Supported metalloporphyrins catalyze the oxidation of isobutane by dioxygen

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Abstract

Metalloporphyrins supported on silica were tested as catalysts for the oxidation of isobutane by dioxygen. Iron *meso*-tetra(pentafluorophenyl)porphyrin ($FeF_{20}TPP$) supported on aminopropyl-functionalized silica was catalytically active (700 turnovers), but degraded quickly. Catalysts prepared by the adsorption of iron or manganese *meso*-tetra(4-*N*-methyl-pyridyl)porphyrin (MTNMePyP, where M = Mn or Fe) on silica were more stable under oxidizing conditions. The Mn catalyst was very active (2800 turnovers), but the activity of the Fe catalyst was much lower (100 turnovers).

Keywords: Catalyst; Oxidation; Porphyrin; Isobutane; Oxygen

1. Introduction

Enzymes such as cytochrome P_{450} are known to catalyze difficult reactions including the partial oxidation of unfunctionalized alkanes to alcohols [1]. Metalloporphyrins have been extensively studied as biomimetic oxidation catalysts, since metalloporphyrins play a key role in the chemistry of some enzymes [2]. Halogenated metalloporphyrins have been reported to catalyze the oxidation of unfunctionalized alkanes to alcohols under mild conditions using molecular oxygen as the oxidant without the need for added co-reductant [3–5]. (Recently, it has been shown that electron deficient perfluoroalkyl porphyrin complexes are active catalysts

for the reaction of isobutane with oxygen and for the decomposition of alkyl hydroperoxides [6]). This work has been replicated in our laboratory, where we have also attempted to design better homogeneous catalysts for this process. Our design attempts focused on incorporating a substrate-binding cavity into the halogenated metalloporphyrin structure. However, these catalysts, although reasonably active, suffered from a lack of stability [7,8].

We have recently initiated an investigation of heterogeneous catalysts consisting of metalloporphyrins on 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

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potentially offer several advantages over homogeneous ones. First, supporting the catalytic centers may increase their stability under oxidizing conditions. Second, the catalyst can be more easily separated from the product and recovered for reuse if it is on a solid support. Furthermore, some supports, such as pillared clays or zeolites, may be able to influence reaction selectivity by controlling the size or orientation of the substrate which can interact with the active catalyst center [9,10].

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 summary of these studies has been published [2]. We now report testing of supported porphyrin catalysts in a reaction of alkane and dioxygen without added sacrificial co-reductant, analogous to the procedure developed at Sun Oil Co. for homogeneous metalloporphyrin oxidation catalysis [5].

2. Experimental

2.1. Preparation of $FeF_{20}TPP / ASiO_2$ catalyst

$FeF_{20}TPP$ (purchased from Midcentury) was attached to the surface of 3-aminopropyl functionalized silica, $ASiO_2$ (purchased from Aldrich), as described in the literature [11] except that ethylene glycol was used as the solvent instead of diglyme. 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. Elemental analysis (F, Fe) of this sample was performed by Galbraith.

Results indicate the catalyst is 9.4% (w/w) porphyrin on silica, which was used in calculating the catalyst turnovers.

2.2. Preparation of $MTNMePyP / SiO_2$ catalyst

$MTNMePyP$, where M = Mn or Fe (purchased from Porphyrin Products), was adsorbed onto silica (Fisher type 150A, 35–60 mesh) from a methanol solution using a procedure similar to that described in [12]. For this preparation, 0.05 g of porphyrin was dissolved in 10 ml of methanol. Silica (0.5 g) 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 of the support with 2 M HCl and quantitating the amount of recovered macrocycle by UV/Vis spectroscopy gave the same result. For the Mn sample, the catalyst is 4.3% (w/w) porphyrin on silica. The iron catalyst is 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 adsorption solution.

2.3. Catalytic testing

Alkane oxidation reactions were performed in a 150 ml teflon-lined stainless steel reactor from Berghof America. For a typical reaction, 25 ml of benzene (Fisher certified ACS) was chilled in an ice/H_2O bath and isobutane (Matheson instrument grade) was bubbled into this cold solvent until approximately 5 g of isobutane was dissolved in the benzene. This isobutane/benzene solution and 20 mg of catalyst (typical amount, varied for some reactions) were sealed into the reactor. Agitation was provided by magnetic stirring. The reactor was heated to 100°C and O_2 was introduced to a pressure of 100 psig. Temperature and pressure were maintained for 6 h. Products were analyzed by stan-

dardized GC–MS. The column used was a 30 m × 0.25 mm HP-Wax column. 1-hexanol was used as an internal standard.

3. Results and discussion

3.1. Blank

Two blank reactions were studied so as to dismiss questions of uncatalyzed autoxidation of isobutane to t-butyl hydroperoxide. In one blank reaction reaction, conditions were followed as described above, minus the catalysts. In the other blank reaction, only silica was used, minus the porphyrin catalyst. The reaction temperatures were set to 100°C for a duration of 6 h. Subsequent GC–MS analysis of the solutions indicated that no products were present; the uncatalyzed control studies did not produce any reaction.

3.2. FeF$_{20}$TPP / ASiO$_2$

The first heterogeneous catalyst we studied was FeF$_{20}$TPP (see Fig. 1) bound to aminopropyl modified silica, denoted FeF$_{20}$TPP/ASiO$_2$. This supported catalyst was chosen for study because the starting porphyrin has been extensively studied by us and others as a homogeneous catalyst [2–7]. Battioni et al. also tested this material as a heterogeneous catalyst with iodosobenzene as the oxidant [11]. We evaluated the activity of this heterogeneous catalyst for the oxidation of isobutane by dioxygen. Results are summarized in Table 1. 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 [5,6]; 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
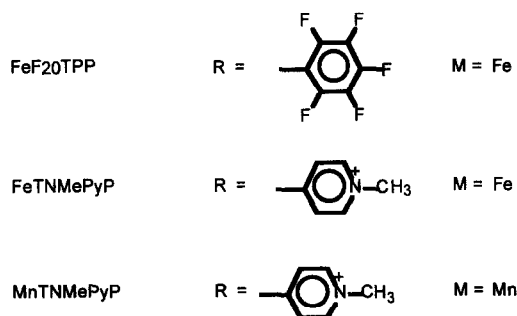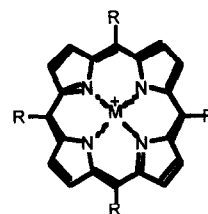
Fig. 1. Porphyrins used for preparing supported catalysts. Counterions (chloride for MP$^+$ and tosylate for N$^+$) are not shown.

(39%), and acetone (17%). It is believed that acetone results from cleavage of the isobutane molecule into a C$_3$ and a C$_1$ fragment [5]. The C$_1$ product was not detected in the liquid phase, and is therefore likely gaseous, perhaps CO.

The catalytic reactivity was accompanied by catalyst decomposition. At the end of a typical 6 h reaction, the initially medium brown solid has lightened to a pale tan, and the benzene solution has turned to a golden yellow. Visible 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 [6,7]. This porphyrin was

Table 1
Summary of catalytic activity and product distribution for supported metalloporphyrin catalyzed isobutane oxidation

Catalyst	Amount of catalyst (mg)	TO [a]	% conversion of substrate	Products (%)		
				t-butyl hydroperoxide	t-butyl alcohol	acetone
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$_2$ [b]	300	300	3	7	22	71
MnTNMePyP/SiO$_2$	20	2800	2	41	47	12
MnTNMePyP/SiO$_2$	100	1000	4	19	54	27

The reactor contained catalyst and approximately 5 g isobutane in 25 ml benzene. The reactor was heated to 100°C while stirring for 6 h under 100 psi of O$_2$. Each experiment was repeated at least three times. Representative data are shown.
[a] TO = catalyst turnovers = total mmol products/mmol porphyrin.
[b] Reaction time is approximately 20 h for this run only. This experiment was not replicated.

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 (perhalogenated porphyrins exhibit improved stability in the homogeneous reaction [5]). 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, the homogeneous reaction can be performed at lower temperatures, thus minimizing catalyst degradation.

An interesting aspect of this chemistry is that utilizing a larger amount of this supported catalyst seems to cause inhibition of the reaction. When 20 mg of FeF$_{20}$TPP/ASiO$_2$ catalyst is utilized for isobutane conversion, oxygenated reaction products are detected, although the amounts are small (2% isobutane conversion in a 6 h reaction). Our expectation was that using 100 mg of catalyst in the same reactor would convert even more of the substrate to products. Instead, if 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 reactions with FeF$_{20}$TPP catalyst at 1 mM reacted for the full six hours (as indicated by continuous usage of oxygen, and a corresponding amount of oxygenated products), other reactions were either completely inactive or were active initially, but quickly deactivated (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.

3.3. MTNMePyP / SiO$_2$

The second type of supported catalysts in this study, MTNMePyP/SiO$_2$, was prepared by adsorption of MTNMePyP (see Fig. 1) on silica. Catalysts were prepared for M = Mn and Fe. These cationic porphyrins have previously been adsorbed onto inorganic supports and evaluated as hydrocarbon oxidation catalysts with the oxidants iodosobenzene [2,9,12–14], and hydrogen peroxide or an organic peroxide [15,16]. These catalysts have also been utilized as oxidation catalysts with dioxygen and a chemical co-reductant [17,18] or electrochemical reduction

[19]. We have 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 1. For the catalyst FeTN-MePyP/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 h 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 [5]. 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 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 h 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$_2$. MnTN-MePyP/SiO$_2$ reacted readily at both 20 and 100 mg levels, although the catalyst turnovers were not the same for both (see Table 1). Because FeTNMePyP/SiO2 was not very active, 300 mg of catalyst was required to produce quantifiable amounts of oxygenated products.

3.4. Product distribution

Another 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 ($\approx$ 90%). The only other liquid product produced in significant quantities is acetone ($\approx$ 10%) [5,6]. 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 [5,6,20,21]. Thus, any hydroperoxide intermediate formed during the course of the reaction is immediately decomposed. If the heterogeneously catalyzed reactions proceed by the same mechanism, one 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 ex-

planation is mass transfer effects due to inadequate catalyst dispersion. In the case of homogeneous catalyst testing, the catalyst is obviously well dispersed. However, in the case of the supported porphyrin catalysts, mass transfer effects may allow ROOH to persist in solution and be detected as a final product. In fact, when the amount of MnTNMePyP/SiO$_2$ was increased from 20 mg to 100 mg, the percentage of t-butyl hydroperoxide in the product mix decreased from 41% to 19% (see Table 1). 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 left to run overnight, and the resulting product distribution in this case was only 7% t-butyl hydroperoxide, 22% t-butyl alcohol, and 71% acetone (see Table 1). Thus, given enough time for mass transfer, the amount of hydroperoxide detected decreased significantly. Another possible explanation is that 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 is required to determine definitively the operative mechanism, and which, if any, of these explanations can account for the differing product distribution.

4. Conclusions

These results indicate that supported metalloporphyrin catalysts 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 the utilization of a heterogeneous porphyrin catalyst for hydrocarbon oxidation by dioxygen without added co-reductant.

Our goal of producing a more stable catalyst by supporting metalloporphyrins was partially achieved. The very active MnTNMePyP/SiO$_2$ catalyst showed good stability, while the FeF$_{20}$TPP/ASiO$_2$ catalyst did not improve in stability with a support. A natural extension of this research would be to support on SiO$_2$ and then test the perhalogenated porphyrins, which homogeneously offer more oxidative stability than FeF$_{20}$TPP [5,6].

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. This differing product distribution may be the result of a different mechanism, mass transfer effects, or a change in the nature of the interaction between the supported catalyst center and the hydroperoxide intermediate. Continued investigation will further increase our understanding of the chemistry and thus provide insights on improving catalyst performance.

Acknowledgements

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