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Novel Metalloporphyrin Catalysts for the Oxidation of Hydrocarbons

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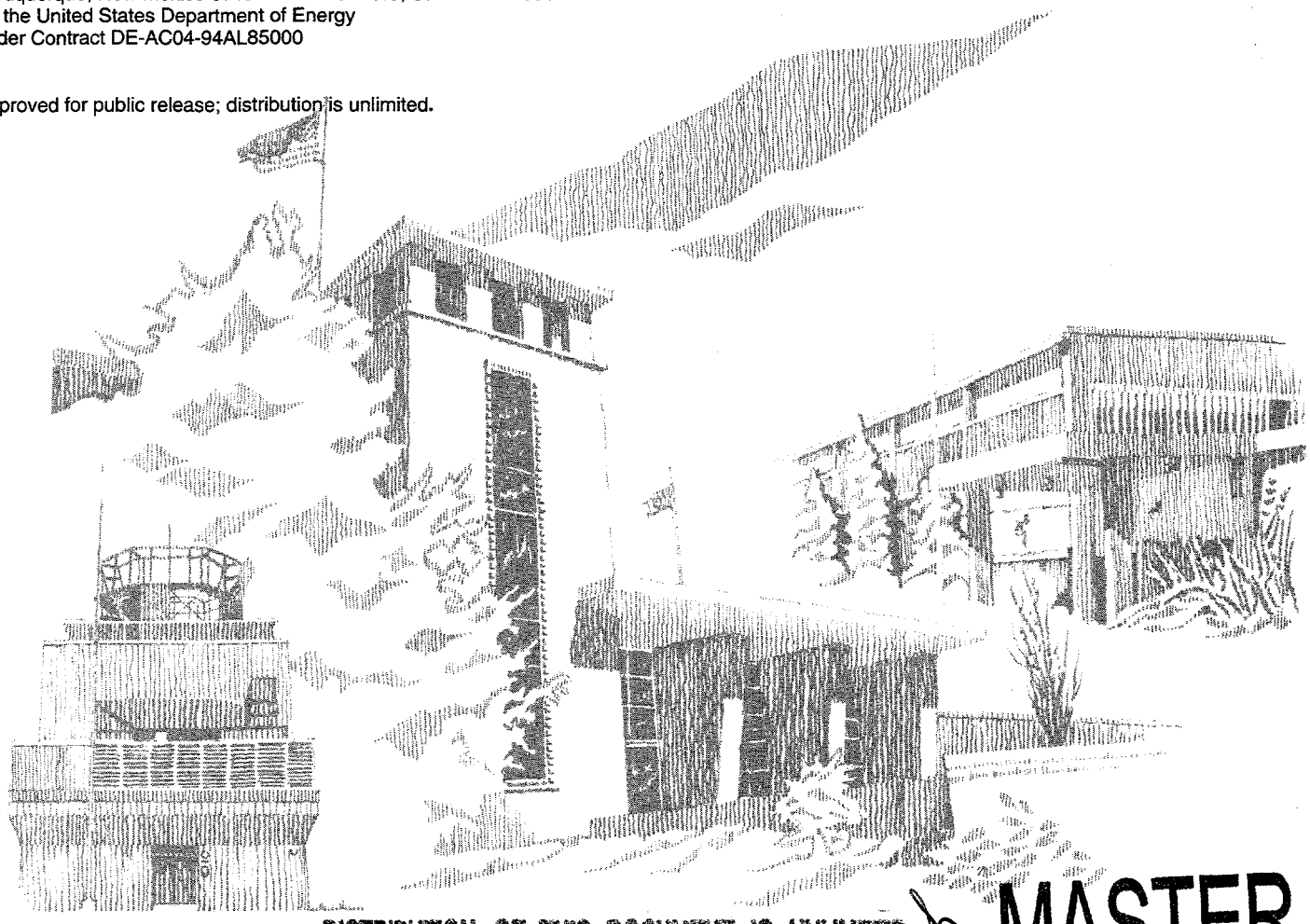

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NOVEL METALLOPORPHYRIN CATALYSTS FOR THE OXIDATION OF HYDROCARBONS

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Albuquerque, NM 87185-0710

Abstract

This report describes work performed in the Advanced Energy Technology Center for developing novel biomimetic oxidation catalysts. Two classes of metalloporphyrin catalysts were studied. The first class of catalysts studied were a novel series of highly substituted metalloporphyrins, the fluorinated iron dodecaphenylporphyrins. These homogeneous metalloporphyrin catalysts were screened for activity as catalysts in the oxidation of hydrocarbons by dioxygen. Results are discussed with respect to catalyst structural features. The second type of catalysts studied were heterogeneous catalysts consisting of metalloporphyrins applied to inorganic supports. Preliminary catalytic testing results with these materials are presented.

Acknowledgments

The US DOE Pittsburgh Energy Technology Center provided financial support for this research under FEW-4262. Special thanks to program managers Arun Bose and Gary Stiegel for this financial support.

This research would not have been possible without the synthetic expertise of Dr. Craig Medforth at the University of California at Davis. Our sincere thanks to Craig for synthesizing and characterizing the DPP catalysts.

Thanks to Drs. Jim Lyons and Paul Ellis of Sun Co. for many helpful discussions and the opportunity to perform some catalyst screening experiments in their laboratories.

Thanks are also extended to Katherine Erkkila and Kenneth Salaz, participants in Sandia'a Outstanding Summer Student Program, for assistance with the technical work.

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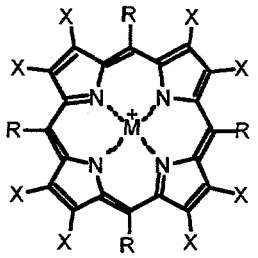
Introduction

The objective of this project was to develop novel catalysts for the direct conversion of hydrocarbons, especially natural gas, to oxygenated liquid products. A catalytic process for the direct conversion of natural gas to liquid fuels and feedstocks would enable more efficient utilization of this natural resource, and prevent the wasteful and polluting practice of flaring. Furthermore, light hydrocarbons are an abundant resource, and new processes are needed for cheap, efficient conversion of hydrocarbons to fuels, feedstocks, and chemicals. Our approach to this problem was to investigate biomimetic metalloporphyrin oxidation catalysts, and design improved catalysts based on structure-activity relationships.

Enzymes such as the cytochromes P450 are known to catalyze the partial oxidation of unactivated alkanes to alcohols.[1] Analysis of these natural systems indicates structural features needed to create a biomimetic catalyst which will mimic the enzyme's high catalytic activity and selectivity. Metalloporphyrins have been extensively studied as biomimetic oxidation catalysts, since metalloporphyrins play a key role in the chemistry of some enzymes.[2,3] Recently, metalloporphyrins have been reported to catalyze the oxidation of light alkanes to alcohols under mild conditions using molecular oxygen as the oxidant without the need for added co-reductant.[4-6] Using computer-aided molecular design (CAMD) coupled with experimental testing, we attempted to develop improved homogeneous catalysts for this process. We also investigated metalloporphyrin catalysts on inorganic supports as an alternative to homogeneous catalysts.

Metalloporphyrin Structures and Abbreviations

Figure 1 shows the structures and abbreviations for metalloporphyrins used in this report. All metalloporphyrins in this research are metal (III) porphyrins, and thus have a (-1) counterion (usually Cl^- or OH^-) which is not shown in the generic drawing in Figure 1. This counterion is sometimes referred to as an axial ligand. In the text, a porphyrin is referred to by the symbol for the metal combined with the symbol for the substituted macrocycle, e.g. $FeF_{20}DPP$. When the nature of the axial ligand is relevant to the discussion, it is designated following the abbreviation for the macrocycle. For example, $FeF_{20}DPPCl$ represents the same porphyrin, but specifically with a Cl counterion or axial ligand. The counterions for the N-methyl pyridinium cation substituents of TNMePyP are tosylates.



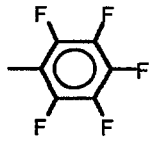
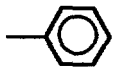
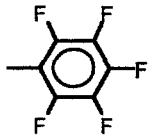
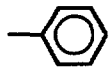
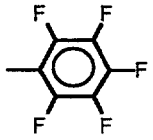
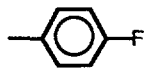
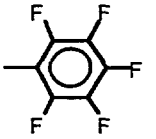
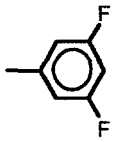
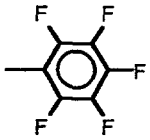
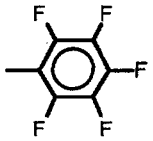
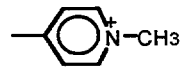
abbreviation	substituents		
F_{20}TPP	R = 		X = H
DPP	R = X = 		
F_{20}DPP	R = 	X = 	
F_{28}DPP	R = 	X = 	
F_{36}DPP	R = 	X = 	
F_{60}DPP	R = X = 		
F_{20}TPPβCl$_8$	R = 		X = Cl
TNMePyP	R = 		X = H

Figure 1. Structures and abbreviations for porphyrin macrocycles as used in this report. Counterions are not shown in these drawings. TPP = tetraphenylporphyrin, DPP = dodecaphenylporphyrin, and TNMePyP = tetra(N-methylpyridyl)porphyrin.

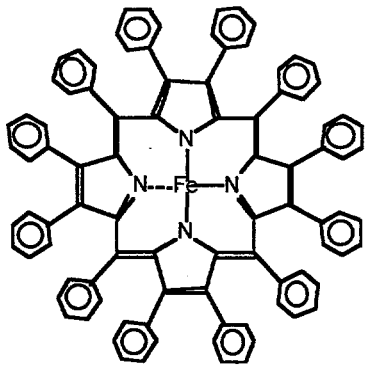
Technical Approach and Results

Fluorinated Dodecaphenyl Porphyrins - A Novel Catalyst Series

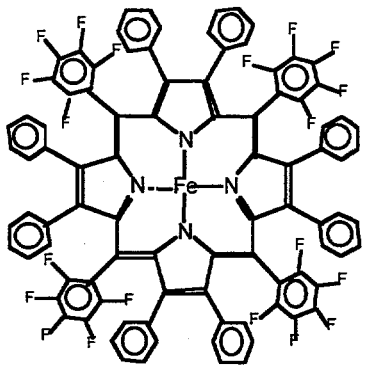
Metalloporphyrins have been shown to catalyze the homogeneous oxidation of light alkanes with oxygen as the oxidant under mild conditions with no added co-reductant.[4-6] Prior work has shown that oxidative catalyst activity is enhanced by the presence of electron withdrawing substituents on the porphyrin ring.[4-9] It has also been shown that steric bulk which prevents close bimolecular face-to-face approach of porphyrin molecules can improve catalyst stability under oxidizing conditions.[8-11] We designed, synthesized, and tested a series of novel catalysts, the fluorinated iron dodecaphenylporphyrins (FeF_xDPP where x = 0, 20, 28, 36). This unique catalyst series, shown in Figure 2, contains the desired structural features of electron withdrawing substituents and steric bulk. This catalyst series also has a third desired structural feature, a rigid cavity adjacent to the metal center. Synthesis and structural characterization of this series of porphyrins has been described elsewhere.[12]

Placing large numbers of bulky substituents, such as phenyl groups, around the periphery of a porphyrin macrocycle causes a nonplanar distortion of the macrocycle which creates a rigid cavity adjacent to the metal center. Figure 3 shows the shape of iron F_{20} dodecaphenylporphyrin ($FeF_{20}DPP$), one of our designed catalysts with a rigid cavity; and for comparison, iron F_{20} tetraphenylporphyrin ($FeF_{20}TPP$), a commercial planar catalyst which has phenyl substituents only at the four *meso* positions. We expected that this cavity would promote substrate binding and trap reactive intermediates adjacent to the metal center. This "micro-reactor" environment could therefore improve catalyst activity and might also influence selectivity. Highly substituted porphyrins such as our iron dodecaphenylporphyrin catalysts should also have improved stability relative to traditional planar porphyrin catalysts because there is considerable steric hindrance to bifacial approach of two porphyrin molecules, thus inhibiting bimolecular catalyst destruction.

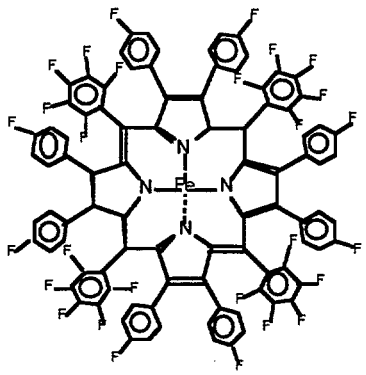
Electron withdrawing groups, such as fluorine, can be substituted on the phenyl rings of FeDPP to create a series of catalysts with a range of overall electron depletion at the metal center. The series of FeF_xDPP catalysts shown in Figure 2 has a range of overall electron depletion which can be estimated by the sum of the Hammett substituent constants ($\Sigma\sigma$) for the twelve substituents around the porphyrin macrocycle. This catalyst series is unique because the bulky phenyl substituents create a nonplanar distortion leading to the formation of a cavity, as discussed above. In addition, these catalysts maintain this same shape across the series, even with the addition of fluorine substituents. In previous investigations of the effect of electron withdrawing substituents on metalloporphyrin catalyst activity,[4-9] the addition of electron withdrawing groups to the porphyrin macrocycle may have been accompanied by a change in the degree of porphyrin nonplanarity. Our unique catalyst series allowed us to study the effect of increased electron depletion of the metal center isolated from a structural change.



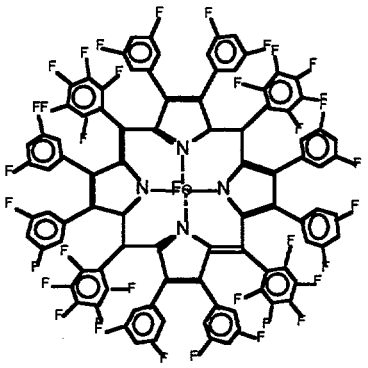
Iron Dodecaphenylporphyrin
FeDPP
$\Sigma\sigma_p = -0.12$ $\Sigma\sigma_m = 0.72$



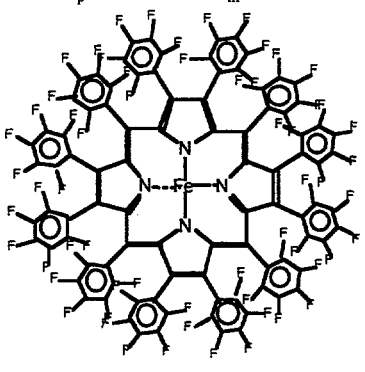
Iron F_{20}-Dodecaphenylporphyrin
$FeF_{20}DPP$
$\Sigma\sigma_p = 1.56$ $\Sigma\sigma_m = 1.84$



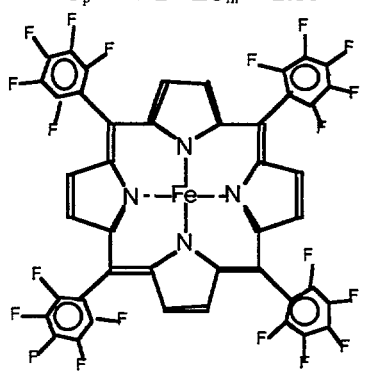
Iron F_{28}-Dodecaphenylporphyrin
$FeF_{28}DPP$
$\Sigma\sigma_p = 1.72$ $\Sigma\sigma_m = 2.16$



Iron F_{36}-Dodecaphenylporphyrin
$FeF_{36}DPP$
$\Sigma\sigma_p = 2.84$ $\Sigma\sigma_m = 2.32$



Iron F_{60}-Dodecaphenylporphyrin
$FeF_{60}DPP$
$\Sigma\sigma_p = 4.92$ $\Sigma\sigma_m = 4.08$



Iron F_{20}-Tetraphenylporphyrin
$FeF_{20}TPP$
$\Sigma\sigma_p = 1.64$ $\Sigma\sigma_m = 1.36$

Figure 2. Porphyrins in the Fluorinated Dodecaphenylporphyrin series. Catalysts with F = 0, 20, 28, 36 have been synthesized and tested. Attempts to synthesize the F = 60 catalyst have been unsuccessful to date. The sum of the Hammett substituent constants ($\Sigma\sigma$) is an approximation of the overall electron depletion of the metal center. Values are shown for the sum of both meta ($\Sigma\sigma_m$) and para ($\Sigma\sigma_p$) constants. $FeF_{20}TPP$, a commercial porphyrin, is shown for comparison.

This FeF_xDPPCl catalyst series was evaluated for activity in the oxidation of isopentane by molecular oxygen. For comparison, we also tested the commercial planar catalyst $FeF_{20}TPPCl$. Reactions were carried out in a teflon-lined stainless steel pressure reactor from Berghof America. In a typical reaction, 10 ml of a benzene solution which was 50 μM in catalyst and 2 M in isopentane was sealed into the reactor. The reactor was pressurized to 10 bar (145psi) with O_2 and heated to 100°C while stirring for 15 hours. Products were analyzed by GC. This reaction was very selective for the production of alcohols. A typical product distribution is 89% tertiary alcohol (2-Methyl-2-butanol), 9% secondary alcohol (3-Methyl-2-butanol), and 2% primary alcohols (mixture of 3-Methyl-1-butanol and 2-Methyl-1-butanol, no attempt was made to separate these primary isomers).

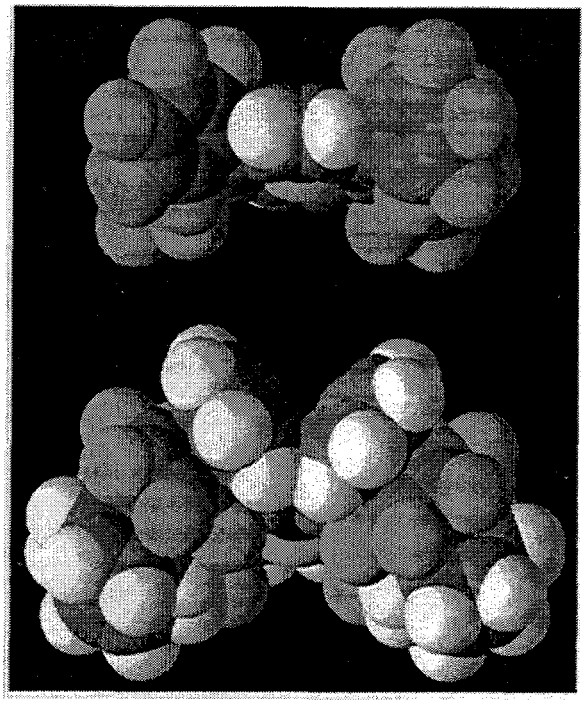


Figure 3. Molecular model showing the shapes of planar $FeF_{20}TPP$ (top) and nonplanar $FeF_{20}DPP$ (bottom).

Figure 4 shows a plot of catalyst activity in turnovers (total mmol alcohol products / mmol catalyst) as a function of the sum of the Hammett substituent constants ($\Sigma\sigma$) for the FeF_xDPPCl catalysts. We observed the predicted trend; that is, catalytic activity increased with the overall electron depletion of the metal center for the FeF_xDPPCl series. However, the overall activity of the FeF_xDPPCl catalysts was much lower than that of the planar catalyst, $FeF_{20}TPPCl$, despite the built-in cavity of the FeF_xDPPCl catalysts. Under the reaction conditions employed in Figure 4, $FeF_{20}TPPCl$ gave 300 catalyst turnovers, which is three times more active than even the most active of the FeF_xDPPCl series.

We observed that the porphyrins tested as oxidation catalysts degraded after several hours, with all catalyst being gone by the end of a 15 hour reaction. Catalyst degradation occurred in this relatively short time period even if a large amount of catalyst was used initially (1mM reaction). Such rapid catalyst deactivation was in conflict with literature reports which indicated that metalloporphyrin catalysts in similar reactions were stable for much longer times.[4-6] Our catalysts were stable at the temperatures and pressures used in catalyst testing. Catalyst degradation was only observed in the presence of a reactive alkane substrate. This indicated that some species formed in the course of the oxidation reaction was responsible for the catalyst degradation.

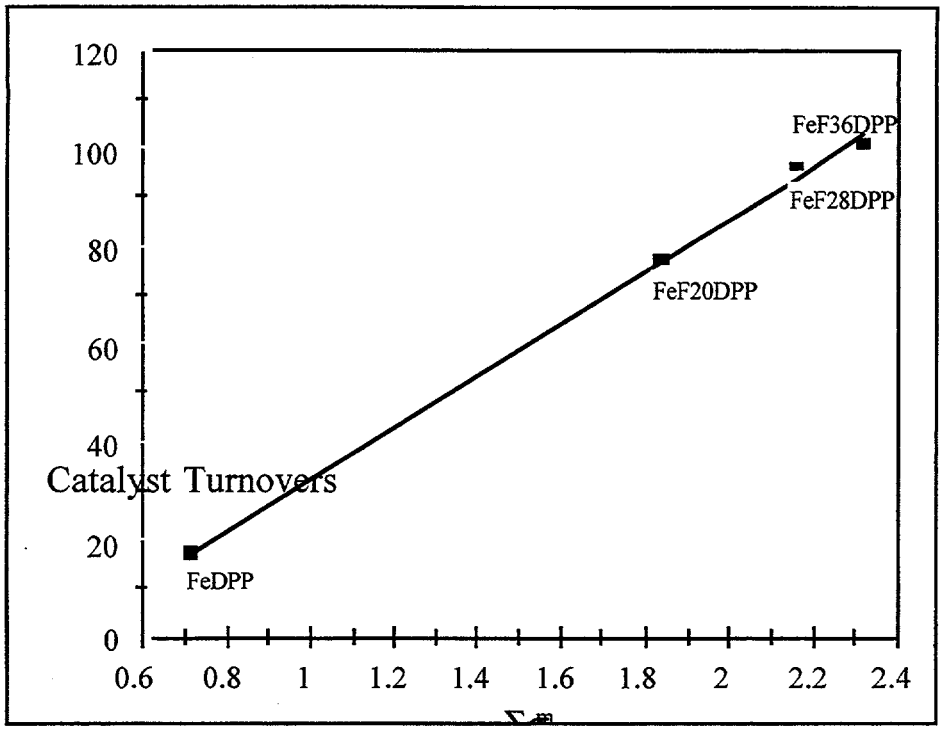


Figure 4. Graph showing the relationship between catalyst turnovers and the sum of the Hammett substituent constants ($\Sigma\sigma_m$) for the FeF_xDPPCl catalyst series. (A similar graph is obtained if $\Sigma\sigma_p$ values are used).

The importance of adding electron withdrawing substituents to alter the redox potential of the metal center was validated by the observed trend of increasing activity with increased degree of fluorination for this structurally homologous series. However, the short life of our catalysts prevented us from making adequate comparisons for our designed catalysts. Although the amount of alcohol produced by $FeF_{20}DPPCl$ was substantially less than the amount produced by $FeF_{20}TPPCl$ under identical experimental conditions, thus yielding a lower value for calculated turnovers, we did not know if this was an indication that the DPP catalyst was less active, less stable, or a combination of both.

Activity Comparison: Sandia vs. Sun Co. Catalysts

Our attempts to measure and compare the activity of Sandia-developed porphyrins as alkane oxidation catalysts were hampered by rapid catalyst decomposition and low apparent activities. Furthermore, such low activities were inconsistent with results reported by other research groups, including scientists at Sun Co.[4-6] At the invitation of Drs. James Lyons and Paul Ellis, Margaret Showalter traveled to the Sun Co. to test some of the Sandia catalysts in the Sun reactors. In this collaborative effort, two different Sandia porphyrins ($FeF_{20}DPPOH$ and

$FeF_{28}DPPCl$) and one Sun porphyrin ($FeF_{20}TPP\beta Cl_8OH$) were tested side-by-side using a catalyst screening experiment developed at Sun for isobutane conversion.

There are three major differences in the Sun catalyst screening procedure and the procedure used previously at Sandia. First, catalyst testing at Sandia had been performed in teflon-lined stainless steel reactors, while the reaction vessel employed at Sun was a glass aerosol tube. Second the scientists at Sun had found that when the axial ligand coordinated to the metalloporphyrin is OH, the reaction is usually easier to initiate than when the ligand is Cl. Thus, Sun preferred to screen potential catalysts as the OH form; however the porphyrins previously tested at Sandia had Cl as the axial ligand. Before traveling to Sun, one of the Sandia catalysts to be tested was converted from the Cl-porphyrin to the OH-porphyrin. Finally, isopentane was the substrate used for screening at Sandia, since this alkane is a liquid and is thus simple to handle in the laboratory. However, the Sun researchers typically screened oxidation catalysts with isobutane as the substrate.

Table 1 summarizes the experiments performed in the joint effort with the Sun Co. researchers. The Sun catalyst, $FeF_{20}TPP\beta Cl_8OH$, which they had previously determined to be very active and robust, performed as expected. Oxygen uptake continued throughout the course of the reaction and no noticeable change in the deepness of color occurred. The first Sandia catalyst, $FeF_{20}DPPOH$, performed well initially, taking up O_2 at a rate comparable to Sun's $FeF_{20}TPP\beta Cl_8OH$ catalyst. However, after a couple of hours, the $FeF_{20}DPPOH$ solutions were noticeably lightened and oxygen consumption slowed. Eventually the solutions lightened to pale reddish-orange and O_2 uptake stopped. This lightening happened more quickly in the 80°C reaction. UV/Visible spectroscopy on the reacted $FeF_{20}DPPOH$ samples indicated that there was no porphyrin left in these pale solutions. Thus, the turnovers achieved by this Sandia catalyst were lower because this porphyrin did not persist in the solution for the entire 6 hour run.

Table 1. Summary of catalytic reactions performed at Sun Co.

Catalyst ID	mmol catalyst	T (°C)	O_2 uptake (mmol)	Turnovers*	Visual observations
$FeF_{20}TPP\beta Cl_8OH$ (Sun catalyst)	0.013	60	25.4	1950	deep brown, constant color
$FeF_{20}DPPOH$ (Sandia catalyst)	0.012	60	13.3	1100	initially dark red, lighter at 2.5 hr, continued lightening to reddish-orange
$FeF_{20}DPPOH$ (Sandia catalyst)	0.017	80	14.5	850	initially dark red, lighter at 1hr, continued lightening to reddish-orange
$FeF_{28}DPPCl$ (Sandia catalyst)	0.013	80	0	0	no reaction, remained dark brown throughout

Reaction solutions contained catalyst and 7g isobutane in 25ml benzene. Solutions were heated while stirring for 6 hours under 100 psi of O_2 in a glass reactor.
*Defined as mmol O_2 consumed /mmol catalyst.

Figure 5 shows O_2 uptake with time for the 60°C reactions, which gives a graphical indication of relative reactivity. Note that initially, Sandia's $FeF_{20}DPPOH$ catalyst consumed oxygen at a rate comparable to Sun's $FeF_{20}TPP\beta Cl_8OH$ catalyst, but O_2 usage by the Sandia catalyst leveled off as the catalyst decomposed. Although the Sandia catalyst was not as stable as desired, the measured catalyst activity was much higher in these experiments than had been determined previously at Sandia using the Cl-porphyrin and isopentane as the substrate.

GC was used to analyze the liquid products formed in these reactions. The only products formed in significant quantities were t-butyl alcohol (the desired product) and acetone, which results from cleavage of the isobutane substrate. The ratio of t-butyl alcohol to acetone is 9:1, thus the selectivity for the desired product is excellent. Approximately 90% of the measured oxygen uptake can be accounted for by these two products.

The second Sandia catalyst, $FeF_{28}DPPCl$, was unreactive, even though the higher temperature of 80°C was used for this compound. This lack of reactivity is consistent with previous observations at Sun that iron porphyrin chlorides are often difficult to initiate. Catalyst testing to date at Sandia had been done with Cl porphyrins, and this warranted change. However, the problem we had had at Sandia was not that the porphyrin did not react at all, but rather that once the reaction was initiated, the porphyrin was short-lived. We had also found that temperatures of 100°C were required. This higher temperature is high enough to cause the relatively unreactive Cl to react, but catalyst decomposition is also accelerated by this higher temperature.

In summary, the initial activity of Sandia's $FeF_{20}DPPOH$ catalyst was comparable to that of $FeF_{20}TPP\beta Cl_8OH$, one of Sun's best catalysts; however the Sandia material was not as robust. The measured activity of $FeF_{20}DPPOH$ was significantly higher as tested at Sun than in previous experiments at Sandia with $FeF_{20}DPPCl$. The second Sandia catalyst, $FeF_{28}DPPCl$, was completely unreactive under the mild conditions used. In the future, axial Cl should be avoided to facilitate easier catalyst screening; conversion to the hydroxide complex should be used to promote catalysis.

After the visit to Sun, we constructed a glass tube reactor in our laboratory at Sandia which is essentially identical to those used at Sun. The glass-tube reactors utilized at Sun provide a quick, easy, reliable method for screening oxidation catalysts, and have the added advantage of allowing visual observation of the reaction in progress. We also added an additional pressure gauge to the teflon lined steel reactors, so that we could more accurately monitor and control the pressure in those reactors.

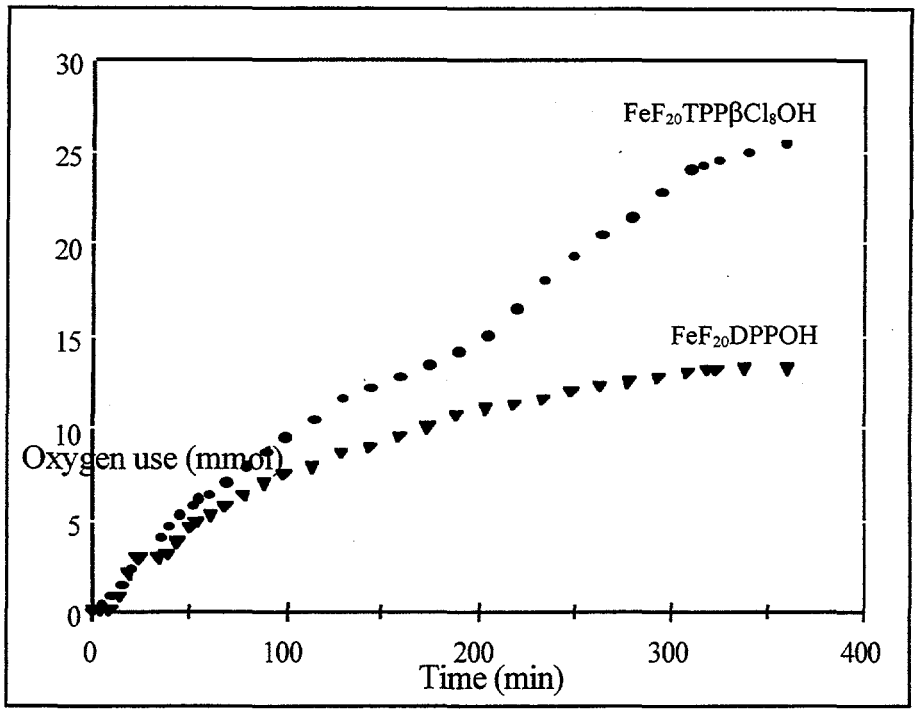


Figure 5. Plot of oxygen usage over time for Sun's $FeF_{20}TPP\beta Cl_8OH$ catalyst (circles) and Sandia's $FeF_{20}DPPOH$ catalyst (triangles).

In an attempt to apply some of the insights gleaned from the collaborative work with Sun, we passed commercial $FeF_{20}TPPCl$ through a column of activated alumina to exchange the axial Cl ligand. (The material obtained from the column appeared to be a mixture of hydroxide and μ-oxo dimer. No attempt was made to separate or purify this mixture. The designation $FeF_{20}TPPOH$ actually refers to this mixture.) We then used this treated porphyrin to catalyze the oxidation of isopentane. However, we found that even with the non-Cl porphyrin, a temperature of 100°C was needed for the reaction to proceed, and the catalyst was consumed quickly at this temperature. When isobutane was used as the substrate, the reaction proceeded at 60-80°C, catalyst decomposition was minimal, and turnovers comparable to those obtained at Sun resulted. Thus it appears that the choice of alkane substrate is as important as the axial ligand of the catalyst in obtaining results consistent with those published by Sun. Also, there does not appear to be any inherent problem with the teflon reactors. We can employ lower reaction temperatures and get excellent catalytic turnovers with minimal catalyst degradation in these reactors when isobutane is used as the substrate and the axial ligand of the porphyrin is not Cl.

Using the improved reaction conditions developed by the Sun scientists, we returned to the problem of comparing the activity of $FeF_{20}DPPOH$ (Sandia-designed catalyst with pocket)

and $FeF_{20}TPPOH$ (commercial catalyst with no pocket). Figure 6 shows oxygen uptake plots for

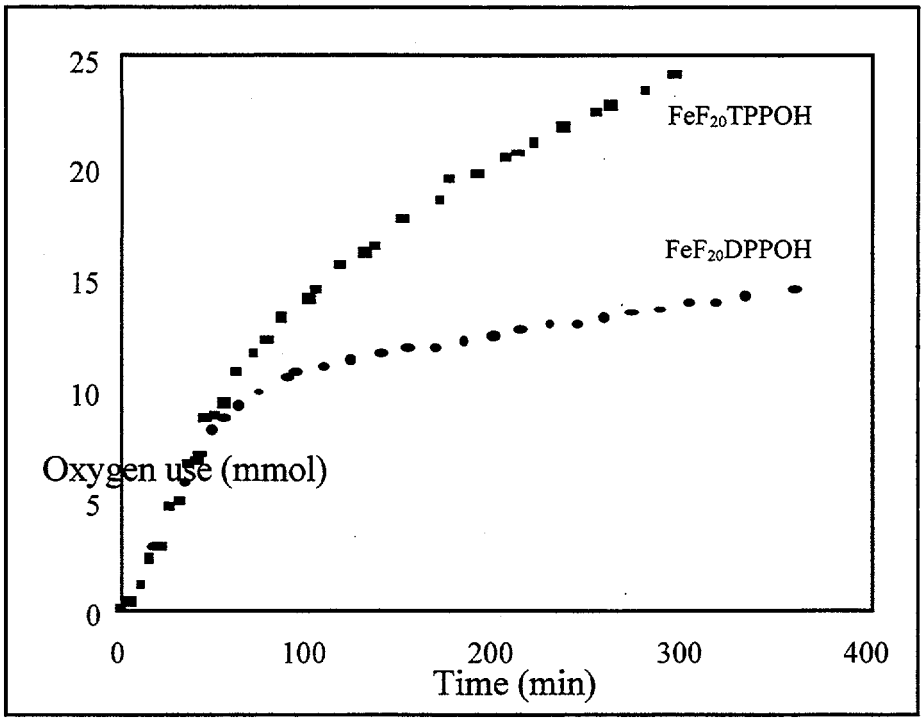


Figure 6. Plot of oxygen usage over time for Sandia's $FeF_{20}DPPOH$ catalyst (circles) and the commercial catalyst $FeF_{20}TPPOH$ (squares).

these two catalysts in isobutane reactions. Note that the oxygen usage, which correlates with catalyst activity, is almost identical for these materials initially. However, the $FeF_{20}DPPOH$ catalyst starts to degrade and thus use oxygen more slowly after only about 1 hour. $FeF_{20}TPPOH$ is more stable, and thus yields a higher activity over the course of the entire reaction. Table 2 shows a comparison of activity for both $FeF_{20}DPP$ and $FeF_{20}TPP$ under the old (Cl axial ligand and isopentane substrate at 100°C, same conditions employed for data in Figure 4) and new (OH axial ligand and isobutane at 80°C) testing conditions. By employing the new reaction conditions, more activity can be squeezed from each catalyst. The intrinsic activity of these catalysts probably has not changed, but rather these improved activity measurements are the result of better catalyst stability at lower temperature. Lower temperatures can be employed when OH is the axial ligand and isobutane is the substrate. Because the relative stability of the $FeF_{20}DPP$ catalyst is lower, $FeF_{20}TPP$ will still outperform this material in a reaction of more than a few hours duration.

In summary, the initial activity of $FeF_{20}DPP$ was comparable to the activity of $FeF_{20}TPP$; however, the bulky DPP catalyst was less stable so the overall performance of this material lagged behind that of $FeF_{20}TPP$. Any enhancement of the catalyst activity or selectivity by the cavity adjacent to the metal center was unable to be verified when O_2 was used as the oxidant.

Table 2. Comparison of the catalytic activity of $FeF_{20}DPP$ and $FeF_{20}TPP$ using different reaction conditions.

Catalyst	Substrate	Temperature (°C)	Turnovers
$FeF_{20}DPPCl$	isopentane	100	80
$FeF_{20}DPPOH$	isobutane	80	950
$FeF_{20}TPPCl$	isopentane	100	300
$FeF_{20}TPPOH$	isobutane	80	1600

Measuring and Comparing Catalytic Activities

As described in the previous section, we have learned that this chemistry can be very tricky, and apparently minor changes in experimental protocol can have a dramatic effect on catalyst activity measurements. We have seen that the axial ligand and substrate can determine what reaction temperature is required, and can thus affect measured activity because decomposition proceeds more rapidly at higher temperature.

We have also noticed additional complicating factors which must be considered when trying to compare the relative activity of catalysts. We have observed that catalyst turnovers (amount of oxygenated products/amount of catalyst) depend on the initial catalyst concentration, as shown in Figure 7. This phenomenon may indicate that true catalytic rates are not being determined under the experimental conditions employed in this research. In an ideal experiment for measuring catalytic activity, doubling the amount of catalyst should lead to a doubling of the amount of product produced, thus yielding the same turnover number. Because these catalysts do show some decomposition during these reactions, that only complicates the relative comparisons of activity even further.

Furthermore, some of the reactions employing a high catalyst concentration suffered from apparent inhibition. Although some of the experiments with catalyst at 1mM concentrations reacted for the full 6 hours, continually using oxygen, and giving high TON, this chemistry is not always reproducible. Some attempted high concentration reactions did not go at all (no oxygen usage, and no oxygenated products). Some of these high catalyst concentrations began normally, consuming O_2, but stopped abruptly (even though catalyst was still present) shortly into the

reaction, and only small quantities of products were produced. When the catalyst concentration was low (i.e. 100μM or less), inhibition was not a problem. The Sun scientists, who routinely screen catalysts at high concentrations, said that they have not seen inhibition near the beginning of the reaction as we have. They have determined that at very high substrate conversions (>30%) there can be enough alcohol product in solution to bind to the porphyrin and thus inhibit further reaction. We have been unable to identify the source of inhibition in our laboratory.

In short, one must be very careful in making comparisons of relative catalytic activity. It is critical to be very careful when comparing catalysts which have not been tested under identical conditions.

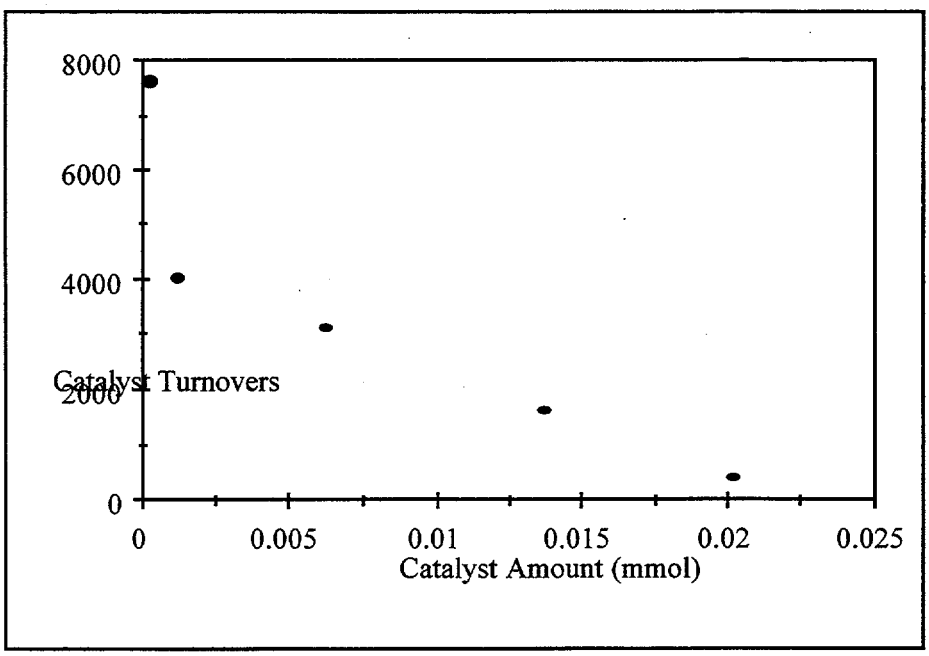


Figure 7. Plot showing the dependence of catalyst turnovers on catalyst concentration. This plot is for $FeF_{20}TPPOH$ catalyzed isobutane conversion at 80°C. A similar trend was observed in $FeF_{20}TPPCl$ catalyzed reactions with isopentane at 100°C.

Mechanistic Implications for Catalyst Design

The rational for studying metalloporphyrins as alkane oxidation catalysts is that they may be able to mimic the high activity and selectivity of some enzymes. Figure 8a shows the key steps of the widely accepted biological mechanism for cytochrome P450 catalyzed oxidation.[1] In their initial reports of homogeneous metalloporphyrin catalyzed alkane oxidation by molecular oxygen without added co-reductant, the Sun researchers proposed a similar "biomimetic" mechanism, shown in Figure 8b.[4] Key to both of these mechanisms is the interaction of the porphyrin catalyst with the dioxygen molecule to form an iron-oxo

intermediate. This iron-oxo intermediate is the species which acts as the oxidant, transferring an oxygen atom to the alkane substrate.

When designing the FeF_xDPP catalysts, we considered design features which would improve catalysis based on the proposed Sun biomimetic mechanism. The pocket created by placing large numbers of substituents around the porphyrin macrocycle was expected to improve catalyst activity by providing a "microreactor" environment for binding substrates, trapping intermediates, and promoting recombination to products. In addition, lining the pocket with fluorine molecules should cause ejection of the polar alcohol molecule, once formed. This ejection of the alcohol would increase activity (by clearing the pocket for next reaction) and improve selectivity (by preventing further oxidation of the alcohol).

According to the proposed biomimetic mechanism, formation of a peroxo dimer, $(FeP)_2O_2$, is necessary to activate the dioxygen molecule. This dimer then splits into an active Fe-O species which reacts with the alkane (RH) to form the alcohol (ROH). Also possible, but undesirable, in this proposed mechanism is the reaction of the intermediate Fe-O species with another catalyst molecule to form a μ-oxo dimer $(FeP)_2O$. The μ-oxo dimer, which does not react with alkane, traps catalyst molecules in an unproductive configuration. Molecular modeling indicated that the steric bulk of the FeF_xDPP catalysts would allow formation of the desired peroxo dimer, while preventing formation of the undesired μ-oxo dimer. Figure 9 shows the energy minimized structures for the μ-oxo and peroxo dimers of $FeF_{20}DPP$. Calculations indicate that formation of the peroxo dimer is energetically favorable, but the μ-oxo dimer is unstable, and thus not likely to form. Therefore, it was thought that these bulky catalysts would be more active than less highly substituted porphyrins such as $FeF_{20}TPP$ which can form a μ-oxo dimer.

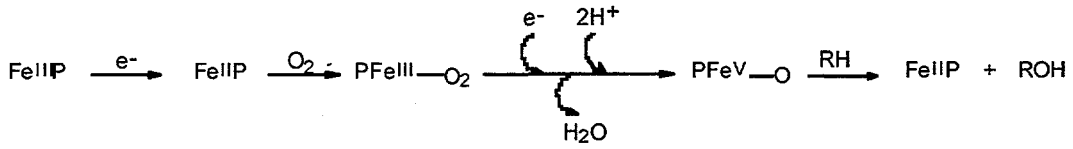
Based on the biomimetic mechanism shown in Figure 8b, the designed features of the DPP catalyst series seemed valid. Now, however, it is generally accepted that these homogeneous reactions proceed via a radical autoxidation mechanism.[6,13,14] Some of the key steps for this mechanism are shown schematically in Figure 8c. Note that in this mechanism, the alkane, not the porphyrin, interacts directly with the dioxygen molecule. The role of the metalloporphyrin in this case is to decompose the alkyl hydroperoxide intermediate. This mechanism does not involve the formation of an iron-oxo intermediate analogous to that of the biological (Fig 8a) and biomimetic (Fig 8b) mechanisms. Evidence for the radical autoxidation mechanism has been published.[6,13,14] Our own catalyst testing results also agree with this published evidence.

In the autoxidation mechanism (Fig. 8c), radical intermediates are abundant. These intermediates are likely the source of catalyst decomposition. Thus adding large numbers of organic substituents, as was done in the FeF_xDPP series, tends to decrease stability instead of increasing it. Stability is diminished because the substituents which give the catalyst its bulk provide more sites for attack by radical intermediates. Bimolecular catalyst destruction by attack of a porphyrin Fe-O intermediate is not a cause for concern here, thus steric bulk which prevents close bifacial approach of porphyrin molecules in unnecessary. What is more important is

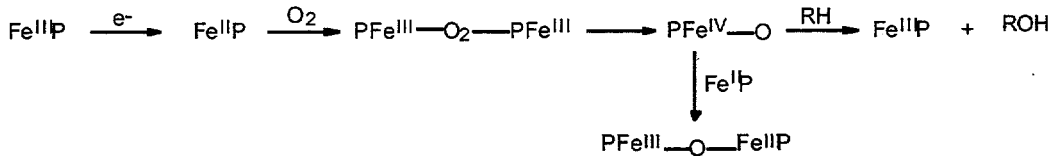
making the porphyrin resistant to radical attack. The Sun Co. researchers have found that perhalogenated porphyrins, such $FeF_{20}TPP\beta Cl_8$, are the most active and most stable catalysts known for this reaction.[6] Halogenation of the porphyrin has two beneficial effects. First, halogenation increases activity by shifting the redox potential of the $Fe^{(III/II)}$ couple to a more positive (thus easier to reduce) value. Second, halogenation improves stability by replacing CH bonds with CX (X = F, Cl, or Br) bonds, which are less susceptible to free radical attack.

Recall that in Figure 2, the fully fluorinated member of the DPP catalyst series, $FeF_{60}DPP$, is shown. Repeated attempts to synthesize this molecule have been unsuccessful. If this molecule is synthesized in the future, it would be interesting to test this porphyrin and compare its performance with a very active and stable catalyst like Sun's $FeF_{20}TPP\beta Cl_8$. In addition to having

a. Biological Mechanism (cP450)



b. Biomimetic Mechanism



c. Radical-chain autoxidation

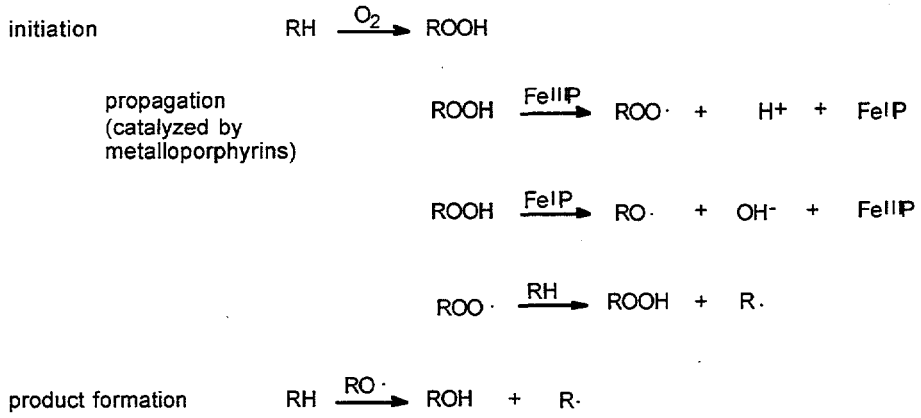


Figure 8. Key mechanistic steps for a) biological oxidation, b) biomimetic oxidation, and c) radical-chain autoxidation. For a more detailed description of each mechanism, see the literature cited in the text.

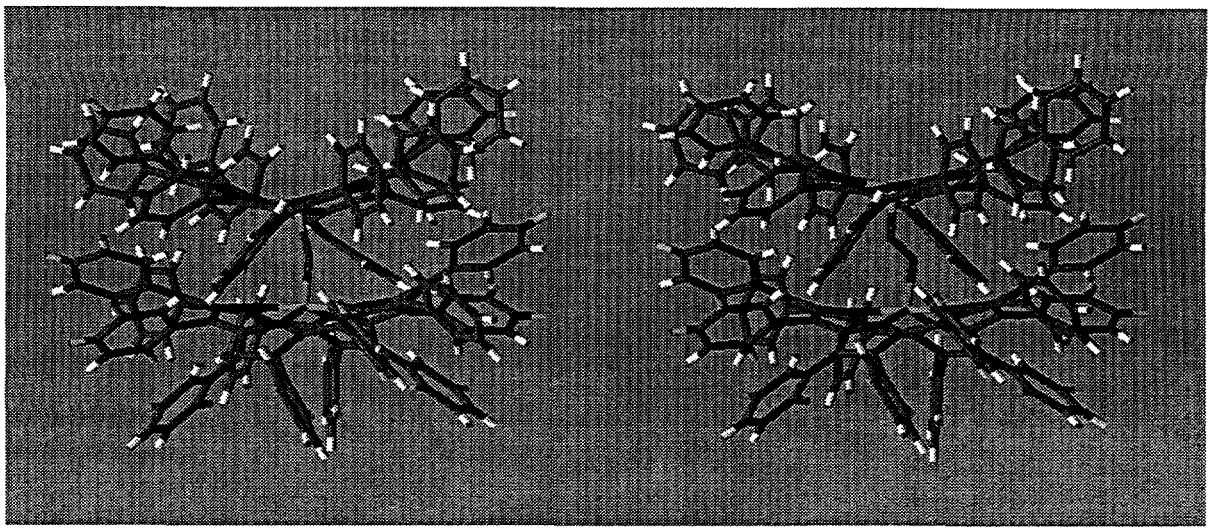


Figure 9. Energy minimized structures for the μ-oxo (left) and peroxo (right) dimers of $FeF_{20}DPP$. Calculations indicate that formation of the μ-oxo dimer is energetically disfavored; however, formation of the peroxo dimer is still possible.

the most electron deficient metal center of the DPP series, this molecule should be more stable because all of the CH bonds (the points most susceptible to radical attack) have been eliminated from this molecule.

One feature which both the biomimetic and radical autoxidation mechanisms shown in Figure 8 have in common, is that the active metal center must cycle between the Fe^{III} -Fe^{II} redox states. Because electron withdrawing groups deplete the electron density around the metal center and make the transition from Fe^{III} to Fe^{II} easier, the presence of electron withdrawing substituents would be advantageous for either mechanism. Thus, even though designed with a biomimetic mechanism in mind, the trend of increased activity with increased fluorination was still observed for the FeF_xDPP catalyst series.

Based on these mechanistic considerations, the performance of the DPP catalyst series was disappointing but not surprising. The DPP catalysts were designed to exert molecular control over the activation and transfer of dioxygen via an iron-oxo intermediate. However, the extensive peripheral substitution which was built into these catalysts for this purpose of molecular control is exactly the property which led to the inferior stability of these materials in a reaction which is now thought to proceed via a radical autoxidation mechanism. If suitable conditions could be found under which a biomimetic mechanism would operate, these catalysts could have real potential.

Supported Metalloporphyrin Catalysts

Our results with the FeF_xDPP series caused us to reconsider the direction of our research. Because the operational mechanism in the homogeneous chemistry seems to be via a radical autoxidation instead of a biomimetic mechanism, designing highly substituted catalysts capable of exerting molecular control of the reaction becomes problematical. Since these highly substituted porphyrins are difficult and expensive to synthesize, and their performance has not justified this expense, we decided to focus on ways to improve the performance (activity and stability) of commercially available porphyrins, which are cheaper and more readily available. Thus, we initiated an investigation of heterogeneous catalysts consisting of readily available commercial metalloporphyrins on common inorganic supports.

Our goal was to determine whether or not such heterogeneous catalysts could catalyze the oxidation of unfunctionalized alkanes by molecular oxygen under mild conditions, as halogenated metalloporphyrins have been shown to do in a homogeneous reaction. Supported porphyrin catalysts potentially offer several advantages over homogeneous ones. First, supporting the catalytic centers may increase their stability under oxidizing conditions (stability was a major problem for our homogeneous catalysts). Second, the catalyst can be more easily separated from the product and recovered for reuse if it is on a solid support. Furthermore, supported catalysts are preferable for the oxidation of gaseous substrates such as methane, because a supported catalyst could be utilized in a gas-phase flow reactor. In addition, some supports, such as pillared clays[15] or zeolites,[16] may be able to influence reaction selectivity by controlling the size or orientation of the substrate as it interacts with the active catalyst center.

Supported metalloporphyrin oxidation catalysts have been prepared and tested by a number of research groups. However, most of these previous studies have utilized oxidants such as iodosobenzene, hydrogen peroxide, organic peroxides, or peracids. There are few literature reports of supported porphyrins being used to catalyze oxidations with dioxygen as the oxidant. These have involved the addition of a chemical co-reductant, or used electrochemical or photochemical activation of dioxygen. An excellent review of these studies has been published.[17] We prepared and tested supported porphyrin catalysts in a reaction of alkane and dioxygen without added sacrificial co-reductant, analogous to the procedure used previously for homogeneous metalloporphyrin oxidation catalysis.[4-6]

$FeF_{20}TPP/ASiO_2$. The first heterogeneous catalyst studied by us was $FeF_{20}TPPCl$ bound to aminopropyl-functionalized silica ($ASiO_2$), denoted $FeF_{20}TPP/ASiO_2$. This material was prepared as described by Battioni, et al,[18] except that ethylene glycol was used as the solvent instead of digylme. In this procedure, the porphyrin is covalently attached to the silica by reaction between a *para*-F of a porphyrin perfluorophenyl substituent and an amino group on the surface of the silica, resulting in a dark brown solid material. We attempted to quantify the amount of Fe incorporated onto the silica by atomic absorption. Hot concentrated HCl was used to extract the Fe for this procedure, but we suspect that extraction was incomplete because much of the brown color remained on the silica even after treatment with the hot HCl. Fe analysis gave

0.18 % Fe (w/w), which corresponds to 3.4 % iron porphyrin on $ASiO_2$. Since this value is lower than the value of 9.7% porphyrin on silica obtained in the literature preparation, and we suspect that recovery of iron in our sample may have been incomplete, we assumed that the coverage of the sample prepared by us is similar to that obtained in the literature preparation, and thus used a value of 9.7 % porphyrin by weight for calculation of catalyst turnovers in this paper.

This supported catalyst was chosen for study because the starting porphyrin has been extensively studied by us and others as a homogeneous catalyst.[2,4-6] Battioni, et al. also tested this material as a heterogeneous catalyst with iodosobenzene as the oxidant.[18] We evaluated the activity of this heterogeneous catalyst for the oxidation of isobutane by dioxygen. Results are summarized in Table 3. The $FeF_{20}TPP/ASiO_2$ catalyst was not active for this reaction at the lower temperatures (60-80°C) under which the homogeneous $FeF_{20}TPP$ catalyzed reaction proceeds; however, if the temperature is increased to 100°C, this catalyst does show some activity. For a reaction of 20 mg of catalyst, 2% of the substrate is converted, corresponding to 700 catalyst turnovers. The detected products for this reaction were t-butyl hydroperoxide (44%), t-butyl alcohol (39%), and acetone (17%). It is believed that acetone results from the cleavage of the isobutane molecule into a C3 and a C1 fragment.[6] The C1 fragment was not detected in the liquid phase, and is therefore likely gaseous, perhaps CO.

Unfortunately, catalytic reactivity was accompanied by catalyst decomposition. At the end of a typical 6 hour reaction, the initially dark brown solid has lightened to a pale tan, and the benzene solution has turned to a golden yellow. UV-visible absorption spectroscopy analysis of the colored solution showed no distinct absorbance bands, especially not any bands characteristic of an intact porphyrin macrocycle. In a blank experiment in which a slurry of catalyst in benzene was heated to reaction temperature under O_2, with no substrate present, the catalyst retained its brown color, and the solution remained colorless. Thus, the decomposition is not simply due to the heat and oxygen required for reaction. Decomposition of the catalyst only occurred when a reactive substrate, in this case isobutane, was present.

A similar observation was made when we tested the parent porphyrin, $FeF_{20}TPP$, as a homogeneous catalyst. This porphyrin was stable when heated to reaction temperature under O_2 in the absence of substrate. However, when a reactive substrate was introduced, alkane oxidation occurred, accompanied by catalyst degradation. These results suggest that the goal of improving catalyst stability by attaching it to a support has not been achieved by this experiment, since the supported $FeF_{20}TPP$ seems just as susceptible as the unsupported porphyrin to oxidative degradation. Furthermore, catalyst decomposition can be minimized in the homogeneous reaction by employing a lower reaction temperature.

A puzzling aspect of this chemistry is that utilizing a larger amount of the $FeF_{20}TPP/ASiO_2$ supported catalyst seems to cause inhibition of the reaction. When 20 mg of catalyst is utilized for isobutane conversion, oxygenated reaction products are detected, although the amounts are small (2% isobutane conversion in a 6 hour reaction). Our expectation was that

using 100 mg of catalyst in the same reactor would convert even more of the substrate to products. Instead, when 100 mg of catalyst is used, no reaction products at all are detected.

We have observed a similar inhibitory phenomenon with the parent homogeneous catalyst, $FeF_{20}TPP$, for reactions with higher concentrations of catalyst (i.e. 1 mM). Although some homogeneous experiments with $FeF_{20}TPP$ catalyst at 1mM reacted for the full six hours (as indicated by continuous consumption of oxygen, and a corresponding amount of oxygenated products), other reactions were either completely inactive or were active initially, but quickly died (even though catalyst was still present). For the heterogeneous $FeF_{20}TPP/ASiO_2$ catalyst, no activity was seen for any of ten reactions performed with 100 mg of catalyst. We have not yet performed a series of reactions with catalyst amounts between 20 and 100 mg to determine what minimum loading is required to cause inhibition of the reaction. Further study is needed to determine why this inhibition occurs, and how to prevent it.

$MTNMePyP/SiO_2$. The second type of supported catalysts in this study, $MTNMePyP/SiO_2$, were prepared by adsorption of iron or manganese tetra(N-methylpyridyl)porphyrin (MTNMePyP) on silica. MTNMePyP, where M = Mn or Fe, was adsorbed onto silica from a methanol solution using a procedure similar to that described in the literature.[19] For this preparation, 0.05g of porphyrin was dissolved in 10 ml of methanol. Silica (0.5g) was added to this solution and the slurry was stirred for one hour. The brown solid was collected by filtration, rinsed with methylene chloride, and dried in air. The amount of porphyrin on the support was determined by elemental analysis (Fe). Dissolving the porphyrin off the support with 2M HCl and quantitating the amount of recovered macrocycle by UV/Vis spectroscopy using a calibration curve prepared from known standards gave the same result. For the Mn sample, the catalyst was 4.3% (w/w) porphyrin on silica. The iron catalyst was 4.0% (w/w). Although these amounts are lower than that reported in the literature (10%), it should be noted that we used different silica and had relatively less porphyrin in the absorption solution.

Table 3. Summary of catalytic activity and product distribution for supported metalloporphyrin catalyzed isobutane oxidation.

				Products		
Catalyst	**Amount catalyst (mg)**	**TO**	**% conversion of substrate**	**% t-butyl hydroperoxide acetone**	**% t-butyl alcohol**	**%**
$FeF_{20}TPP/ASiO_2$	20	700	2	44	39	17
$FeF_{20}TPP/ASiO_2$	100	0	0	0	0	0
$FeTNMePyP/SiO_2$	20	0	0	0	0	0
$FeTNMePyP/SiO_2$	300	100	1	46	39	15

$FeTNMePyP/SiO_2$*	300	300	3	7	22	71
$MnTNMePyP/SiO_2$	20	2800	2	41	47	12
$MnTNMePyP/SiO_2$	100	1000	4	19	54	27

Reactor contained catalyst and 5g isobutane in 25ml benzene. Reactor was heated to 100°C while stirring for 6 hours under 100psi of O_2. Each experiment was repeated at least three times. Representative data are shown.
TO = catalyst turnovers = total mmol products / mmol porphyrin.
*Reaction time is approximately 20 hours for this run only. This experiment was not replicated.

These cationic porphyrins have previously been adsorbed onto inorganic supports and evaluated as hydrocarbon oxidation catalysts with the oxidants iodosobenzene,[2,15,19-21] and hydrogen peroxide or an organic peroxide.[22,23] Similar catalysts have also been utilized as oxidation catalysts with dioxygen and a chemical co-reductant[24,25] or electrochemical reduction.[26] We performed catalytic testing of these supported catalysts with dioxygen as the oxidant and no added co-reductant. We have not tested the parent MTNMePyP porphyrins in an analogous homogeneous experiment because the cationic substituent groups render these molecules insoluble in the benzene solvent used for these reactions.

Both the iron and manganese tetra pyridinium-substituted supported porphyrins were evaluated for activity in the oxidation of isobutane by dioxygen. A summary of results can be found in Table 3. For the catalyst $FeTNMePyP/SiO_2$, only small amounts of oxygenated products were detected, and the overall activity of this catalyst was relatively low – 1% substrate conversion and 100 turnovers for 300 mg of catalyst in a typical 6 hour reaction. However, when the catalyst $MnTNMePyP/SiO_2$ was prepared and tested under similar conditions to those used previously for Fe, this Mn catalyst was found to be much more active. A typical reaction of 20 mg of the Mn catalyst gives 2% substrate conversion and 2800 turnovers. This is in contrast to the relative activity of Fe and Mn halogenated tetraphenyl porphyrins for homogeneous oxidation reported in the literature.[6] Although it would be interesting to investigate this difference in relative metal reactivity further, it should be pointed out that these are different porphyrins (the substituents on the basic porphyrin macrocycle are different), and the supported catalysts require a higher reaction temperature, so it might not be expected that the metals would have the same relative reactivity.

The $MTNMePyP/SiO_2$ catalysts appear to be more stable under the employed reaction conditions than the previously described $FeF_{20}TPP/ASiO_2$ catalyst. These dark brown solid catalysts retained all or most of their color throughout a typical 6 hour reaction. In some experiments, a slight lightening of the catalyst was observed, but it was not dramatic like the $FeF_{20}TPP/ASiO_2$ catalyst, which lost almost all of its color.

Furthermore, the $MTNMePyP/SiO_2$ catalysts do not seem to inhibit the reaction at higher catalyst concentrations, as was observed in the case of $FeF_{20}TPP/ASiO_2$. $MnTNMePyP/SiO_2$ reacted readily at both 20 and 100 mg levels, although the catalyst turnovers

were not the same for both (see Table 3). Because FeTNMePyP/SiO_2 was not very active, 300 mg of catalyst was required to produce quantifiable amounts of oxygenated products.

Product Distribution. An interesting observation of the current research is that the product distribution for these heterogeneously catalyzed isobutane oxidations differs from that resulting from the homogeneously catalyzed reaction. In the homogenous $FeF_{20}TPP$ catalyzed reaction of isobutane with dioxygen, the major product is t-butyl alcohol (ca 90%). The only other liquid product produced in significant quantities is acetone (ca 10%). However, when the heterogeneous catalysts MTNMePyP/SiO_2 (M = Mn, Fe) or $FeF_{20}TPP/ASiO_2$ are employed in the oxidation of isobutane under similar reaction conditions (reaction conditions are not identical as a higher temperature is required for the heterogeneous reactions), a typical product distribution is 44% t-butyl hydroperoxide, 39% t-butyl alcohol, and 17% acetone. The major product in this case, t-butyl hydroperoxide, is not detected at all in the homogeneous reaction.

It has been suggested that the reason $FeF_{20}TPP$ and similar halogenated porphyrins readily catalyze the homogeneous oxidation of isobutane is that they are extremely active hydroperoxide decomposition catalysts.[6,13,14] Thus, any hydroperoxide formed during the course of the reaction is immediately decomposed. If the heterogeneously catalyzed reactions proceeded by the same mechanism, you would not expect to detect any hydroperoxide; however, this is the major product for these reactions.

Although the differing product distribution could suggest a different mechanism, there are other plausible explanations. One possible explanation is mass transfer effects due to inadequate catalyst dispersion. In the case of homogeneous catalyst testing, the catalyst is obviously well dispersed. Thus, at any point in the solution where a ROOH molecule forms, there is a catalyst molecule in close proximity which can decompose this ROOH molecule. However, in the case of the supported porphyrin catalysts, although magnetic stirring is used to suspend the catalyst particles in the liquid solution, there may be areas of solution not in contact with a catalyst particle. ROOH molecules formed in these pockets of solution which are not in contact with catalyst particles may thus persist in solution and be detected as final products. In fact, when the amount of MnTNMePyP/SiO_2 was increased from 20 to 100 mg, the percentage of t-butyl hydroperoxide in the product mix decreased from 41% to 19% (see Table 3). This observation is consistent with mass transfer limited ROOH decomposition, because a larger amount of catalyst in the same volume of solution improves the chance of contact between catalyst and ROOH. Furthermore, in one experiment with FeTNMePyP/SiO_2, the reactor was accidentally left on overnight, and the resulting product distribution in this case was only 7% t-butyl hydroperoxide, 22% t-butyl alcohol, and 71% acetone (see Table 3). Thus, given enough time for mass transfer, the amount of hydroperoxide detected does decrease significantly.

Although mass transfer limitation is a plausible explanation for the observance of t-butyl hydroperoxide as a final product in reactions with the heterogeneous catalysts, there may also be other explanations. For example, the steric or electronic environment of the porphyrin molecule may be changed due to its adsorption on the support, and such a change may affect the ability of

the porphyrin to interact with and decompose ROOH. Further experimentation would be required to determine definitively the operative mechanism, and the reason for the differing product distribution.

These initial results are promising because they indicate that supported metalloporphyrin catalysts do have potential as oxidation catalysts when dioxygen is utilized as the oxidant. One of the goals of supporting metalloporphyrins was to provide a more stable catalyst. For the $FeF_{20}TPP/ASiO_2$ catalyst tested in this research, the goal of improved stability was not achieved. However, the very active $MnTNMePyP/SiO_2$ catalyst showed good stability.

The product distribution for these heterogeneous reactions differed from the previously studied homogeneous reactions in that t-butyl hydroperoxide, which is not detected at all in the homogeneous reactions, is detected in significant quantities in the heterogeneous reactions. Possibile explanations for this differing product distribution include a different mechanism, a mass-transfer limit on ROOH decomposition due to inadequate catalyst dispersion, or a change in the nature of the interaction of ROOH with the catalytic center when the catalyst is applied to a support.

Conclusions

Fluorinated Iron Dodecaphenylporphyrin Catalysts

We developed and tested a series of fluorinated dodecaphenyl substituted iron porphyrin catalysts (FeF_xDPP) which have three desired structural features: 1) a rigid substrate binding cavity adjacent to the metal center, 2) a systematic variation of the redox potential of the Fe center caused by increasing numbers of fluorine substituents, and 3) steric bulk to prevent close bifacial approach of independent catalyst molecules. This catalyst series is unique because the bulky phenyl substituents create a nonplanar distortion leading to the formation of a cavity. In addition, these catalysts maintain this same shape across the series, even with the addition of fluorine substituents. In most other investigations of the effect of electron withdrawing substituents on metalloporphyrin catalyst activity, the addition of electron withdrawing groups to the porphyrin macrocycle has been accompanied by a change in the degree of porphyrin nonplanarity. Our unique catalyst series allowed us to study the effect of increased electron depletion of the metal center isolated from significant structural variation.

Catalyst testing verified the predicted trend -- catalytic activity increased with the overall electron depletion of the metal center for this structurally homologous series. However, the overall performance of the FeF_xDPP series was compromised by a lack of stability. A direct comparison of $FeF_{20}DPPOH$ and $FeF_{20}TPPOH$ shows that the initial activity of these materials is almost identical; however, $FeF_{20}TPPOH$ out-performs $FeF_{20}DPPOH$ over the course of the reaction because this less bulky catalyst is more stable and thus continues reacting for a longer

period of time. Although the poor stability of our DPP catalysts is disappointing, it is not unexpected given that this chemistry is now believed to proceed via an autoxidation type of free-radical chain mechanism instead of via the biomimetic route for which these catalysts were designed.

Supported Metalloporphyrin Catalysts

Our initial results with supported metalloporphyrin catalysts are promising because they indicate that these materials do have potential as oxidation catalysts. These results are also significant because there are few examples in the literature of supported metalloporphyrin oxidation catalysts which utilize dioxygen as the oxidant, and those which are reported utilize either a sacrificial co-reductant or photochemical or electrochemical activation of the dioxygen. Herein, we report of the utilization of a heterogeneous porphyrin catalyst for hydrocarbon oxidation by dioxygen without added co-reductant.

One of the goals of supporting metalloporphyrins was to provide a more stable catalyst. Unfortunately, for the $FeF_{20}TPP/ASiO_2$ catalyst tested in this research, the goal of improved stability was not achieved. It would be interesting to prepare and test similar heterogeneous catalysts from some of the perhalogenated porphyrins (i.e. Sun's $FeF_{20}TPP\beta Cl_8$) which have been shown to be more stable in the homogeneous reaction than $FeF_{20}TPP$. If the perhalogenated catalysts which are very active and stable in the homogeneous reaction are able to exhibit similar activity and stability when supported, these already excellent catalysts would have the added benefit of ease of recovery for reuse.

The $MTNMePyP/SiO_2$ catalysts showed good stability. Activity for these catalysts varied greatly depending on the metal center. The Mn catalyst was very active, but the Fe catalyst exhibited a very low activity. Since these porphyrins show potential for catalysis with oxygen as the oxidant, further work is warranted. Further work should include experiments to optimize catalyst activity, and experimentation with other support materials. It may be possible, by judicious selection of support, to develop a catalyst in which the activity is provided by the metalloporphyrin, and the selectivity is enhanced by the steric constraints of the support.

The product distribution for the heterogeneous metalloporphyrin catalysts differed from the previously studied homogeneous catalysts in that tertiary butyl hydroperoxide, which is not detected at all in the homogeneous reactions, is detected in significant quantities in the heterogeneous reactions. One plausible explanation is that poorer catalyst dispersion in the heterogeneous reaction allows some of the intermediate hydroperoxide to persist in the reaction solution. Another possibility is that the reaction is not mass-transfer limited, but rather, the actual nature of the catalyst center is changed by its application to a support, thus rendering the interaction of the metal center and ROOH less effective. More work is needed to determine

which, if any, of these possibilities are valid. Further investigation should lead to a better understanding of the chemistry and thus provide insights on improving catalyst performance.

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