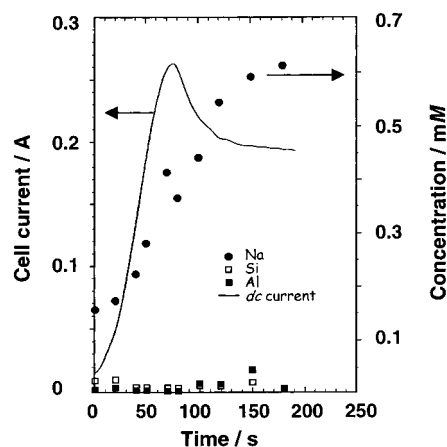
**FIGURE 1.** Current as a function of applied voltage gradient for 18 M $\Omega$ -cm H<sub>2</sub>O, dilute NaOH solutions (4 and 400  $\mu$ M), and a dispersion of 2.5 mg of 5 wt % Pt–NaY/mL pf H<sub>2</sub>O (Pt feeder electrodes;  $\sim$ 1  $^{\circ}$ C).<sup>26</sup> The polarizations in dilute NaOH show the relative ineffectiveness of electrolysis at the Pt feeder electrodes in the absence of zeolite particulates.

current, it takes  $\sim$ 3 million years to make 1 mol of a one-electron reaction product.<sup>19</sup> Zeolites provide a useful scaffold to support numerous nanoscale electrodes because the porous structure, with its molecular size specificity, permits a templated synthesis of nanoscale particles.<sup>20</sup> These nanoscale particles, once collectively assembled in a statistically useful number and charged at a feeder electrode of a dispersion electroreactor, behave as an ensemble capable of effective electrosynthesis.<sup>21</sup>

We initiated research in the area of electrified microheterogeneous catalysis (EMC) by accessing zeolite-associated electrocatalysts that had been physically dispersed in solvent in a two-electrode cell.<sup>21–24</sup> Zeolite-supported nanocrystallites are electrically charged when they physically contact the feeder electrodes and so behave as dispersed electrodes (Scheme 2), which obviates the need to individually wire each particle. Microheterogeneous dispersions of zeolite-supported Pt nanocrystallites (Pt–NaY<sup>21,22</sup>) effectively electrolyze water, to which no electrolyte has been deliberately added, upon applying a dc voltage gradient  $>25$  V/cm between two feeder electrodes. No significant water electrolysis occurs at the feeder electrodes in the absence of dispersed Pt–NaY (Figure 1).<sup>21</sup>

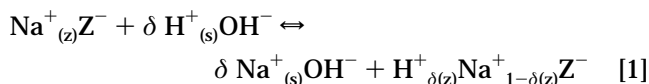
Low-field electrolyses ( $<300$  V/cm) involving electroactive species either capable of sorbing into zeolite type Y (water, H<sub>2</sub> dissolved in water, ferrocene in neat acetonitrile) or size-excluded [bis(1,2-dibenzylcyclopentadienyl)iron(II)] established that electrolysis occurs only at boundary-sited Pt particles.<sup>22</sup> The enormous intrazeolitic Pt surface area (for 1 wt % Pt–NaY, estimated at  $2.5 \times 10^4$  cm<sup>2</sup>/g for supercage-encapsulated, 1-nm Pt) is faradaically silent. Even though only boundary-sited Pt is electrochemically active, zeolite-supported Pt dispersions give current densities 1–2 orders of magnitude higher than other types of dispersed Pt microelectrodes (1 wt % Pt supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub><sup>21,22</sup> or unsupported Pt microspheres<sup>25</sup>).

**EMC and Ionics.** Electric-field effects are observed when alkali-ion-compensated zeolites (such as NaY) are



**FIGURE 2.** Temporal character of the dc current flowing through a dispersion of 2.5 mg of NaY zeolite/mL of 18 M $\Omega$ -cm H<sub>2</sub>O upon electrifying at 50 V/cm;  $\sim$ 1  $^{\circ}$ C. The concentrations of Na, Si, and Al are monitored by sampling aliquots from the electrified microheterogeneous dispersion with time and analyzing the filtrate.<sup>27,29</sup>

electrified in high-impedance water.<sup>26,27</sup> These experiments are a necessary control when studying redox-modified zeolites, and they monitor the ionic conductivity of a dispersion containing water and zeolite over the ohmic (linear) region of the  $i$ – $V$  polarization curve, before water electrolysis dominates. Placing zeolites in water induces a coupled equilibrium whereby extraframework cations exchange with the protons that form during autoprotolysis of water.<sup>28</sup> An ionic strength is thus unavoidably generated in salt-free water by zeolite-promoted autoprotolysis, as shown in eq 1 for a Na<sup>+</sup>-compensated zeolite, where Z<sup>–</sup> represents a fixed negative charge in the



zeolite lattice, (z) and (s) represent zeolitic and solution phases, respectively, and  $\delta$  indicates the fraction of exchange that occurs between zeolitic Na<sup>+</sup> and H<sub>2</sub>O-derived H<sup>+</sup>. These zeolite-derived, solution-phase cations equilibrate to submillimolar concentrations (for  $\sim$ 5 g of NaY/L H<sub>2</sub>O); thus, electrolyte-free conditions cannot be attained. However, separating these low concentrations of electrolyte from product is no longer a significant disadvantage of the electrochemical technique.

The equilibrium that develops upon immersing a zeolite (MZ, where M is an alkali or alkaline earth cation) in water (eq 1) takes hours to establish, but the same levels of MOH<sub>(s)</sub> are reached in seconds when an aqueous dispersion of MZ is electrified.<sup>23,26,27</sup> This accelerated steady-state arises from the high activity of H<sup>+</sup> at the positive feeder electrode as water is oxidized to O<sub>2</sub> and protons. As can be seen in Figure 2, the dc current that flows through the microheterogeneous medium as a function of time (at a constant voltage gradient) exhibits a maximum in the  $i$ – $t$  plot before a steady-state current is achieved in  $\sim 10^2$  s. This maximum does not arise from any faradaic process, as the same feature (in shape and

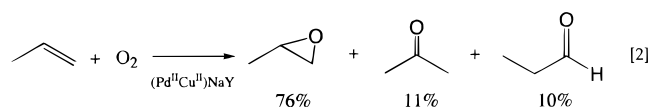
timing) is measured if the temporal dependence of the conductivity is monitored at constant applied field.<sup>27</sup>

The concentration of Na<sup>+</sup> in filtered aliquots of the electrified NaY microheterogeneous medium ([Na<sup>+</sup>]<sub>(s)</sub>) increases with time, but the approach to steady state is monotonic and does not exhibit a maximum. Although aluminosilicate zeolites dealuminate in the presence of H<sub>3</sub>O<sup>+</sup>,<sup>28</sup> neither aluminum nor silicon is measured at significant levels as [Na<sup>+</sup>]<sub>(s)</sub> and current/conductivity reach steady state (Figure 2). The approach to the maximum conductivity of the microheterogeneous medium can be modeled well when based on the proposed H<sup>+</sup>/Na<sup>+</sup> interactions and the measured solution concentration of Na<sup>+</sup>, but the (relatively rapid) relaxation to steady state is not predicted.<sup>29</sup>

Absent a maximum in the [Na<sup>+</sup>]<sub>(s)</sub>-*t* plot, we infer that the surge in the ionicity of the medium arises from the ionic nature at the zeolite boundary as the particles contact the anode and react with electrogenerated interfacial protons. Due to the transient ionic conductivity of microheterogeneous dispersions when first electrified, substrates (other than water) are not added to the medium in our experiments until a steady-state current is obtained.

The time to maximum current/conductivity (*t*<sub>max</sub>) depends on the extraframework cation, the dimensionality of the zeolite's porosity, and the magnitude of the applied field—but not the applied voltage or the nature of the anode (platinum vs stainless steel). The Group I series of zeolite type Y tracked the expected trend for ionic mobility of the alkali cation in infinitely dilute (aqueous) solutions; i.e., *t*<sub>max(V/cm)</sub> for dispersions of LiY >> NaY > KY ~ RbY > CsY.<sup>26</sup> The dependence of *t*<sub>max</sub> on the dimensionality of the zeolite reflects the strength of the local electrostatic field between the mobile cation and the zeolite framework and depends on the valency of the cation and its siting in the specific zeolite structure. For instance, CaY, which is calculated to have ~2 times the local electrostatic field relative to Na<sup>+</sup> in type Y zeolite,<sup>30</sup> requires twice as strong a voltage gradient to achieve a *t*<sub>max</sub> comparable to that for a NaY dispersion.<sup>6,26</sup>

**EMC and Selective Partial Oxidation.** Electrifying a dispersion of zeolite-supported molecular catalyst drives selective organic redox reactions with voltage or field, rather than temperature or pressure, and does so at low ionic strength. We demonstrated the selective partial oxidation of propene to propylene oxide (eq 2) using low-ionic-strength aqueous dispersions of (Pd<sup>II</sup>Cu<sup>II</sup>)NaY,<sup>23</sup> i.e., NaY chemically modified with the Wacker homogeneous oxidation catalyst. The EMC reaction occurs at 0 °C and at applied gradients > 25 V/cm; in the absence of an applied gradient, no product forms.



Unlike the products obtained for this reaction by thermally driven homogeneous<sup>31</sup> or heterogeneous forms<sup>32</sup> of this bifunctional catalyst, the primary EMC partial

oxidation product is propylene oxide rather than acetone. Although total product yields are low due to the limited solubility of propene in water, the selectivity of the oxidation (see eq 2) is good.<sup>33,34</sup> Electrifying aqueous dispersions of propene and either NaY/H<sub>2</sub>O or (Pd<sup>II</sup>Cu<sup>II</sup>)-NaY/0.1 M NaOH produces >12 partial oxidation products.<sup>23</sup> These two control experiments show that both the molecular catalyst and a low-ionic-strength medium are necessary to achieve selective partial oxidation of propene.

Mechanistically, the EMC process mimics Wacker oxidation of an olefin: both Pd<sup>2+</sup> and Cu<sup>2+</sup> are required; the customary oxygen-transfer agent, water, is copiously present in the microheterogeneous medium; and molecular oxygen (the oxidant used to cycle Cu<sup>+</sup> to Cu<sup>2+</sup>) is constantly being electrogenerated at the anode. Yet propylene oxide is not customarily obtained for the Pd<sup>2+</sup>/Cu<sup>2+</sup> bifunctional system, even in Cl<sup>-</sup> and H<sup>+</sup>-free media, such as (Pd<sup>II</sup>Cu<sup>II</sup>)NaY in the gas phase at temperatures >60 °C.<sup>32</sup> An indication that π-bonded, Pd-coordinated propene interacts with an oxygen-transfer species other than water during EMC reactions at (Pd<sup>II</sup>Cu<sup>II</sup>)NaY comes from the observation that when the feeder anode is stainless steel rather than Pt, the oxidation of propene does not occur.<sup>34</sup> Because Pt can catalyze the one-electron oxidation of OH<sup>-</sup> to hydroxyl radical<sup>35</sup> and propylene oxide is the primary EMC oxidation product, it is plausible that a Pt-oxidized -OH species at the zeolite boundary, rather than water, acts as the oxygen-transfer species to a neighboring Pd-coordinated olefin.

**EMC and Molecular Decomposition.** We also explored the oxidative effectiveness of EMC in the absence of a zeolite-supported molecular catalyst as a means to decompose chlorinated aromatics (Cl<sub>x</sub>Ar) and chlorofluorocarbons.<sup>24,36,37</sup> Polyhalogenated organic compounds decompose at 0 °C to water-soluble fragments (including chloride and fluoride) when aqueous dispersions of NaY and the organic substrate are electrified via EMC.<sup>24</sup> The primary variable limiting degradation of water-immiscible Cl<sub>x</sub>Ar is its poor phase transfer to the aqueous phase (demonstrated using chloronaphthalene as a model substrate). Organic cosolvents used to increase Cl<sub>x</sub>Ar solubility in the medium (e.g., acetone or propylene carbonate) improve the fraction of Cl<sub>x</sub>Ar decomposed without appearing to affect the decomposition mechanism (although acetone reacted to form chromophoric byproducts).<sup>36</sup> Under constant reaction conditions with aqueous dispersions of synthetic faujasite zeolites, EMC degradation of 1,2-dichlorobenzene improves as the ratio of Al to Si is increased. Aluminum offers multiple means to affect reactivity: it establishes electrostatic fields in the zeolite lattice, determines the cation-exchange capacity of the zeolite, and acts as a Lewis acid.

Analogously to the EMC-driven selective oxidation of propene in (Pd<sup>II</sup>Cu<sup>II</sup>)NaY dispersions, the effectiveness of EMC decomposition of Cl<sub>x</sub>Ar is poor in dilute NaOH controls (in the absence of NaY) and excellent with Pt, rather than stainless steel, as the feeder anode.<sup>36,37</sup> The dependence on Pt for effective EMC oxidation again implies that Pt electrocatalyzes a key reaction intermediate

on the surface of the zeolite. Anatase titania, with a surface known to sustain hydroxyl radicals, is also effective for decomposition of  $\text{Cl}_x\text{Ar}$  when aqueous titania dispersions are electrified, although the ability to form water-soluble fragments is higher at zeolite NaY.<sup>37</sup>

EMC experiments with water-soluble 2,3-dichlorobenzoic acid dissolved in  $\text{D}_2\text{O}$  permit the kinetics of decomposition to be studied by NMR spectroscopy.<sup>37</sup> The reaction supernatant contains only trace quantities of the chlorinated organic after 6 h of EMC reaction and none (even with signal averaging) after 23 h. Only one H-containing product is observed, which is identified by NMR spectroscopy and capillary electrophoresis as chloromalonate. Chloride production is linear over the first 10 h of EMC reaction, after which its concentration in the aqueous phase decreases, with all  $\text{Cl}^-$  consumed at the end of a 23-h reaction.  $\text{Cl}_2$  can be trapped from the effluent once the concentration of organic substrate becomes negligible in the microheterogeneous medium, which indicates that  $\text{Cl}^-$  becomes a secondary oxidation substrate.<sup>37</sup> Although electrified aqueous dispersions of zeolite Y degrade chlorinated aromatic organics to water-soluble products (and do so more effectively at high concentrations ( $\geq$  millimolar) of organic than does photocatalysis), the necessity of Pt anodes and the post-decomposition reaction of  $\text{Cl}^-$  to molecular chlorine limits the practicality of this process.

## Electrosynthesis Using Nanoelectrode-Modified Zeolites

Dispersions of zeolite-supported nanoelectrodes are also effective for controlled potential electrolyses and offer a simple means to introduce minute quantities of an expensive electrocatalyst into an electroreactor. We explored issues of electrolyte nature, ionic strength, and the type and concentration of the zeolite-supported electrocatalytic nanoelectrodes on the electrolytic efficiency of a model "synthetic" substrate:  $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ .<sup>38-40</sup>

In high-ionic-strength electrolytes containing  $\text{Cl}^-$ ,  $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$  is a reversible couple.<sup>41</sup> The faradaic yield of  $[\text{Fe}(\text{CN})_6]^{3-}$  reduction (and reoxidation) at a reticulated vitreous carbon (RVC) feeder electrode in phosphate buffer/0.2 M KCl ( $\mu = 0.3$  M) is the same with or without zeolite-supported nanoelectrodes. However, the addition of dispersed nanoelectrodes increases the rate of reaction as measured by the total electrolysis time (reduction and reoxidation). Electrolysis time decreased 55% with dispersed 1 wt % Pt–NaY and 26% with 5 wt %  $\text{RuO}_2$ –NaY as compared to electrolysis without dispersed nanoelectrode-modified zeolites.<sup>40</sup> As with water electrolysis at zeolite-supported Pt,<sup>21,22</sup> 1 wt % Pt–NaY is more effective for ferri-/ferrocyanide electrolysis than 5 wt % Pt–NaY, which we attribute to an improved metal particle–(zeolite)–ion interface for the smaller Pt particles supported on 1 wt % Pt–NaY ( $\sim 2.5$  vs  $\sim 20$  nm, respectively<sup>22</sup>).

Increased rates of reaction without an improvement in yield indicate that zeolite-supported Pt or  $\text{RuO}_2$  nanoscale particles act as electron-transfer mediators rather

than as the controlling heterogeneous electron-transfer surface. The dispersed nanoelectrodes effectively increase the surface area of the RVC feeder electrode, as expected for redox solutes with fast heterogeneous electron-transfer rate constants, so that faster bulk conversion of substrate into product occurs. This rate enhancement is of practical importance because less electricity is used (and process costs are lowered), and it was achieved with a total of only 25  $\mu\text{g}$  of zeolite-supported Pt nanoelectrodes dispersed at a low-cost feeder electrode.

Without added  $\text{Cl}^-$ , the yield for bulk electrolysis of  $[\text{Fe}(\text{CN})_6]^{3-}$  increased from ca. 51% at RVC alone to 66% with 1.0 mg/mL of dispersed 1 wt % Pt–NaY, and the latter proceeded 44% faster.<sup>40</sup> The improved faradaic efficiency indicates that the electron-transfer reaction shifts to the dispersed Pt nanoelectrodes, which act as an electrocatalytic surface for ferri-/ferrocyanide in the absence of  $\text{Cl}^-$ . The faradaic efficiency was even higher at dispersed 5 wt %  $\text{RuO}_2$ –NaY, indicating that  $\text{RuO}_2$  has a higher innate exchange current density (i.e., heterogeneous electron-transfer rate) for ferri-/ferrocyanide than does Pt.

Bulk electrolysis of  $[\text{Fe}(\text{CN})_6]^{3-}$  was also investigated in low-ionic-strength solutions (650  $\mu\text{M}$ ), where the electrolyte could either participate in  $\text{H}^+_{(s)}-\text{Na}^+_{(z)}$  exchange ( $\text{HClO}_4$ ,  $\text{NaOAc}$ ) or not ( $\text{NaOH}$ ). With 1 wt % Pt–NaY dispersions, the average faradaic yields were much higher (84%) than those at RVC alone, again indicating that the site of electroreduction was divorced from the carbon electrode and moved to the zeolite-supported electrocatalyst. The reaction time depended on the possibility of  $\text{H}^+_{(s)}-\text{Na}^+_{(z)}$  exchange (eq 1), with faster electrolytic rates obtained when solution-phase protons could exchange into the zeolite (pure  $\text{H}_2\text{O} < \text{HClO}_4 < \text{NaOAc}$ ).<sup>40</sup> The slowness of  $[\text{Fe}(\text{CN})_6]^{3-}$  electrolysis in 650  $\mu\text{M}$   $\text{NaOH}$  indicates that even at a comparable ionic strength, the  $\text{Na}^+$  self-exchange reaction  $[\text{Na}^+_{(s)} \leftrightarrow \text{Na}^+_{(z)}]$  did not facilitate the electron-transfer reaction at zeolite-supported Pt.

Finally, in nonaqueous solutions where no electrolyte is added (Co(salen) in neat  $\text{CH}_3\text{CN}$ , salen = *N,N'*-bis(salicylidine)ethylenediamine), electrolysis at zeolite-supported nanoscale particles occurs only at large overvoltages when compared to the same reaction in standard concentrations of electrolyte. Because the microheterogeneous medium is stirred and many nanoscale electrodes are present, insufficient charge-compensating ions are available to establish a double layer at each nanoelectrode,<sup>40</sup> so redox activity is slow or absent until charge compensation can occur via the high interfacial fields that develop at large overvoltages. Our observations are consistent with those of Gao and White, who compared the use of quiescent and rotated microelectrodes and found that a rotated microelectrode (which swept the few charge-compensating ions away from the electrode surface) needed an applied overvoltage before the faradaic reaction could again be observed.<sup>42</sup>

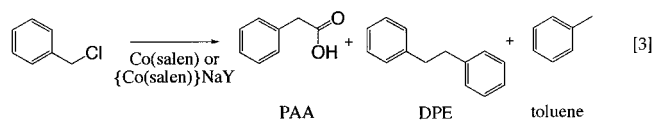
Even though  $[\text{Fe}(\text{CN})_6]^{3-}$  is not an ideal electrosynthetic substrate, we used it to gauge how to vary electrolyte

conditions to manipulate both the rate of bulk electrolysis and the electrode surface at which electron-transfer predominates. We have shown that these same concepts can, indeed, be transferred to organic substrates by characterizing the selective electrooxidation of *p*-methoxybenzyl alcohol to aldehyde at NaY-supported Pt and RuO<sub>2</sub> dispersed nanoelectrodes.<sup>43</sup> It is now possible to design electroorganic syntheses that use a miniscule amount of an expensive electrocatalyst (supported on zeolite crystals) and inexpensive (and durable) feeder electrodes, while easily separating the electrosynthesized product from low concentrations of ions.

## Electrocatalyzed Synthesis Using Microheterogeneous Dispersions of Zeolite-Associated Transition Metal Complexes

The ultimate goal when combining electrochemistry (electronic control) with zeolite scaffolding (steric control) is selective conversion of reagents to products at high yield. An important advantage of electrocatalyzed reactions with dispersed redox- (or electrode-) modified zeolites is that the electron is an environmentally friendly reactant; additional chemical oxidants and reductants are not required. We investigated this premise for the catalyzed electrosynthesis of phenylacetic acid at homogeneous Co(salen) and at microheterogeneous dispersions of the zeolite-associated complex, {Co(salen)}NaY.<sup>44</sup>

The reaction of benzyl chloride with CO<sub>2</sub>, as catalyzed by electrogenerated [Co<sup>I</sup>(salen)]<sup>-</sup>,<sup>45</sup> produces a mixture of phenylacetic acid (PAA), 1,2-diphenylethane (DPE), and toluene (eq 3).



Catalyst	Total turnovers in 2 h mol of product/mol of catalyst	PAA / %	DPE / %	Toluene / %
Co(salen)	34	88	8	4
{Co(salen)}NaY	270 (~ 8 × 10 <sup>4</sup> )	95	2	3

As the homogeneous and heterogeneous product distributions are the same (within error), no change in the catalytic mechanism is indicated. This comparability implies that the substrate samples only the exterior topography of the zeolite structure, as the presence of pores, cages, and channels has no influence on product ratios.

Homogeneous Co(salen) produced 34 turnovers (moles of product per mole of Co catalyst) in 2 h. {Co(salen)}-NaY produced 270 turnovers in 2 h, as based on the bulk analysis of Co<sup>2+</sup> ions and the assumptions that encapsulated Co(salen) was formed quantitatively from Co<sup>2+</sup> ions and that all encapsulated Co(salen) was electrochemically accessible on the time scale of the experiment; i.e., this turnover represents the lower limit for catalyst productivity. When the electrocatalytic turnovers from {Co-

(salen)}NaY are calculated using the moles of electroactive Co(salen), as determined by integrating the voltammetric wave for the Co(II/I) reduction according to Faraday's law,<sup>46</sup> the true electrocatalytic turnover number for {Co(salen)}NaY is estimated at 8 × 10<sup>4</sup>, or ca. 3000 times that of homogeneous Co(salen).<sup>47</sup>

This large increase in turnovers upon zeolitic association of the transition metal catalyst has several possible causes: (1) framework zeolite oxygens may act as Lewis bases in the mechanism<sup>48</sup> (a role normally played by Cl<sup>-</sup>); (2) the substrate may "dock" into the supercage, as facilitated by weak van der Waals interactions;<sup>49</sup> (3) the cavity-trapped guest may experience electronic confinement;<sup>50</sup> and (4) Cl<sup>-</sup> may be Donnan excluded (i.e., electrostatically repelled) by the negatively charged zeolite lattice and thereby expedite the rate of ligand substitution by [Co<sup>I</sup>(salen)]<sup>-</sup>. It is not yet possible to distinguish the contribution of any or all of these possibilities to the enhanced catalytic efficiency, but because the activity arises from boundary-sited complexes, this reaction joins the class of reactions guided by the zeolite surface.

Finally, zeolite-imposed isolation of the Co(salen) catalyst increases its lifetime by at least 200%.<sup>44</sup> The accumulated faradaic charge (measured in coulombs) transferred to homogeneous Co(salen) plateaus after ~120 min, while that transferred to {Co(salen)}NaY continues to increase. The relative durability of the zeolite-associated Co<sup>I</sup>(salen) electrocatalyst most likely arises from topological minimization of the conditions that deactivate the homogeneous catalyst: intermolecular Co<sup>I</sup>(salen) interactions or irreversible CO<sub>2</sub> adduct formation.

## The Region of Activity

As with the other examples of liquid-phase catalysis with redox- or electrode-modified zeolites discussed above, the activity of {Co(salen)}NaY is attributed to boundary-sited complexes only. The mechanism of electron transfer to zeolite-associated redox species has been a subject for serious debate.<sup>6-8,51,52</sup> It is now well agreed, however, that in the absence of zeolite-mobile electron-transfer mediators, electrochemical access to zeolite-included, redox-active species is possible only to those species sited on the exterior of the zeolite superstructure and not to those in the interior.

Only a minor fraction of the total zeolite-associated redox-active species (usually <1%) accounts for the profound reactivity of metal- or complex-modified zeolites during catalysis. This active fraction is difficult to characterize as it cannot be physically separated from the bulk species, nor can most analytical measurements characterize this minor component in competition with the bulk. Most current characterization methods (spectroscopy, diffraction, etc.) provide information averaged over the (usually highly ordered) bulk of a material, which hinders understanding the defects, amorphous phases, or minor carriers that dictate technologically relevant properties, including electrochemical ones, in many materials.<sup>52b,53</sup>

The identity and nature of the bulk may or may not

represent the identity and nature of the boundary. For redox-modified zeolites, where the relevant region from which the electrochemical signal arises is boundary, bulk characterization methods provide information on an irrelevant region—one from which electron transfer is not occurring. When key properties arise from disordered surface species, even though ordered domains exist in the material, the surface-mediated properties are completely unpredicted by X-ray diffraction or X-ray absorption spectroscopy.<sup>54</sup> X-ray photoelectron spectroscopy and electrochemistry have proven to be two techniques that offer (near-)surface-specific information of relevance to redox-active zeolites because they average the physico-chemical character of the active species and its environment over less of the bulk.

## Conclusions and Outlook

The intersection of electrochemical methods with zeolitic structure yields new understanding of the nature and mechanisms of reactivity at interfaces. We have gained insight into (1) the effects of applied electric fields on ionic transport in zeolites through studies involving electrified microheterogeneous catalysis; (2) the effects of nanoscale particle size and site on electrosynthesis through studies using nanoelectrode-modified zeolites; and (3) reaction kinetics and mechanisms and molecular confinement through studies involving the use of zeolite-associated, redox-active coordination complexes.

Notably, the study of zeolite-influenced electron transfer continues to give rise to important questions, the understanding of which will improve our general application of electron transfer and catalytic chemistries. Key questions will include whether full three-dimensional control of the reaction space is required or if topological control of key reaction coordinates is sufficient. Answering these questions requires continued improvement in characterizing disordered or amorphous species and differentiating boundary-associated species from bulk species. Surface-specific analyses can only improve our understanding of boundary topological redox isomers,<sup>46,55</sup> which are currently the only zeolite-associated electron-transfer communicators of electrocatalytic relevance.

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## References

- Rolison, D. R. Zeolite-modified electrodes and electrode-modified zeolites. *Chem. Rev.* **1990**, *90*, 867–878.
- Ozin, G. A.; Kuperman, A.; Stein, A. Advanced zeolite materials. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 359–376.
- Rolison, D. R.; Nowak, R. J.; Welsh, T. A.; Murray, C. G. Analytical implications of zeolites in overlayers at electrodes. *Talanta* **1991**, *38*, 27–35.
- Bard, A. J.; Mallouk, T. E. Electrodes modified with clays, zeolites, and related microporous solids. In *Molecular Design of Electrode Surfaces*; Murray, R. W., Ed.; Wiley: New York, 1992; pp 271–312.
- Baker, M. D.; Senaratne, C. Electrochemistry of clays and zeolites. In *Electrochemistry of Novel Materials*; Lipkowsky, J., Ross, P. N., Jr., Eds.; VCH: Amsterdam, 1994; pp 339–380.
- Rolison, D. R. The intersection of zeolites with electrochemistry. *Stud. Surf. Sci. Catal.* **1994**, *85*, 543–586.
- Walcarius, A. Zeolite-modified electrodes: analytical applications and prospects. *Electroanalysis* **1996**, *8*, 971–986.
- Bedioui, F. Synthèse critique de la caractérisation électrochimique de zéolithes et d'aluminophosphates chimiquement modifiés. *Can. J. Chem.* **1998**, *76*, 1886–1909.
- Walcarius, A. Zeolite-modified electrodes in electroanalytical chemistry. *Anal. Chim. Acta* **1999**, *384*, 1–16.
- Hölderich, W.; Hesse, M.; Naumann, F. Zeolites: Catalysts for organic syntheses. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 226–246.
- (a) Sheldon, R. A. Heterogeneous catalytic oxidation and fine chemicals. In *Heterogeneous Catalysis and Fine Chemicals II*; Guisnet, M., et al., Eds.; Elsevier: Amsterdam, 1991; pp 33–54. (b) Arends, I. W. C. E.; Sheldon, R. A.; Wallace, M.; Schuchardt, U. Oxidative Transformations of Organic Compounds Mediated by Redox Molecular Sieves. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1144–1163.
- Perot, G.; Guisnet, M. Advantages and disadvantages of zeolites as catalysts in organic chemistry. *J. Mol. Catal.* **1990**, *61*, 173–196.
- Intrazeolitic water solvates the extraframework cations, thereby creating the equivalent of a several molal salt solution—a medium which is inhospitable to most organic molecules.
- Attempts to synthesize “molecular wires” within microporous zeolites did not produce effective intrazeolitic electron paths. See, e.g.: Zuppiroli, L.; Beuneu, F.; Mory, J.; Enzel, P.; Bein, T. The low-field conductivity of zeolite-encapsulated molecular wires. *Synth. Met.* **1993**, *57*, 5081–5087.
- Martens, J. A.; Souverijns, W.; Verrelst, W.; Parton, R.; Gromont, G. F.; Jacobs, P. A. Selective isomerization of hydrocarbon chains on external surfaces of zeolite crystals. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2528–2530.
- Ernst, S. Selective catalytic reactions at the external surface of zeolite catalysts. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 63–64.
- Fleischmann, M.; Pons, S.; Rolison, D. R.; Schmidt, P. P. *Ultra-microelectrodes*; Datatech Systems: Morganton, NC, 1987.
- Heinze, J. Ultramicroelectrodes in electrochemistry. *Angew. Chem., Int. Ed. Engl.* **1993**, *30*, 1268–1288.
- At constant current,  $q = it$ ; by Faraday's law:  $q = nFm$  (where  $q$  is charge (coulombs),  $i$  is current (amperes),  $t$  is time (seconds),  $n$  is the number of electrons transferred,  $F$  is Faraday's constant ( $9.5 \times 10^{-4}$  coulombs/mol), and  $m$  is moles of product).
- Metal Microstructures in Zeolites: Preparation—Properties—Applications*; Jacobs, P. A., Jaeger, N. I., Jiru, P., Schultz-Ekloff, G., Eds.; Elsevier: Amsterdam, 1982.
- Rolison, D. R.; Nowak, R. J.; Pons, S.; Ghoroghchian, J.; Fleischmann, M. Zeolite-supported ultramicroelectrodes. In *Molecular Electronic Devices III*; Carter, F. L., Siatkowski, R. E., Wohltjen, H., Eds.; Elsevier: Amsterdam, 1988, pp 401–410.
- Rolison, D. R.; Hayes, E. A.; Rudzinski, W. E. Electrode-modified zeolites: electrode microstructures contained in and on a heterogeneous catalyst. *J. Phys. Chem.* **1989**, *93*, 5524–5531.
- Rolison, D. R.; Stemple, J. Z. Electrified microheterogeneous catalysis in low ionic strength media. *J. Chem. Soc., Chem. Commun.* **1993**, 25–27.
- (a) Rolison, D. R.; Stemple, J. Z. Electrified microheterogeneous catalysis. U.S. Patent 5,296,106, 1994. (b) Rolison, D. R.; Stemple, J. Z. Oxidation of organic materials by electrified microheterogeneous catalysis. U.S. Patent 5,288,371, 1994. (c) Rolison, D. R.; Stemple, J. Z. Decomposition of halogenated and polyhalogenated organic materials by electrified microheterogeneous catalysis. U.S. Patent 5,282,936, 1994.
- Fleischmann, M.; Ghoroghchian, J.; Rolison, D.; Pons, S. Electrochemical behavior of dispersions of spherical ultramicroelectrodes. *J. Phys. Chem.* **1986**, *90*, 6392–6400.
- Rolison, D. R.; Stemple, J. Z.; Curran, D. J. Electrochemical and electric-field effects at dispersions of zeolites. In *Proceedings of the 9th International Zeolite Conference*; von Ballmoos, R., Higgins, J. B., Treacy, M. M. J., Eds.; Butterworth-Heinemann: Stoneham, MA, 1993; pp 699–706.
- Blaich, D. N.; Rolison, D. R. Application of AC impedance for in-situ, real-time measurements of changes in the bulk conductivity of aqueous zeolite dispersions during electrolysis. *J. Electroanal. Chem.* **1994**, *370*, 305–308.

- (28) Breck, D. W. *Zeolite Molecular Sieves*; Wiley: New York, 1974; pp 578–585.
- (29) Blauch, D.N.; Stemple, J. Z.; Rolison, D.R. Investigation of conduction in aqueous zeolite dispersions. *Extended Abstracts*; Electrochemical Society: Pennington, NJ, 1993; PV 93-1, #1874.
- (30) Dempsey, E. *Molecular Sieves*; Society of Chemical Industry: London, 1968; p 293.
- (31) Henry, P. M. *Palladium Catalyzed Oxidation of Hydrocarbons*; Reidel: Boston, 1989; Chapter 2.
- (32) Espeel, P. H.; Tielen, M. C.; Jacobs, P. A. Palladium copper-exchanged Y-type zeolites—a true heterogeneous Wacker catalyst. *J. Chem. Soc., Chem. Commun.* **1991**, 669–671.
- (33) When the EMC reaction is run at constant current rather than under an applied voltage gradient, the selectivity for production of propylene oxide improves to 90%.<sup>34</sup>
- (34) Stemple, J. Z.; Rolison, D. R. Oxidation of propene by electrified microheterogeneous catalysis. *Extended Abstracts*; Electrochemical Society: Pennington, NJ, 1993; PV 93-2, p 926.
- (35) Wroblowa, H.; Piersma, B. J.; Bockris, J. O'M. Studies of the mechanism of the anodic oxidation of ethylene in acid and alkaline media. *J. Electroanal. Chem.* **1963**, 6, 401–416.
- (36) Hayes, E. A.; Stemple, J. Z.; Rolison, D. R. Destruction of polychlorinated organics by electrified microheterogeneous catalysis. In *Water Purification by Photocatalytic, Photoelectrochemical, and Electrochemical Processes*; Rose, T. L., Conway, B. E., Murphy, O. J., Eds.; Electrochemical Society: Pennington, NJ, 1994; 94-19, pp 121–130.
- (37) Osburn-Atkinson, E. O.; Feng, Z.; Rolison, D.R. Manuscript in preparation.
- (38) Ferri-/ferrocyanide—and many organic substrates<sup>39</sup>—do not have ultrafast electron-transfer kinetics, so variations in rate and faradaic yield result as a function of the nature of the electrode and the constituents of the electrolyte.
- (39) Lund, H.; Baizer, M. M. *Organic Electrochemistry: An Introduction and A Guide*, 3rd ed.; Marcel Dekker: New York, 1991; pp 253–331.
- (40) Bessel, C. A.; Rolison, D. R. Microheterogeneous dispersion electrolysis with nanoscale electrode-modified zeolites. *J. Electroanal. Chem.* **1997**, 439, 97–105.
- (41) Adams, R. N. *Electrochemistry at Solid Electrodes*; Marcel Dekker: New York, 1969; pp 218, 223.
- (42) Gao, X.; White, H. S. Rotating microdisk voltammetry. *Anal. Chem.* **1995**, 67, 4057–4064.
- (43) Cepak, V. M.; Rolison, D. R. Manuscript in preparation.
- (44) Bessel, C. A.; Rolison, D. R. Electrocatalytic reactivity of zeolite-encapsulated Co(salen) with benzyl chloride. *J. Am. Chem. Soc.* **1997**, 119, 12673–12674.
- (45) Folest, J.-C.; Duprilot, J.-M.; Perichon, J.; Robin, Y.; Devynck, J. Electrocatalyzed carboxylation of organic halides by a cobalt-salen complex. *Tetrahedron Lett.* **1985**, 26, 2633–2636.
- (46) Bessel, C. A.; Rolison, D. R. Topological redox isomers: the surface chemistry of zeolite-encapsulated Co(salen) and [Fe-(bpy)<sub>3</sub>]<sup>2+</sup> complexes. *J. Phys. Chem. B* **1997**, 101, 1148–1157.
- (47) Further proof that the moles of catalytic Co(salen) in {Co(salen)}-NaY equaled the moles of electroactive Co(salen) came from studies of {Co(salen)}NaY prepared without a surface excess of Co:<sup>44</sup> this zeolite-associated complex exhibited neither electroactivity<sup>46</sup> nor activity for electrocatalysis of benzyl chloride.<sup>44</sup>
- (48) Teunissen, E. H.; van Santen, R. A.; Jansen, A. P. J.; Van Duijneveldt, F. B. NH<sub>4</sub><sup>+</sup> in zeolites—coordination and solvation effects. *J. Phys. Chem.* **1993**, 97, 203–210.
- (49) (a) Derouane, E. G.; Andre, J. M.; Lucas, A. A. Surface curvature effects in physisorption and catalysis by microporous solids and molecular-sieves. *J. Catal.* **1988**, 110, 58–73. (b) Chen, N. Y.; Degnan, T. F., Jr.; Smith, C. M. *Molecular Transport and Reactions in Zeolites*; VCH: New York, 1994; p 110.
- (50) Zicovich-Wilson, C. M.; Corma, A.; Viruela, P. Electronic confinement of molecules in microscopic pores—a new concept which contributes to explain the catalytic activity of zeolites. *J. Phys. Chem.* **1994**, 98, 10863–10870.
- (51) Senaratne, C.; Zhang, J.; Baker, M. D.; Bessel, C. A.; Rolison, D. R. Zeolite-modified electrodes: intra- versus extrazeolite electron transfer. *J. Phys. Chem.* **1996**, 100, 5849–5862.
- (52) See the point and counterpoint in the following: (a) Bedioui, F.; Devynck, J.; Balkus, K. J., Jr. Comment on “Zeolite-modified electrodes: intra- versus extrazeolite electron transfer”. *J. Phys. Chem.* **1996**, 100, 8607–8609. (b) Rolison, D. R.; Bessel, C. A.; Baker, M. D.; Senaratne C.; Zhang, J. Reply to the comment on “Zeolite-modified electrodes: intra- versus extrazeolite electron transfer”. *J. Phys. Chem.* **1996**, 100, 8610–8611.
- (53) Eckert, J.; Stucky, G. D.; Cheetham, A.K. Partially disordered inorganic materials. *Mater. Res. Soc. Bull.* **1999**, 24, 31–41.
- (54) (a) Kaatz, F. H.; Harris, V. G.; Kurihara, L.; Rolison, D. R.; Edelstein, A. E. Slow oxidation of Cu–Co nanocrystals. *Appl. Phys. Lett.* **1995**, 67, 3807–3809. (b) Swider, K. E.; Merzbacher, C. I.; Hagans, P. L.; Rolison, D.R. The synthesis of RuO<sub>2</sub>–TiO<sub>2</sub> aerogels—redistribution of electrical properties on the nanoscale. *Chem. Mater.* **1997**, 9, 1248–1255. (c) Rolison, D. R.; Hagans, P. L.; Swider, K. E.; Long, J. W. The role of hydrous ruthenium oxide in Pt–Ru direct methanol fuel cell anode electrocatalysts—the importance of mixed electron/proton conductivity. *Langmuir* **1999**, 15, 774–779.
- (55) Turro, N. J.; Garcia-Garibay, M. Thinking topologically about photochemistry in restricted spaces. In *Photochemistry in Organized Media*; Ramamurthy, V., Ed.; VCH: New York, 1991; pp 1–38.

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