

Final Technical Report

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Project Title: Mediation of Heterogeneous Oxidation of Aliphatic Hydrocarbons
Through System Specific Optimization of Photo-induced Charge Carrier Separation Distance on
TiO₂, Pt/TiO₂ and Iron Oxide/TiO₂ Particulate Photocatalysts.

Abstract. Our research has as its primary objective the development and mechanistic investigation of suitable photocatalytic surfaces, as mediators of energy-efficient heterogeneous oxidation of aliphatic hydrocarbons. Particular emphasis is placed on mixed iron(III)/titanium(IV) oxide semiconductor particulates, featuring low %Fe content, for which a novel synthetic protocol has been developed in this laboratory, relying on sol-gel hydrolysis of high purity iron and titanium isopropoxide precursors, followed by thermal treatment to develop the active anatase phase. This methodology leads to replacement of Ti(IV) ions by Fe(III) sites in the TiO₂ (anatase) lattice, and is contrasted to samples prepared by physical mixing of nanometer-sized γ -Fe₂O₃ (gift from MACH I, Inc.) and TiO₂ (Degussa P-25).

Mechanistic understanding of these systems involves multifaceted approaches. Our unique ability to evaluate charge-carrier separation distances, as measured by time-resolved photocharge experiments (TRPC) on instrumentation pioneered by Dr. Levy, permits correlation of this important photophysical property to photocatalytic efficiency and reaction mechanism. A major redesign of our benchmark TRPC apparatus was recently undertaken, which provides for controlled environments during measurement, i.e., vacuum; controlled atmosphere (inert or reactive); and

temperature control (-100 to + 150 °C). Operation of this new TRPC cell necessitated insulation from RF noise, which was achieved by employing a walk-in Faraday enclosure to house the apparatus and supporting instrumentation. Previous work has shown that charge-carrier separation distances (CCSD) for Pt doped TiO₂ pass through a maximum at very low %Pt content. A similar region of maximum CCSD has now been tentatively identified with samples of □-Fe₂O₃/TiO₂ (0 – 0.02 %Fe) under ambient conditions. Interestingly, the decay portion of the TRPC waveform (charge recombination) exhibits significant delay, by an order of magnitude, under vacuum conditions. Under high vacuum (10⁻⁷ torr), reversal of the signal sign is frequently observed, further underscoring the importance of the surface condition in controlling CCSD values. Experimentation with inert gas atmospheres is currently under way to assist in the interpretation of these observations. Surprisingly, maximum CCSD values have been shown not to correlate always with maximum photocatalytic activity in the oxidation of hydrocarbons. As the oxidation products derive from precursors that combine radical species generated via the action of both photoholes (organic peroxy radicals) and photoelectrons (superoxide), it is postulated that the maximum in photocatalytic activity will occur at a balance point between maximum CCSD and minimum distance crossover for the resulting radicals. The generality of this premise with respect to the present iron-doped TiO₂ preparations remains to be verified.

In a complimentary approach, in order to explore the possible active oxidants that may develop on iron-oxide doped photocatalytic surfaces, we rely on model compounds that can mimic the structural and functional aspects of the active site. One such system is formulated on the well-known oxo-bridged, triiron core structure [Fe^{III}₃O], which, in the presence of dioxygen and a reducing agent, or alternatively upon action of hydrogen peroxide, can generate a structure that fuses two [Fe^{III}₃O] units via a peroxo moiety. This hexairon(III) peroxide reacts directly with alkanes under stoichiometric conditions, albeit at elevated temperatures. Under catalytic conditions ([Fe^{III}₃O]_{cat}, O₂, reducing agent), the same system has been shown to produce reactive hydroxyl and alkoxyl radicals under ambient conditions. These results indicate that the role of Fe(III) sites on semiconductor

surfaces need not be limited to photoelectron trapping, as usually discussed in the literature, but may be actively involved in generating potent oxidants via sequential reduction of dioxygen.

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Detailed Progress Report

Specific Goals. The research aims of this work have remained the same throughout the grant period. Our research has as its primary objective the development and mechanistic investigation of suitable photocatalytic surfaces, as mediators of energy-efficient heterogeneous oxidation of aliphatic hydrocarbons. Particular emphasis is placed on mixed iron/titanium oxide semiconductor particulates, for which novel synthetic protocols, based on organometallic precursors, have been developed. Mechanistic understanding of these systems involves multifaceted approaches. Our unique ability to measure charge-carrier separation distances, using instrumentation recently developed in this laboratory to perform time-resolved photocharge measurements under variable pressure and temperature conditions, allows us to correlate this important photophysical property to photocatalytic efficiency and reaction mechanism. Simultaneous interrogation of iron-centered thermal and photochemical systems that permit oxidation of hydrocarbons under similar mechanistic pathways, has proven indispensable in refining our mechanistic scenarios and for providing mechanistic probes. The desirable practical goals are the synthesis of commodity oxo chemicals from aliphatic hydrocarbons, and the photo-degradation of organic pollutants.¹

Hypotheses under Investigation. Recombination of photoelectrons with photoholes is traditionally considered a major cause for low quantum efficiencies in heterogeneous photocatalytic processes. Based largely on intuitive reasoning, it has frequently been assumed in the literature that maximized efficiency can be achieved by increasing the charge carrier separation distance (CCSD), thereby decreasing the probability of recombination prior to reaction of the desired chemical reagents with photoelectrons and photoholes. However, our work (vide infra) has indicated that for oxygenation processes, which frequently depend on generation and coupling of surface bound radicals, optimization than maximization of CCSD correlates better with maximum photocatalytic efficiency.² The present work explores the generality of this premise and the details of the underlying mechanistic picture by means of novel photocatalytic materials, in conjunction with

parallel investigations of thermal homogeneous or heterogeneous oxygenation systems.^{3,4} Both photocatalytic and thermal oxygenation systems are based on oxygen and carbon-centered radicals, which are surface bound or diffusively free, respectively. In photocatalytic systems, photoholes are traditionally associated with the generation of potent hydroxyl radicals via oxidation of water, while photoelectrons are usually trapped by dioxygen to form superoxide and/or hydrogen peroxide. In contrast, thermal oxygenation systems develop their active oxidant (which can still be hydroxyl radicals) by means of sequential reduction of dioxygen, to form intermediate superoxo and/or peroxo species at transition metal centers. The site of reduction coincides therefore with the site of oxidant development. This operational mode has not been adequately addressed with photocatalytic surfaces. The concept of charge-carrier separation has been intuitively associated with a sharp distinction in terms of the area of action of oxidizing and reducing equivalents. While this concept may be fundamentally true, it is not inconceivable that, in the presence of redox-active metals such as iron, the sites of electron capturing by dioxygen may also be involved in the generation of active oxidants. This work, and that of others,^{5,6} shows that at least the products of oxygenation processes combine elements generated by the action of both oxidizing and reducing equivalents. According to one interpretation,² superoxide radicals (O_2^- , $^{\bullet}O_2H$), generated via one-electron reduction of dioxygen by photoelectrons, and organic peroxy radicals ($ROO^{\bullet}$), formed by the oxidizing action of photoholes, diffuse on the surface and combine into tetraoxo intermediates that are immediate precursors of the final products (usually alcohol and ketone, for oxidation of alkanes). This process is also consistent with variations in measured charge-carrier separation distances in relation to photocatalytic activity. An alternative explanation, under investigation, is the aforementioned site coincidence of reducing power and oxidizing activity.

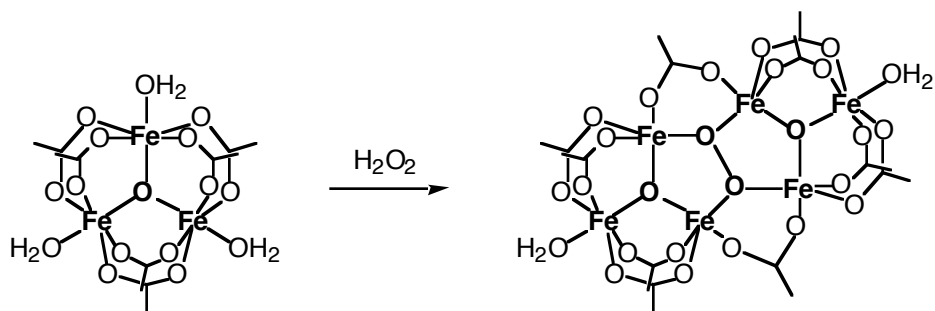
Results and Discussion

(i) **Mechanistic Investigations: Nature of Intermediates.** In order to explore the possible active oxidants that may develop on iron-oxide doped photocatalytic surfaces, we rely on model compounds that can mimic the structural and functional aspects of the active site. One such system

is formulated on the well-known oxo-bridged triiron core structure ($[\text{Fe}_3\text{O}]^+$, core atoms in bold in Scheme 1), which is a pervasive feature in many metal oxo complexes. Supporting ligands are provided by carboxylates, which are frequently used for attaching metal sites on surfaces, but most importantly are employed here for generating a ligand field rich in oxo moieties. Each iron atom is octahedrally coordinated by six oxygen atom residues. The model thus generated is not unlike local structural units on metal oxide semiconductor surfaces.

From a functional standpoint, electrochemical experiments indicate that the all-ferric $[\text{Fe}^{\text{III}}_3\text{O}]^{7+}$ core can be reduced via sequential one-electron steps to the mixed-valence clusters $[\text{Fe}^{\text{III,II,II}}_3\text{O}]^{6+}$ and $[\text{Fe}^{\text{III,II,II}}_3\text{O}]^{5+}$. The former one-electron reduction is electrochemically reversible; chemical reductions confirm that the so generated mixed-valence cluster retains the Fe_3O core. The second one-electron step is typically quasi-reversible, and since the resulting cluster is not easily isolable by chemical means, it is currently unclear whether the Fe_3O unit is preserved intact. In any event, the all-ferric $\text{Fe}^{\text{III}}_3\text{O}$ core is a suitable starting unit for redox-active transformations.

Scheme 1



Reactivity studies show that the all-ferric species $[\text{Fe}_3\text{O}(\text{O}_2\text{CCMe}_3)_6(\text{OH}_2)_3]^+$ is converted by the action of O_2/Zn (Zn acts as a source of reducing equivalents), or more cleanly by H_2O_2 , to afford the remarkable hexairon(III) cluster $[\text{Fe}_6(\text{O}_2)(\text{O})_2(\text{O}_2\text{CCMe}_3)_{12}(\text{OH}_2)_2]$ (Scheme 1). The cluster features a O_2 -peroxo unit trapped at the center of a $[\text{Fe}_6(\text{O}_2)(\text{O})_2(\text{O}_2\text{CCMe}_3)_{12}(\text{OH}_2)_2]$ core (core atoms in bold).⁷ The structure can be rationalized as the product of fusion of two $\text{Fe}^{\text{III}}_3\text{O}$ units by means of a peroxo and two carboxylate moieties, the latter derived via minimal structural rearrangement of two carboxylate moieties per starting Fe_3O unit (one of these carboxylates along with two water

molecules per Fe_3O are eliminated). The structure is remarkable in its simplicity and highly relevant to surface-bound events, as the local environment of an initial iron-oxo lattice can be minimally perturbed to incorporate a reactive peroxo unit (see below).

The interconvertible use of O_2 /reducing agent or H_2O_2 (already reduced dioxygen) to generate the cluster is typical in catalytic oxidation chemistry. Reducing equivalents produce the necessary Fe(II) sites for the activation of dioxygen. These are provided by abundant photoelectrons on semiconductor surfaces. Alternatively, H_2O_2 circumvents the need for reducing power and acts directly on Fe(III) sites with similar results. Hydrogen peroxide is copiously generated on illuminated TiO_2 and is responsible for the purplish color evidenced on TiO_2 surfaces due to generation of titanium peroxides. The role of these metal peroxides as potential oxidizing agents has not been adequately addressed.

Oxygenation of Substrates. The possibility that the peroxo moiety observed in a number of complexes containing the $[\text{Fe}_6(\text{O}_2)(\text{O})_2]$ unit may be involved in oxo transfer and/or hydrogen-abstraction chemistry was explored with suitable substrates. First, we employed phosphines (PPh_3 , (*p*-tolyl) $_3\text{P}$) to ensure that the cluster does not undergo simple oxo-transfer chemistry due to the bridging oxo moieties. Indeed, when $[\text{Fe}_6(\text{O}_2)(\text{O})_2(\text{O}_2\text{CCMe}_3)_{12}(\text{OH}_2)_2]$ is exposed to PPh_3 (1–18 equiv.) or (*p*-tolyl) $_3\text{P}$ (1–5 equiv.) in degassed C_6D_6 and the reaction is followed by ^{31}P and/or ^1H NMR spectroscopy, phosphine oxide is not detected either in free or metal-bound form even after prolonged periods (several weeks) of heating (70 °C (PPh_3), 45 °C ($\text{P}(\text{p-tolyl})_3$)).

A typical olefin such as *cis*-stilbene undergoes oxygenation by these peroxo-containing complexes, albeit at a slow rate. The reaction of *cis*-stilbene (3.3 μmol , 1 equiv. over iron complex) in C_6D_6 (70 °C) under N_2 was followed by ^1H NMR to reveal generation of benzaldehyde (0.3 μmol) and *trans*-stilbene oxide (0.5 μmol). These amounts double if the catalyst is allowed to react with 2 equivalents of *cis*-stilbene (7 μmol). The products are most likely formed due to direct interaction of *cis*-stilbene with the peroxo unit. The product profile indicates that a step-wise rather than a concerted mechanism is involved, featuring radical and/or carbocationic intermediates.

Stoichiometric oxidations of a diagnostic alkane such as adamantane (0.10 mmol, 1 equiv. over iron complex) by the peroxo-containing species, in the presence of pyridine as a good radical trap, affords oxygenation products upon heating at 66 °C. Low yields of 1-adamantanol (0.4 μ mol), adamantanone (0.4 μ mol), 2-(1-adamantyl)pyridine (0.9 μ mol), and 2-(2-adamantyl)pyridine (0.1 μ mol) are obtained. The presence of adamantylpyridines denotes the intermediacy of adamantyl radicals, although the selectivity obtained for the oxidation of the tertiary over secondary positions (*tert/sec* $\approx$ 8) suggests that the active oxidant, probably the peroxo unit per se or a hydroperoxo version, is fairly selective and certainly different from the corresponding oxidant (*tert/sec* $\approx$ 3–5) of the catalytic versions (see below). The aforementioned stoichiometric reactions indicate that despite the low yields of the substrate oxidation reaction, the peroxo-containing iron compound can effect direct substrate oxidation. Under the high-temperature operational conditions of heterogeneous catalysts, analogous surface-bound peroxo units should be taken into consideration as potential oxidants.

Catalytic oxidations of adamantane (5 mmol) mediated by the all-ferric, oxo-bridged triiron compound $[\text{Fe}_3\text{O}(\text{O}_2\text{CCMe}_3)_6(\text{OH}_2)_3]^+$ (0.2 mmol), and supported by either Zn (20 mmol)/O₂ (4% in N₂ or 100%) or H₂O₂ (2 mmol) provide a cautionary note. In the presence of pyridine, the product profile is composed of oxo adamantyl species (1-ol, 2-ol, 2-one) and adamantylpyridines (2-(1-Ad)py, 4-(1-Ad)py, 2-(2-Ad)py, 4-(2-Ad)py). Under increasing partial pressures of dioxygen the amounts of all adamantylpyridines are decreased in favor of the corresponding oxo adamantyl products due to competition of dioxygen and pyridine in trapping *tert*- and *sec*-adamantyl radicals. Furthermore, the amounts of *sec*-adamantylpyridines are more seriously affected with increasing O₂ (reduced to almost trace amounts under pure O₂), due to the inferior rate constant (reportedly by two orders of magnitude) for capturing *sec*-adamantyl versus *tert*-adamantyl radicals by pyridine. All these results are consistent with a mechanism that invokes radical abstraction of H atoms from both tertiary and secondary C-H bonds of adamantane to generate diffusively free *tert*- and *sec*-adamantyl radicals. These radicals are captured by dioxygen (and/or pyridine) to form the corresponding peroxy radicals (and/or adamantylpyridines). In turn, peroxy radicals decompose

via well known pathways (in particular bimolecular Russell disproportionation) to afford the observed alcohol and ketone. More important in this regard is the nature of the active oxidant(s) involved. As noted above, these are different from those observed in stoichiometric reactions, underscoring the importance of distinguishing between stoichiometric and catalytic versions. The *tert/sec* selectivity (3–5) obtained in catalytic reactions suggests that a much less selective oxidant is here at work, most likely involving a combination of hydroxyl and alkoxy radicals. The presence of hydroxyl radicals was further confirmed by means of their diagnostic reaction with dimethyl sulfoxide, and via measurements of deuterium kinetic isotope effects on deuterated adamantane. These results cannot determine whether both the present oxidants *and* the iron-peroxo compound (generated in situ) are operative in the catalytic reaction, owing to the low yields anticipated for the latter compound.

The present results strongly suggest that similar iron oxo species on semiconductor surfaces can generate potent active oxidants in close proximity to the site of reduction. These active oxidants can vary according to reaction conditions, and may include diffuse oxyl radicals *and* metal peroxo moieties.

(ii) Mixed Iron/Titanium Oxide Semiconductor Particulates: Synthesis and Characterization. Two types of mixed iron/titanium oxides have been prepared for further evaluation of their electronic properties by time-resolved photocharge measurements (TRPC) and subsequent correlation with photocatalytic oxidation efficiency as a function of %Fe content. In one synthetic protocol sol-gel techniques are utilized to incorporate Fe(III) ions in the TiO₂ matrix by means of metal substitution at low %Fe content. The second preparative method seeks to generate mixed Fe₂O₃/TiO₂ heterojunctions by virtue of mortar-and-pestle mixing of nanometer-sized □-Fe₂O₃ and TiO₂. The metal oxides used are prepared by MACH I, Inc. (□-Fe₂O₃) and Degussa (TiO₂) via proprietary supersonic nozzle techniques.

The sol-gel dependent methodology involves high purity organometallic precursors. Suitable starting complexes are iron and titanium alkoxides, in particular isopropoxides which are readily amenable to sol-gel hydrolysis. The selection is also influenced by the fact that among all titanium

alkoxides $\text{Ti}(\text{O}^i\text{Pr})_4$ is commercially available at very high purity (99.999%). Iron(III) isopropoxide is ill defined in the literature and had to be synthesized by the reaction of anhydrous FeCl_3 and sodium isopropoxide in anhydrous isopropanol. The yellow-brown crystals of $[\text{Fe}(\text{O}^i\text{Pr})_3]_n$ have not provided so far a specimen suitable for X-ray analysis, thus the nuclearity (n) of the discrete molecule remains unidentified, although molecular weight measurements suggest a value of 2 or 3. Reportedly, samples of commercially available iron alkoxides, synthesized by employing sodium alkoxides, retain oxo or hydroxo bridges between Fe(III) centers. To eliminate this possibility, we have started employing thallium alkoxides, as Tl(I) is known to precipitate efficiently not only TlCl but also TlOH . The so generated $[\text{Fe}(\text{O}^i\text{Pr})_3]_n$ (solid) is dissolved in $\text{Ti}(\text{O}^i\text{Pr})_4$ (liquid) in a dry atmosphere box at desired molecular ratios (usually 0 – 5% Fe). Anhydrous isopropanol or ethanol is used to dilute the mixed Fe/Ti alkoxide solution, followed by fast addition, via anaerobic funnel and under vigorous stirring, of an alcohol solution containing water in amounts exceeding by five fold the required stoichiometric amounts for complete hydrolysis. Stirring is continued at very slow speed for another hour, followed by centrifugation and resuspension of the solid in water by means of sonification and centrifugation (the cycle repeated three times). The solid is finally dried under vacuum. The so obtained material is crystallographically amorphous and shows virtually no TRPC signal, as expected for amorphous TiO_2 which is known to possess minimal photocatalytic activity. In order to activate the material by inducing formation of the anatase phase, the solid was placed in platinum boats and stepwise heated in a tube furnace to 450 °C under a slow stream of pure O_2 . The procedure is also effective in removing all remaining organic matter. The resulting solid exhibits high photocatalytic activity as evidenced by TRPC measurements.

Mixed iron oxide/ TiO_2 heterojunctions were prepared by employing pre-synthesized $\alpha\text{-Fe}_2\text{O}_3$ and Degussa P-25 TiO_2 . Alpha type Fe_2O_3 was provided as a gift by MACH I, Inc.. Its physical form appearance is that of a free flowing brown powder (aerosol), composed of 0.003 micron particles of surface area 250 m^2/g . The material is hygroscopic and requires handling in a dry atmosphere box. This $\alpha\text{-Fe}_2\text{O}_3$ is mixed carefully with P-25 TiO_2 by using a mortar and pestle to ensure homogeneous mixing. As the mol% Fe is usually kept at low levels (0 – 5 %), a method of

stepwise dilutions with TiO_2 is employed, starting from an equimolar mixture of $\alpha\text{-Fe}_2\text{O}_3$ and Degussa P-25 TiO_2 . As indicated below, TRPC measurements largely demonstrate decreasing charge-carrier separation distance with increasing %Fe(III), save for an important region at very low %Fe which is subsequently discussed.

Photophysical Properties. Typical TRPC waveforms for pure TiO_2 and Fe/ TiO_2 photocatalysts at high Fe% loadings have been discussed in previous progress reports. Our analysis is based on the premise that the maximum amplitude, V_m , of the transient signal is proportional to the charge-carrier separation distance (CCSD). As noted previously, we have undertaken a major redesign of our benchmark TRPC apparatus, which provides for controlled environments during measurement, i.e., vacuum; controlled atmosphere (inert or reactive); temperature control (-100 to +150 °C), and lowered background noise by inclusion of light traps fabricated from non-photoconducting materials. This apparatus makes possible, for the first time, the measurement of the intrinsic charge carrier dynamics of photoconducting materials in vacuum and allows for in-situ determinations during photocatalysis in reactive atmospheres. Pictures of this new apparatus have been included in previous progress reports.

Smooth operation of this new TRPC apparatus was initially impeded by high RF noise levels. This was particularly true for several samples of mixed iron/titanium oxides described in the preceding section that exhibit small maximum photocharge amplitudes. Our benchmark TPRC cell, much smaller in size than the current advanced version and without the vacuum related extensions of the present equipment, was designed to operate embedded in a handy RF-shielded box. The present version necessitated construction of a sizeable, custom-made Faraday enclosure (dimensions: 8 ft (l) $\times$ 4 ft (w) $\times$ 8 ft (h); walk-in style) to house the TRPC cell and supporting equipment. Appropriate inlets for the light path and provisions for electric/vacuum connections were suitably accommodated. Armed with this significant reconfiguration of the instrumentation setup we were able to acquire useful TRPC data under both ambient and low-pressure conditions.

The current TPRC measurements address variations in the maximum photocharge amplitude (a direct measure of charge-carrier separation distance) as a function of mol % Fe, in a region of low

Fe doping (0 – 0.5 %). For samples composed of α -Fe₂O₃/TiO₂ particulate heterojunctions, a progressive decrease of the maximum value of the TRPC signal (negative signal) is observed with increasing mol% Fe in the region of 0.03 – 0.5%. However, at very low %Fe (0 – 0.02%), the maximum photocharge amplitude goes through a maximum value at approximately 0.0005 to 0.01 %. Owing to the low %Fe content, further experimentation will be needed to explore the credibility and scope of the curvature. However, similar maxima in charge-carrier separation distance have been previously observed² with Pt-doped TiO₂ samples at very low %Pt content. Both platinum and Fe(III) particles act as deep traps of photoelectrons and, therefore, their density and dispersion controls the extent of charge-carrier separation. As argued previously, at a critically small number of photoelectron traps, the charge-carrier separation distance can be maximized.

The reproducibility of the TRPC measurement is reasonably good, especially if TRPC waveforms are collected for a large number of samples in short order. Ambient conditions, as those employed in the series of measurements noted above, introduce day-to-day variations (especially in terms of water content), which can affect reproducibility of what is known to be a very sensitive signal. Nevertheless, the present TRPC cell is designed to circumvent these problems by providing ways of controlling the local atmosphere. Of particular interest are experiments under vacuum conditions. The generic characteristics of the TRPC signal are significantly altered upon increasing vacuum levels. The most pronounced effect is a delay of the signal decay time by at least an order of magnitude versus ambient conditions. The phenomenon relates to an anticipated decrease in the rate of reaction between photocarriers and water/dioxygen, as the amount of these common traps is progressively reduced under evacuation conditions. At higher vacuum regimes (10^{-4} – 10^{-7} torr), the intensity of the TRPC signal is progressively reduced to very low levels, and, with several samples, even reversal of the sign of the waveform is observed, yielding a small positive signal. While no firm rationalization for the signal reversal can be offered at the present time, we consider likely that the effect of particle aggregation may be reduced with decreasing water content, thereby enhancing electron back-scattering in the opposite direction with respect to light incidence.

Photocatalytic Properties. A wide range of alkenes and alkanes, including the substrates used in model chemistry, have been scheduled to undergo in situ photocatalytic exploration. This work has been delayed due to the need to insulate the TRPC cell in a Faraday box, as noted above. We are now fully equipped to screen the photocatalytic efficiency of these substrates over semiconductor particulates covering the entire range of %Fe content explored in photophysical measurements. Particular emphasis will be placed on samples residing in the region of high maximum photocharge amplitude.

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