# Oxidation of Alkenes with Hydrogen Peroxide Catalyzed by Iron Porphyrins Immobilized to Imidazole Groups in a Hydrophobic Environment on a Modified Silica Surface

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A biomimetic model of a monooxygenase enzyme was designed and synthesized on a silica surface using a facile procedure, for the purpose of direct functionalization of hydrocarbons. Immobilization and isolation of simple and bulky forms of iron tetraphenylporphyrin was accomplished by coordinative ligation to anchored imidazolyl groups in hydrophobic cavities formed by alkyl chains attached to the surface. The synthesized catalyst was dispersed in an aqueous solution with alkenes. The substrates were catalytically epoxidized by $H_2O_2$ as the oxygen donor in the presence of imidazole. The high catalytic activity for the epoxidation of alkenes is discussed with respect to the characteristics of the novel catalyst structure and of the applied reaction system.

In recent years, much attention has been focused on mimicking monooxygenase enzymes, such as cytochrome P450, which oxidizes lipophilic hydrocarbons with the use of dioxygen and NADPH or a single oxygen donor.[1,2] The direct functionalization of hydrocarbons under mild conditions is an industrially important target and is also of biological interest. Groves et al. first reported that (5,10,15,20-tetraphenylporphinato)iron(III) chloride (**FeTPPCl**) catalyzed oxygen atom transfer from iodosylbenzene (**PhIO**) to alkanes and alkenes.[3] Since that time, numerous synthetic metalloporphyrin catalysts using single oxygen donors have been developed.[4—13] In particular, Traylor et al. have synthesized [5,10,15,20-tetrakis(2,6-dichlorophenyl)porphinato]iron(III) chloride (**FeTDCPPCl**) which shows an extremely high turnover number for alkene epoxidation. They suggest that the substitution of bulky and highly electronegative[4] atoms on the phenyl rings in **FeTPPCl** may be responsible for the prevention of aggregation and the increased stability to oxidative destruction of the porphyrin molecule.

By contrast Mansuy et al. found that metalloporphyrins oxidize alkanes and alkenes in the presence of imidazole and either $H_2O_2$ or alkyl hydroperoxides.[15,16] The epoxidation of alkenes by $H_2O_2$ with **FeTDCPPCl** in the absence of imidazole has also been reported, recently.[17] $H_2O_2$ is a very attractive oxygen donor because it is inexpensive and because the oxidized products may be easily separated from the oxidant residue. These characteristics suggest a potential advantage of such a system for preparative oxidation and have stimulated recent progress of highly active catalytic systems of manganese porphyrins and $H_2O_2$.[18—21]

Another attempt to use porphyrin catalysts for preparative reactions involves the immobilization of them on inorganic supports such as silica, alumina and montmorillorite.[22—24] By attaching the porphyrins to such supports, the catalyst efficiency is enhanced as well as the selectivity when **PhIO** is used as the oxygen donor.

The prosthetic group of native cytochrome P450 is a simple iron protoporphyrin(IX) structure which is bound to a cysteine thiolate group of the protein chain. The active center is buried in a hydrophobic environment within polypeptide chains; it catalyzes the epoxidation of cyclohexene by $\alpha$-cumyl hydroperoxide and the hydroxylation of cyclohexane and adamantane by the same.[25] The purposes of the present work are to 1) build a biomimetic model of the active site which is coordinatively immobilized in a hydrophobic pocket and 2) to model the catalytic oxidation of hydrocarbons at the active site. We describe the procedure for immobilization and isolation of the bulky form of iron porphyrin on a silica surface that yields a hydrophobic reaction site on the porphyrin plane. We also describe the epoxidation of alkenes with catalyst by $H_2O_2$ in the presence of imidazole.

## Experimental

Capillary column gas chromatography was performed on a Shimadzu GC-9A instrument with flame-ionization detector. Visible spectra were measured on a Photal MCPD-110 spectrophotometric system. FT-IR spectra were obtained on a JEOL JIR 3510 instrument. Solid-state $^{29}Si$ CP/MAS NMR spectrum was measured at JEOL Co. Ltd. Elemental analyses were performed on a Yanagimoto MT-5 instrument.

**Materials.** Amorphous silica powder, Aerosil 200 (specific surface area, 200 $m^2 g^{-1}$) was obtained from Nippon Aerosil Co., Ltd., and dried under vacuum at 110 °C overnight before use. All reagents or solvents were purchased commercially and used as supplied except where stated. Toluene and benzene were purified by standard methods and subsequently distilled from $CaH_2$. Bis(pyridine)(phthalocyaninato)iron(II) (**FePcpy$_2$**) was obtained by the recrystallization of phthalocyaninatoiron(II) (**FePc**) in pyridine. **FeTPPCl** was prepared by a previously reported procedure.[26] All alkenes were passed through basic alumina prior to use.

**Preparation of Catalyst.** Aerosil 200 (90 g) was dispersed in toluene to which *N*-[3-(triethoxysilyl)propyl]imidazole (1.15 g) was added. Refluxing overnight and removal of

solvent under vacuum produced the support-anchored silica, **S-1**. Elemental and quantitative FT-IR analyses indicated the supports (3-imidazolylpropylsilyl groups, **IPS**) loading of $4.5\times10^{-2}$ mmol $g^{-1}$ of silica.

**S-1** (61.2 g) was dispersed in pyridine, to which **FePcpy$_2$** (1.81 g) was added under an argon stream. The mixture was refluxed overnight with stirring. The solid collected by filtration was washed with pyridine and then acetone until the filtrate became colorless. Drying at 50 °C under vacuum gave a pale blue solid, **S-2** ($\lambda_{max}$=450, 590 (sh), and 650 nm). The loading level of iron phthalocyanine monopyridine (**FePcpy**) complex on **S-2** was estimated to be $2.9\times10^{-2}$ mmol $g^{-1}$ of silica by elemental analysis.

**S-2** (15.0 g) was dispersed in $CH_2Cl_2$, to which dodecyltriethoxysilane (2.5 g) was added under argon stream. After stirring for 1 h and removing $CH_2Cl_2$ under vacuum, the container was evacuated, sealed, and heated for 24 h at 150—160 °C. The same process was repeated twice. It was then opened, cooled, and washed with acetone and $CH_2Cl_2$ resulting in a pale blue solid, **S-3**. The visible spectrum of **S-3** ($\lambda_{max}$=660 nm), however, exhibited absorptions corresponding to the **FePc** complex rather than to **S-2**, other bisadducts of bases,[27] or $\mu$-oxo dimers.[28] A detailed description of the coordination state of iron could not be determined from the adsorption spectra. Therefore we assumed an **FePc** structure[29] in this work, and calculated an **FePc** loading of $1.6\times10^{-2}$ mmol $g^{-1}$ of silica on **S-3**.

Removal of the **FePc** complex on **S-3** by Soxhlet extraction with pyridine for 72 h yielded a white solid, **S-4**. Elemental analysis showed the attachment of $4.13\times10^{-1}$ mmol dodecylsilyl (**DDS**) groups per gram of silica.

**S-4** (5.2 g) was dispersed in benzene, to which **FeTPPCl** (70 mg) was added, again under argon. After refluxing 48 h with stirring, the solid was collected by filtration and washed with $CH_2Cl_2$ until the filtrate turned colorless. The dark green solid obtained, **S-5**, had a loading of iron tetraphenylporphyrin (**FeTPP**) complex of $1.1\times10^{-2}$ mmol $g^{-1}$ of silica as determined from the quantitative analysis of iron.

By the same procedure, **S-2** (14.8 g) was modified to **S-6**, on which octadecylsilyl (**ODS**) groups and **FePc** complex ($1.4\times10^{-2}$ mmol $g^{-1}$ of silica) were loaded. Soxhlet extraction of **S-6** with pyridine for 96 h yielded **S-7**, on which $4.15\times10^{-1}$ mmol **ODS** groups per gram of silica were attached. A final loading of **FeTPPCl** on **S-7** yielded the product **S-8**, with an **FeTPP** complex loading of $9.1\times10^{-3}$ mmol $g^{-1}$ of silica.

**Oxidation of Alkenes.** The catalyst ($4\times10^{-4}$ mmol) was dispersed in 4 ml of deionized water, to which substrate (0.3—0.4 mmol), imidazole (0.4 mmol), and $H_2O_2$ (0.4 mmol) were added. The vial containing the mixture was sealed with a septum and shaken at 150 strokes/min and 40 °C using a Bio-shaker for a desired reaction time. For anaerobic assays, manipulations were done in a glove box.

After reaction, decane was added to the mixture as a GC internal standard. The mixture was then extracted with diethyl ether and filtered for GC analysis. Each oxidation reaction was repeated two to four times.

## Results

**Preparation of Catalyst.** An amorphous silica was employed for the experiment. $^{29}$Si-solid state NMR spectrum of the silica showed the presence of 81% single hydroxyl and 19% geminal hydroxyl groups on the surface. Thus it was assumed that the surface was composed predominantly of the 111-face of $\beta$-cristobalite model, in which there are 4.6 single hydroxyl groups $nm^{-2}$ located 0.5 nm apart in a hexagonal array.[30,31]

For the active center, we have chosen **FeTPPCl**, so that our results may be compared with published data. **IPS** bearing an imidazolyl group was used for the formation of the support. It is anchored to silanol functions on the silica surface and immobilizes the **FeTPP** complex by coordinative bonds. In order to isolate the immobilized iron porphyrin, alkanes (**DDS** and **ODS** groups) were selected as fence molecules because of their resistance to oxidation.

Synthetic pathway of the catalyst is shown in Fig. 1. The attachment of a dilute concentration of support, **IPS**, gave a loading of 3.0% of total silanols on the 111-face model. By treatment with **FePcpy$_2$**, a concentration of **FePcpy** complex equal to 1.9% of total silanols was immobilized on the supports. However, anchoring of alkylsilyl groups caused a reduction of the amount of **FePc** complex to 1.1% of total silanols. Several attempts to vary the loading of **FePc** complex yielded nearly identical final loadings after the attachment of fence molecules.

Removal of **FePc** complex was done by Soxhlet extraction using pyridine. The complete elimination of **FePc** complex was confirmed by elemental analysis and quantitative analysis of iron. As a final step, **FeTPPCl** was inserted into the cavity, and occupied 69 and 66% of the cavity enclosed with **DDS** and **ODS** groups, respectively. The formation of $\mu$-oxo dimer was ruled out based on examination of the visible spectrum of the catalyst (Fig. 2).

**Oxidation of Alkenes.** Substrates for the oxidation reaction were *trans*-$\beta$-methylstyrene (**MS**), *cis*-stilbene (**SB**), and *cis*-cyclooctene (**CO**). Prior to the oxidation study, we examined the effect of pyridine, *N*-methylimidazole, and imidazole addition on the epoxidation of **MS** and found that the most efficient acceleration of the reaction occurred with imidazole. The oxidation rate was dependent on the amount of imidazole. Under aerobic conditions, the yields of oxide and benzaldehyde from **MS** increased with increasing imidazole, up to slightly more than 1/2 equivalent of imidazole in $H_2O_2$ (Table 1, Entries 5—7). As a result, equal mol of imidazole in $H_2O_2$ was added for the epoxidation of substrates.

The results of oxidation of alkenes are shown in Tables 1, 2, and 3. In this reaction system, no reaction product was detected in the absence of either catalyst

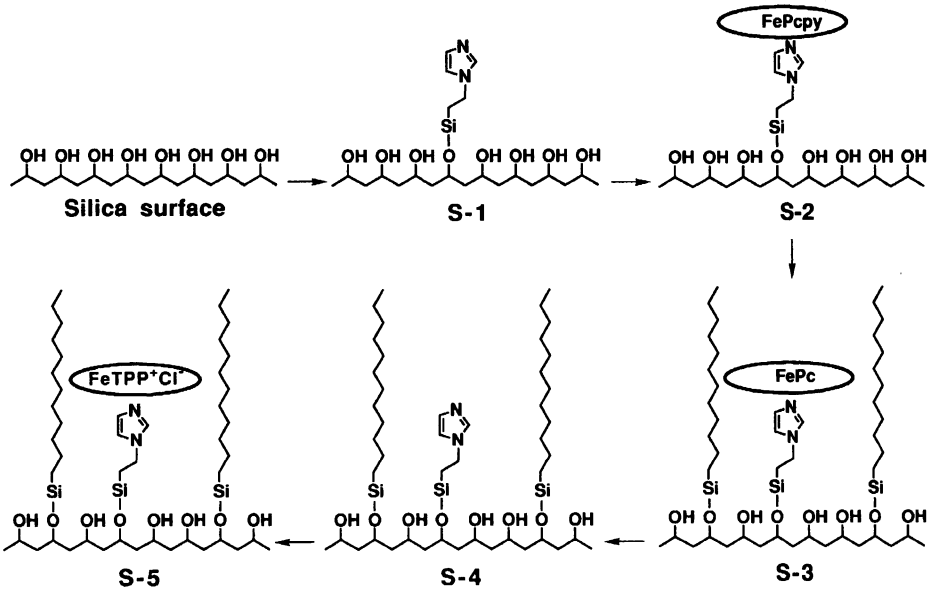


Fig. 1. Synthetic pathway of catalyst.

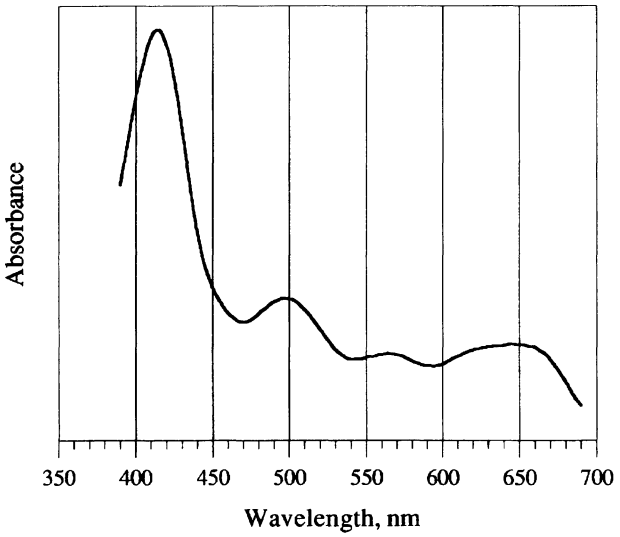


Fig. 2. Visible spectrum of **S-5**.

or $H_2O_2$. The material balance was over 97% in all experiments.

Oxidation of **MS** (Table 1) demonstrated the remarkable differences between aerobic and anaerobic conditions. Large quantities of benzaldehyde were produced in the presence of oxygen (Entries 1 and 3). In the absence of oxygen, the formation of aldehyde became insignificant but a slight decrease in the yield of oxide occurred (Entries 2 and 4). Oxidation of **SB** (Table 2) yielded predominantly *cis*-oxide as well as small amount of benzaldehyde, *trans*-stilbene oxide and benzophenone. The catalyst which has **DDS** fences seems to be more efficient for epoxidation of **SB**. The removal of oxygen decreased the yields of by-products. The conversion of **CO** (Table 3) was considerably lower than the other two substrates and was not improved by extending the reaction time.

Table 1. Oxidation of *trans*-β-Methylstyrene by Immobilized FeTPP Complex and $H_2O_2$[a)]

| Entry | Catalyst | Imidazole[c)] | Atmosphere | Product yield[b)] Oxide | Benzaldehyde |
|---|---|---|---|---|---|
| 1 | **S-5** | 0.4 | Aerobic | 144 | 88 |
| 2 | **S-5** | 0.4 | Anaerobic | 121 | 9 |
| 3 | **S-8** | 0.4 | Aerobic | 120 | 69 |
| 4 | **S-8** | 0.4 | Anaerobic | 111 | 8 |
| 5[d)] | **S-8** | 0 | Aerobic | 8 | 14 |
| 6[d)] | **S-8** | 0.2 | Aerobic | 78 | 49 |
| 7[d)] | **S-8** | 0.4 | Aerobic | 98 | 51 |

a) Alkene/$H_2O_2$/catalyst=0.4 mmol/0.4 mmol/$4\times10^{-4}$ mmol in $H_2O$ (4 ml) at 40 °C for 4 h. b) Yields based on equivalents of catalyst used. c) Mmol. d) Reaction time; 2 h.

## Discussion

Polymer-supported manganese tetraphenylporphyrin has been reported as a model for cytochrome P450.[32)] The enhancement of catalytic activity by site isolation is described for the epoxidation of cyclohexene. However, a decrease in the epoxidation rate attributable to diffusion limitations or shielding of the metalloporphyrin has been observed when a cross-linked polymer was used as the support. The present work attempts to solve this problem which is often seen in such polymer-supported catalysts by the construction of enzyme-like three dimensional structures consisting of a metal complex in a microenvironment on a silica surface.

**Creation of Active Site on Silica Surface.** In order to build an active site on the silica surface, it was necessary to consider the approximate maximum size of the molecules which function as support, protection groups for the open space, fence and **FeTPPCl**.

Table 2. Oxidation of *cis*-Stilbene by Immobilized FeTPP Complex and $H_2O_2$[a)]

| Entry | Catalyst | Atmosphere | Product yield[b)] | | | |
|---|---|---|---|---|---|---|
| | | | *cis*-Oxide | *trans*-Oxide | Benzaldehyde | Benzophenone |
| 1 | **S-5** | Aerobic | 97 | 7 | 9 | 6 |
| 2 | **S-5** | Anaerobic | 99 | 6 | 5 | 5 |
| 3 | **S-8** | Aerobic | 74 | 6 | 6 | 5 |
| 4 | **S-8** | Anaerobic | 79 | 5 | 4 | 3 |

a) Alkene/$H_2O_2$/imidazole/catalyst=0.3 mmol/0.4 mmol/0.4 mmol/$4\times10^{-4}$ mmol in $H_2O$ (4 ml) at 40 °C for 4 h. b) Yields based on equivalents of catalyst used.

Table 3. Oxidation of *cis*-Cyclooctene by Immobilized FeTPP Complex and $H_2O_2$[a)]

| Entry | Catalyst | Atmosphere | Oxide yield[b)] |
|---|---|---|---|
| 1 | **S-5** | Aerobic | 54 |
| 2 | **S-5** | Anaerobic | 47 |
| 3 | **S-8** | Aerobic | 36 |
| 4 | **S-8** | Anaerobic | 40 |

a) Alkene / $H_2O_2$ / imidazole / catalyst = 0.4 mmol/0.4 mmol/0.4 mmol/$4\times10^{-4}$ mmol in $H_2O$ (4 ml) at 40 °C for 4 h. b) Yields based on equivalents of catalyst used.

The maximum lateral and perpendicular extensions of an **FeTPPCl** molecule are approximately 1.8 and 0.45 nm, respectively. The substrates are oxidized on the upper porphyrin plane. To create a hydrophobic environment there, it is required that the fence molecules being long enough to shield the supported iron porphyrin. The maximum distance from the Si to the N of the imidazole structure in **IPS** is estimated to be 0.75 nm. The length of the coordination bond is about 0.2 nm;[33)] therefore the maximum distance from Si to the mean plane of the porphyrin is roughly calculated to be 0.95 nm, which corresponds to the length of a heptylsilyl group. As a result, the **DDS** and **ODS** groups were chosen as fence molecules in this work.

The catalytic activity is significantly affected by the iron porphyrin loading. Both the highest loading of iron porphyrin and complete isolation must be achieved concurrently. However, if there is a high density of anchored alkylsilyl groups on the surface, the imidazolyl groups of the supports will be buried and shielded under the fences formed by the alkylsilyl groups. In addition, the space between the fences will be too small to accept the large porphyrin molecule. Therefore, prior to the introduction of the fence, we tried to secure sufficient space in the vicinity of the support so that it would be capable of receiving the iron porphyrin which would be loaded during the last synthetic stage. Such an area was protected from reaction with alkylsilyl groups by temporary ligation of **FePcpy** complex to the support.

If we assume that the highly mobile support[34)] rotates about the Si-$C_1$ axis with a distance from $C_1$ to Fe of 0.65 nm, then the **FePcpy** complex ligating to the support sweeps out a projected circle of roughly 2.5 nm maximum diameter, in which a maximum of 24 silanols are present on the 111-face model (Fig. 3). Because a **DDS** group is placed on approximately every third silanol site under these experimental conditions, at least eleven alkylsilyl groups are required to encircle the area. That approximates a hexagonal arrangement with two alkylsilyl groups on a side. Consequently the most efficient site isolation seems to be accomplished by creating an extended packing distribution of the spherical projection of the **FePcpy** complex and three alternate sides of the hexagonal fence (Fig. 4). A single **FePcpy** complex must accompany the sum of silanols covered by it (24), and those needed for binding the 6 alkylsilyl fence groups (18); this corresponds to 2.4% of total silanol sites on 111-face model.

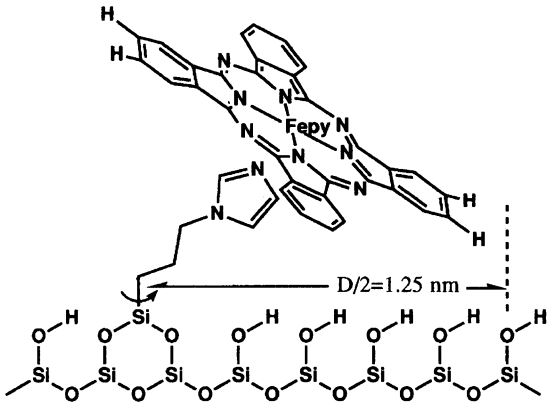


Fig. 3. Swept out area of **FePcpy** complex.

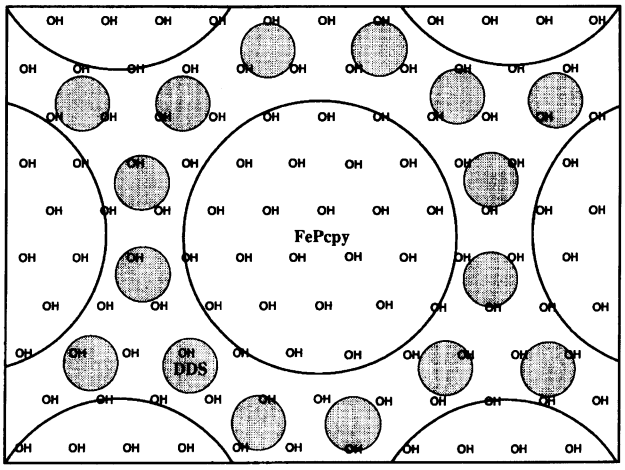


Fig. 4. Ideal maximum packing of **FePcpy** and fences.

As described before, however, the packing of alkylsilyl groups has excluded some of **FePcpy** complex and caused a decrease in the loading level to 56% of the ideal value. This decrease in loading may be due to nonidealities of the actual surface of amorphous silica such as the arrangement of silanol groups which emerge from the surface, and/or decomposition of coordination bonds followed by removal of the complex during the packing of fences.

The loading of **DDS** groups after removal of **FePc** complex was 38% of the available silanol sites. Available silanol sites include those that were not already occupied holding the supports or protected by the **FePc** complex. Highly packed fences surround the cavity (Fig. 5).

In the study of immobilization of iron deuteroporphyrin(IX) dimethyl ether chloride by coordination to imidazolyl groups in a flexible polymer, the iron centers have been shown to possess two axial ligands.[35] But one is readily exchangeable and may be replaced by solvent. On the synthesized catalyst, the **FeTPP** complex is thought to be isolated by the coordinative ligation on one axial imidazolyl group, as is its accompanying $Cl^-$. The similarity of the visible spectra of the catalyst and **FeTPPCl** is comparable to the findings of Traylor et al. using chelated protoheme.[36]

**Oxidation of Alkenes by Synthesized Catalyst.** The oxidation of alkenes was performed in aqueous solution, because it is assumed that lipophilic substrates are condensed on the surface due to hydrophobic interactions as in the native enzyme[1] and occupy the cavity containing the active center.

In the study of the epoxidation of alkenes with iron and manganese porphyrin by alkyl hydroperoxide in the presence of imidazole, Mansuy et al. suggest that the heterolytic cleavage of hydroperoxide to give high valent metal oxo species occurs in the presence of imidazole.[15] Groves et al. investigated the effect of imidazole addition on the oxidation of *cis*-$\beta$-methylstyrene with manganese porphyrin by $H_2O_2$ and suggested that heterolysis of $H_2O_2$ is predominant, independent of the presence of imidazole.[37] The increased yield of epoxidation products has been attributed to the effect of imidazole ligation promoting heterolysis as well as to the function of the general base catalyst.[36] Labeque and Marnett have reported the stereospecific epoxidation of **SB** to *cis*-oxide in the presence of imidazole with **FeTPPCl** by alkyl hydroperoxide, but reported nonstereospecific oxidation in the absence of imidazole.[38] They attributed the results to the change from homolysis to heterolysis due to the ligation of imidazole and to its role as a general base catalyst.

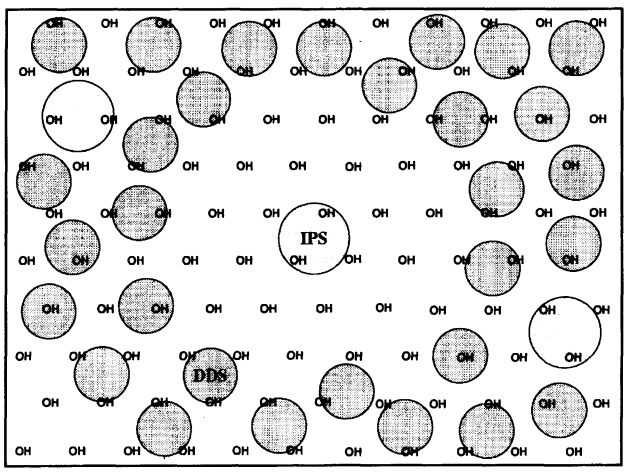


Fig. 5. Cavity formed by synthesis on silica surface.

The fact that *cis*-oxide is obtained as a main product from **SB** in this work (Table 2) is consistent with the findings of Labeque and Marnett and indicates that the heterolysis of $H_2O_2$ yielding active iron oxo species predominates. The heterolytic cleavage of the O–O bond is also proposed by Traylor et al. in their kinetic study using imidazolyl group chelated iron porphyrin chloride and $H_2O_2$.[39] On the other hand, although the iron centers have an axial imidazole ligand in this catalyst, the improvement in yields of oxides produced from alkenes were primarily due to the addition of imidazole. The function of imidazole as a general base catalyst is apparently quite important for the epoxidation of alkenes in this reaction system.

The high yield of benzaldehyde from **MS** under aerobic conditions is a characteristic aspect of this work (Table 1). In the presence of **PhIO**, iron porphyrins are known to catalyze **MS** or styrene to oxides with a high selectivity either in the presence or in the absence of oxygen.[40] Fontecave and Mansuy have shown a huge production of benzaldehyde from styrene and a loss of stereospecificity in the epoxidation of **SB** by **PhIO** with non-porphyrin iron catalyst.[41] They attributed these findings to the formation of alkene derived free radical intermediates. Groves et al. have revealed that large quantities of benzaldehyde as well as cinnamaldehyde are yielded in the epoxidation of *cis*-$\beta$-methylstyrene with manganese porphyrin catalyst under aerobic conditions.[37] The alkene carbon radical is proposed as the intermediate which is trapped by oxygen and produces an alkylperoxyl radical. However, in the same report, when $H_2O_2$ is used in the presence of imidazole, they suggest that the formation of active species different from those leading to such radical chain reactions are responsible for aldehyde production.

Among the several intermediates in the proposed mechanisms for alkene epoxidation,[42,43] another, capable of participating with oxygen, is involved in the alkene carbocation radical pathway. Castellino and Bruice suggested such an intermediate in the epoxidation of **SB** with electronegatively substituted **FeTPPCl** by **PhIO**.[44] The product distribution and reaction behavior in the present work (Table 2) are almost identical with those results. The single exception is the for-

mation of dibenzophenone as a rearrangement product instead of the diphenylacetaldehyde and deoxybenzoin identified by them. It seems likely that the same intermediate accounts for the high yield of benzaldehyde in the presence of oxygen.

A catalyst which immobilizes and isolates simple and fragile **FeTPP** complex demonstrates a high activity for the epoxidation of alkenes by $H_2O_2$ in the presence of imidazole. This improvement of catalytic activity is partly due to the formation of a hydrophobic environment in the area surrounding the active site. The hydrophobic nature of the catalyst and the condensation of lipophilic substrates previously mentioned apparently inhibit contact between the active center and $H_2O_2$; $H_2O_2$ is repelled by surrounding paraffinic fences and is only slightly soluble in the alkene phase. The low concentration of $H_2O_2$ near the active site may inhibit the decomposition of **FeTPP** complex. It may also hinder the prevention of epoxidation of alkenes by the formation of hydroperoxyl and alkoxyl radicals derived from the reaction between iron oxo species and hydroperoxide.[45,46] However, the activity of the catalysts of the present work is still far from those of synthetic metalloporphyrins. Further research is in progress.

## References


1) T. J. McMurry and J. T. Groves, "Cytochrome P-450," ed by P. R. Ortiz de Montellano, Plenum Press, New York (1986).
2) D. Mansuy, *Pure Appl. Chem.*, **59**, 759 (1987).
3) J. T. Groves, T. E. Nemo, and R. S. Myers, *J. Am. Chem. Soc.*, **101**, 1032 (1979).
4) C. K. Chang and F. Ebina, *J. Chem. Soc., Chem. Commun.*, **1981**, 778.
5) J. T. Groves and T. E. Nemo, *J. Am. Chem. Soc.*, **105**, 5786 (1983).
6) J. T. Groves and T. E. Nemo, *J. Am. Chem. Soc.*, **105**, 6243 (1983).
7) J. P. Collman, T. Kodadek, S. A. Raybuck, and B. Meunier, *Proc. Natl. Acad. Sci.*, **80**, 7039 (1983).
8) S. Takagi, E. Takahashi, T. K. Miyamoto, and Y. Sasaki, *Chem. Lett.*, **1986**, 1275.
9) T. G. Traylor, T. Nakano, B. E. Dunlap, P. S. Traylor, and D. Dolphin, *J. Am. Chem. Soc.*, **108**, 2782 (1986).
10) T. G. Traylor and S. Tsuchiya, *Inorg. Chem.*, **26**, 1338 (1987).
11) S. Tsuchiya and M. Seno, *Chem. Lett.*, **1989**, 263.
12) T. G. Traylor and A. R. Mikszal, *J. Am. Chem. Soc.*, **111**, 7443 (1989).
13) J. F. Bartoli, O. Brigaud, P. Battioni, and D. Mansuy, *J. Chem. Soc., Chem. Commun.*, **1991**, 440.
14) P. S. Traylor, D. Dolphin, and T. G. Traylor, *J. Chem. Soc., Chem. Commun.*, **1984**, 279.
15) D. Mansuy, P. Battioni, and J-P. Renaud, *J. Chem. Soc., Chem. Commun.*, **1984**, 1255.
16) J-P. Renaud, P. Battioni, J. F. Bartoli, and D. Mansuy, *J. Chem. Soc., Chem. Commun.*, **1985**, 888.
17) T. G. Traylor, W-P. Fann, and A. Bandyopadyay, *J. Am. Chem. Soc.*, **111**, 8009 (1989).
18) P. Battioni, J-P. Renaud, J. F. Bartoli, and D. Mansuy, *J. Chem. Soc., Chem. Commun.*, **1986**, 341.
19) P. L. Anelli, S. Banfi, F. Montanari, and S. Quici, *J. Chem. Soc., Chem. Commun.*, **1989**, 779.
20) S. Banfi, A. Maiocchi, A. Moggi, F. Montanari, and S. Quici, *J. Chem. Soc., Chem. Commun.*, **1990**, 1794.
21) S. Banfi, F. Legramandi, F. Montanari, G. Pozzi, and S. Quichi, *J. Chem. Soc., Chem. Commun.*, **1991**, 1285.
22) P. Battioni, J-P. Lallier, L. Barloy, and D. Mansuy, *J. Chem. Soc., Chem. Commun.*, **1989**, 1149.
23) L. Barloy, P. Battioni, and D. Mansuy, *J. Chem. Soc., Chem. Commun.*, **1990**, 1365.
24) P. Battioni, J. F. Bartoli, D. Mansuy, Y. S. Byun, and T. G. Traylor, *J. Chem. Soc., Chem. Commun.*, **1992**, 1051.
25) M-B. McCarthy and R. E. White, *J. Biol. Chem.*, **258**, 9153 (1983).
26) A. D. Alder, F. R. Longo, F. Kampas, and J. Kim, *J. Inorg. Nucl. Chem.*, **32**, 2443 (1970).
27) G. V. Ouedraogo, C. More, Y. Richard, and D. Benlian, *Inorg. Chem.*, **20**, 4387 (1981).
28) C. Ercolani, M. Gardini, F. Monacelli, G. Pennesi, and G. Rossi, *Inorg. Chem.*, **22**, 2584 (1983).
29) D. V. Stynes and B. R. James, *J. Am. Chem. Soc.*, **96**, 2733 (1974).
30) D. W. Sindorf and G. E. Maciel, *J. Am. Chem. Soc.*, **103**, 4263 (1981).
31) D. W. Sindorf and G. E. Maciel, *J. Phys. Chem.*, **86**, 5208 (1982).
32) A. W. van der Made, J. W. H. Smeets, R. J. M. Nolte, and W. Drenth, *J. Chem. Soc., Chem. Commun.*, **1983**, 1204.
33) S. C. Tang, S. Koch, G. C. Papaefthymiou, S. Foner, R. B. Frankel, J. A. Ibers, and R. H. Holm, *J. Am. Chem. Soc.*, **98**, 2414 (1976).
34) D. Slotfeldt-Ellingsen and H. A. Resing, *J. Phys. Chem.*, **84**, 2204 (1980).
35) J. Grimshaw and J. Trocha-Grimshaw, *J. Chem. Soc., Chem. Commun.*, **1990**, 157.
36) T. G. Traylor, W. A. Lee, and D. V. Stynes, *J. Am. Chem. Soc.*, **106**, 755 (1984).
37) J. T. Groves and M. K. Stern, *J. Am. Chem. Soc.*, **110**, 8623 (1988).
38) R. Labeque and L. J. Marnett, *J. Am. Chem. Soc.*, **111**, 6621 (1989).
39) T. G. Traylor and J. P. Ciccone, *J. Am. Chem. Soc.*, **111**, 8413 (1989).
40) J. T. Groves and R. S. Myers, *J. Am. Chem. Soc.*, **105**, 5791 (1983).
41) M. Fontecave and D. Mansuy, *J. Chem. Soc., Chem. Commun.*, **1984**, 879.
42) J. P. Collman, P. D. Hampton, and J. I. Brauman, *J. Am. Chem. Soc.*, **112**, 2977 (1990).
43) J. P. Collman, P. D. Hampton, and J. I. Brauman, *J. Am. Chem. Soc.*, **112**, 2986 (1990).
44) A. J. Castellino and T. C. Bruice, *J. Am. Chem. Soc.*, **110**, 158 (1988).
45) T. G. Traylor and F. Xu, *J. Am. Chem. Soc.*, **109**, 6201 (1987).
46) T. G. Traylor and F. Xu, *J. Am. Chem. Soc.*, **112**, 178 (1990).