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Characterization of Iron(III) Tetramesitylporphyrin and Microperoxidase-8 Incorporated into the Molecular Sieve MCM-41

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Introduction

Chemical manufacturers, especially those involved in the synthesis of fine chemicals, seek robust catalysts that can (1) promote selective oxidation reactions using inexpensive oxidants and (2) do so without generating toxic waste. A number of metalloenzymes can promote selective oxidations using O_2 or H_2O_2 but lack the stability necessary for most industrial processes. An attractive solution is to use zeolites, crystalline aluminosilicates with cage sizes of up to 1.3 nm, which can serve as a hosts for biomimetic compounds. Phthalocyanines reportedly have been prepared in faujasite-type zeolites by a "ship-in-the-bottle" technique;[1,2] embedding zeolite-encaged phthalocyanines into a polymer leads to an efficient mimic of cytochromes P450.[2] The "ship-in-the bottle" approach is not, however, a viable method for stabilizing the more biologically relevant and catalytically active porphyrins on a solid support.[3] Recently a family of regularly arrayed, large-pore molecular sieves has been developed: MCM-41, for example, contains channels with pore diameters ranging from 2 to 10 nm .[4] These channel systems permit the introduction of large molecules such as porphyrins[5−8] or even small proteins,[9] circumventing the need for the "ship-in-the-bottle" synthesis.[10]

A number of methods have been reported in the literature for associating transition metal complexes or other large molecules with MCM-41. These methods include simply stirring the guest and host,[11−14] grafting the guest to the host,[5,8,13] including the guest in the organic surfactant that serves as the template for pore formation,[7] and modifying the host after the guest is presumably encapsulated to prevent escape.[9] Porphyrins have been incorporated into MCM-41 by several of these methods. Kevan and co-workers reported associating free-base porphyrins with MCM-41 by stirring porphyrins and MCM-41 in chloroform for 24 h and then removing the solvent under vacuum.[6] Che and co-workers reported associating ruthenium porphyrins with MCM-41 after modifying MCM-41 with an organosilane, which provided an amine to serve as an axial ligand for the porphyrin.[5,8] Recently Stein and co-workers published a report in which they studied the encapsulation, stabilization, and catalytic properties of several metalloporphyrins in MCM-41.[7]

We report here the first example of transforming a water-insoluble porphyrin, hydroxo(5,10,15,20-tetramesitylporphinato)iron(III) ($Fe^{III}(TMP)(OH)$) into a catalytically competent water-soluble catalyst by means of embedding it into MCM-41. Furthermore, using the operationally unstable heme-containing octapeptide microperoxidase, known to be inactivated within 1 min of catalytic turnover,[22] we also investigated whether embedding heme-based catalysts into MCM-41 would provide increased operational stability due to better shielding of the heme moiety. This was done because previous studies indicate that increased polypeptide chain length provides some protection against inactivation during catalytic activity[15] and we wondered if the solid matrix would function in a similar manner. Electron paramagnetic resonance (EPR) spectroscopy confirms that the iron is still ligated to the porphyrin macrocycle after the stabilization in MCM-41. The hydroxylation of aniline with

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H_2O_2 as the oxidant has been utilized to probe the catalytic activity of the water-insoluble model porphyrin in a water-soluble MCM-41 system and to investigate the catalytic activity and operational stability of microperoxidase-8 upon its incorporation into MCM-41. Our results demonstrate that metalloporphyrins supported on MCM-41 can catalyze cytochrome P450-like reactions in aqueous solutions. Control experiments using MCM-41 alone or MCM-41 with iron(III) in a non-heme environment show essentially no catalytic activity, ruling out Fenton-type chemistry and proving that iron porphyrins are essential for the catalytic activity reported. Because iron porphyrin-mediated oxidations show greater selectivity than radical-induced oxidations[16] and because hydrogen peroxide is an inexpensive and clean oxidant, the systems described show some promise for industrial applications where "greener" methods are desired. However, experiments done with uncalcined MCM-41, where the pores are still filled with the organic templating agent, and zeolite Y, which has cavity openings that are too small to permit metalloporphyrin diffusion into the pores, indicate that a critical analysis of the unique benefits of MCM-41 as a solid support, including a direct comparison with other well-characterized aluminosilicates, is warranted.

Experimental Section[17]

General Information for Syntheses. All starting materials were used as received, except for pyrrole, which was distilled prior to use, and toluene, which was dried and distilled prior to use. All chemicals were purchased from Aldrich, except for sodium aluminate, which was purchased from Crescent Chemical Co. TMP was synthesized by the standard Lewis acid-catalyzed condensation of aryl aldehydes with pyrrole[18] and metalated by refluxing with iron pentacarbonyl in dry toluene. MP-8 was prepared by peptic and tryptic digestion of horse-heart ferricytochrome *c*.[19] MCM-41 was synthesized according to a literature method.[20] Reduced aluminum levels were obtained by reducing or eliminating the sodium aluminate used in the synthesis, in accordance with the reported procedure.[20] Small-angle X-ray diffraction indicated a well-formed pore structure with a diameter of 2.5 ± 0.3 nm.[6] Well-formed pores were also visible by transmission electron microscopy. Three other MCM-41 samples, with pore sizes of 2, 3.4, and 4 nm, were provided as gifts. Zeolite Y was a gift from Grace Davidson.

Synthesis of Metalloporphyrin/MCM-41 Complexes. Metalloporphyrin/MCM-41 complexes were prepared by two methods: (1) direct encapsulation and (2) modification of MCM-41 followed by encapsulation. Both methods are similar to those used by Kevan[6] and Che.[5,8]

For direct encapsulation, typically 100 mg of MCM-41 was dehydrated under vacuum (10^{-2} mbar). A heating rate of 0.5 K/min was employed up to 523 K. The final temperature was maintained for 12 h. For samples containing the synthetic porphyrin $Fe^{III}(TMP)(OH)$, the dehydrated MCM-41 was impregnated under Ar with 1 mL of CH_2Cl_2 containing $Fe^{III}(TMP)(OH)$ (concentration: 3 mg of $Fe^{III}(TMP)(OH)$/mL). The samples were stirred (stirring times were varied from 1 to 5 days) and then filtered. The resulting solids were washed three times successively with acetone, methylene chloride, and DMF. Soxhlet extractions with the same solvents led to no differences in the amount of porphyrin retained on the MCM-41. For samples containing MP-8, dried MCM-41 was stirred with 1 mL of a 0.1 M phosphate buffered solution (pH 7.6) of MP-8 under argon. The samples were cooled to 77 K and the water was pumped off during thawing, followed by washing three times with doubly distilled water.

In the second method, MCM-41 was modified with (3-aminopropyl)triethoxysilane to provide an axial ligand for the iron porphyrin,[5,8] thus making this method suitable only for the synthetic porphyrin $Fe^{III}(TMP)(OH)$, which has a more labile axial ligand. In a typical preparation, MCM-41 (500 mg) was dried under vacuum for 12 h prior to modification. A 25 mL portion of a 0.1 M solution containing (3-aminopropyl)triethoxysilane in dry chloroform was added, and the mixture was stirred under argon for 24 h. Afterward, the reaction mixture was filtered, and the solid was dried. $Fe^{III}(TMP)(OH)$ (100 mg) was dissolved in methylene chloride (50 mL), the solution was added to the modified MCM-41, and the mixture was stirred for 4 days. The resulting solid was filtered off and washed three times successively with acetone, DMF, and methylene chloride. Soxhlet extractions with the same solvents led to no differences in the amount of porphyrin retained on the MCM-41.

Synthesis of Metalloporphyrin/Zeolite Y Complexes. For comparison, $Fe^{III}(TMP)(OH)$ complexes with zeolite Y were synthesized by following both procedures outlined above for the synthesis of Fe(TMP)(OH)/MCM-41 complexes, except that zeolite Y was substituted for MCM-41.

Synthesis of Fe(MCM-41). For comparison, material containing non-heme iron was synthesized by stirring 2 mL of $Fe(CO)_5$ in 10 mL of CH_2Cl_2 with 100 mg of dried MCM-41 for 24 h. The resulting material was filtered off, rinsed thoroughly, and dried.

Chemical Analysis. The concentration of iron was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Perkin-Elmer Optima 3000 with an rf power of 1300 W. Samples for ICP were digested with an acid solution (1:1:1 $HF-HNO_3-HCl$) at room temperature for 12−24 h. All analyses were done with matrix-matched blanks and standards. Iron content of samples ranged from 0.002% to 0.6% by weight. Samples were also analyzed by Galbraith Laboratories, Knoxville, TN.

Evidence that essentially all the iron detected by ICP was still ligated to a porphyrin was provided by EPR spectroscopy. Electron paramagnetic spectroscopy was performed on a Bruker X-band EPR spectrometer equipped with an Oxford cryostat or on a JEOL TE100 spectrometer equipped with an Oxford ESR900A cryostat at liquid helium temperature (4−10 K).

Catalysis. The reactivity of iron porphyrin/MCM-41 complexes was characterized by monitoring the hydroxylation of aniline using H_2O_2 as the oxygen atom source.[21,22] In a typical experiment, 5 mg of an iron(III) porphyrin/MCM-41 complex (containing, on average, 1×10^{-8} mol of iron porphyrin) was added to 0.45 mL of a 0.1 M phosphate buffered solution (pH 7.6). Aniline (0.050 mL) from a 1 M stock solution in DMSO was then added to achieve a final concentration of 10 mM (1×10^{-5} mol of aniline). The solution was allowed to equilibrate at 37 °C for 2 min. Then H_2O_2 was added (30 wt %; titrated before use using a thiosulfate standard) to achieve a final peroxide concentration of 2 mM (0.2×10^{-5} mol of peroxide). After 1 min, 0.150 mL of trichloroacetic acid (20% mass/volume) was added to quench the reaction, and the reaction mixture was centrifuged. To the supernate was added 0.10 mL of a sodium carbonate solution together with 0.10 mL of phenol in NaOH (final concentration 2.8 mM) to form the blue indophenol.[23] After 1 h, the absorbance was measured at 630 nm, and the concentration of hydroxylated aniline was determined from the extinction coefficient of indophenol, $\epsilon = 30.5$ mM^{-1} cm^{-1} (confirmed by generating a standard curve with 4-hydroxyaniline). Turnover numbers are reported as nmol of product formed/nmol of iron porphyrin. Turnover frequencies are turnover numbers per unit time (either per minute or per second, depending upon the experiment). The amount of iron were determined from ICP data; EPR data confirmed that essentially all iron was ligated to porphyrin.

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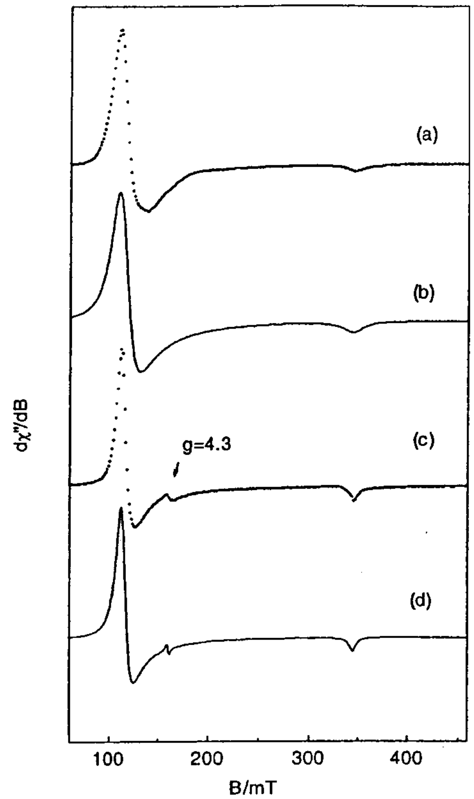

Figure 1. (a) EPR spectrum of solid Fe^{III}(TMP)(OH). (b) Simulation of (a) assuming a Lorentzian line shape with $g_{\perp}^{eff} = 6.0$ and $g_{\|}^{eff} = 2.0$ and with line widths $\Gamma_{\perp} = 26$ mT and $\Gamma_{\|} = 25$ mT. (c) EPR spectrum of Fe^{III}(TMP)(OH)/MCM-41 (association method 1). (d) Simulation of (c) with the same *g* values as used in (b) but with line widths $\Gamma_{\perp} = 15$ mT and $\Gamma_{\|} = 8$ mT. The signal at $g^{eff} = 4.3$ represents traces of non-heme iron (0.1% relative contribution). Experimental conditions: temperature 10 K; microwave frequency 9.646 GHz; modulation frequency 100 kHz; modulation amplitude 5 G; microwave power 20 μW.

Results and Discussion

Porphyrin Incorporation. Both techniques (methods 1 and 2) of incorporating iron porphyrins into MCM-41 yielded light brown to dark brown solids, even after extensive washing and Soxhlet extraction. The clearest evidence that iron porphyrins were incorporated into MCM-41 comes from EPR spectroscopy. The EPR spectra of Fe^{III}(TMP)(OH)/MCM-41 (stirred and modified) show that essentially all EPR-active iron is ligated to a porphyrin (Figure 1). The spectra can be simulated with a spin Hamiltonian that describes the spin manifold of Fe(III) bound to a porphyrin. In contrast, partially destroyed iron porphyrins usually show an EPR absorption near $g = 4.3$, a signal that was present only as a minor impurity in the spectra of our samples. The relative contribution of the non-heme iron ranges from 0.1% in Fe^{III}(TMP)(OH)/MCM-41 (Figure 1d) to a maximum value of 5% in MP-8/MCM-41 (data shown as Supporting Information). As additional experiments with non-heme iron in MCM-41 showed no catalytic activity (discussed below), the small amount of non-heme iron seen in some samples is not significant. The simulation of the EPR spectrum of Fe^{III}(TMP)(OH)/MCM-41 yields line widths that are reduced compared to the line widths of solid Fe^{III}(TMP)(OH) by a factor of 1.7 for the $g_{\perp}^{eff}$ resonances and 3 for the $g_{\|}^{eff}$ resonance. The spectra and simulations do not differ between the two Fe^{III}(TMP)(OH)/MCM-41 preparations. The decrease in line widths can be explained by a decrease in the spin−spin relaxation rate[24] caused by the higher dispersion of the iron porphyrins in MCM-41 as compared with that in the crystalline state.

We studied the amount of iron porphyrin incorporated into MCM-41 as a function of the amount of time Fe^{III}(TMP)(OH) was stirred in solution with MCM-41, the amount of aluminum in the MCM-41, the method of association used (stirring vs silanol modification), and the presence or absence of organic templating material. We found that after 48 h of stirring the iron porphyrin solution with MCM-41, the amount of iron that could be incorporated into MCM-41 reached a maximum. Additional stirring did not lead to an increase in the amount of iron that could be incorporated. No statistically significant difference was seen in the amount of iron porphyrin that could be associated with MCM-41 when the concentration of aluminum in MCM-41 was varied. There was also no statistically significant difference in the amount of iron porphyrin that was retained in MCM-41 in the two different procedures used to associate iron porphyrins with MCM-41. Both procedures yielded iron levels that averaged 0.1 wt %. Four separate experiments in which Fe^{III}(TMP)(OH) was stirred, under identical conditions, with both uncalcined and calcined MCM-41, showed that the amount of iron porphyrin retained in MCM-41 was essentially the same regardless of whether the pores contained the organic templating agent. The average amount of iron retained in the calcined material was 0.0242% (w/w) ± 0.0046%, and in the uncalcined material it was 0.0252% (w/w) ± 0.0082%. The relative amount of porphyrin retained is similar to the amount reported in other studies involving clays or MCM-41.[5,8,16,25−28]

A thorough review of the literature shows that definitive methods for conclusively demonstrating that a guest molecule is located exclusively inside the pores of MCM-41 are scarce and are infrequently used. The most compelling case to be made for materials being located inside the pores is simply that the overall surface area in a sample of MCM-41 is dominated by the surface area of the pore walls. Over 97% of the total surface area, which averages around 1000 m^2/g for a typical sample of MCM-41, is estimated to be interior surface.[29] Assuming that each iron porphyrin requires 2.25 nm^2, even loading 1% iron porphyrin by weight (which is higher than the concentration of porphyrin used for catalysis or electron transfer by Che,[8] Stein,[7] and Kevan[6]) does not require that catalysts be located on the interior pores. Therefore, at this time, we do not claim that the iron porphyrins associated with MCM-41 in our samples are embedded solely within the pores of MCM-41.

Catalytic Activity. Bioinorganic chemists have long searched for a way of harnessing the monooxygenase activity of cytochromes P450 for industrial applications. However, models of cytochromes P450 have been hampered by several problems, including their tendency to autooxidize, difficulties with catalyst recovery that are especially acute, given the expense of metalloporphyrin synthesis, and their solvent restrictions. Solid supports have the potential to alleviate all of these problems. The limitations of zeolites, largely a function of the narrow pore

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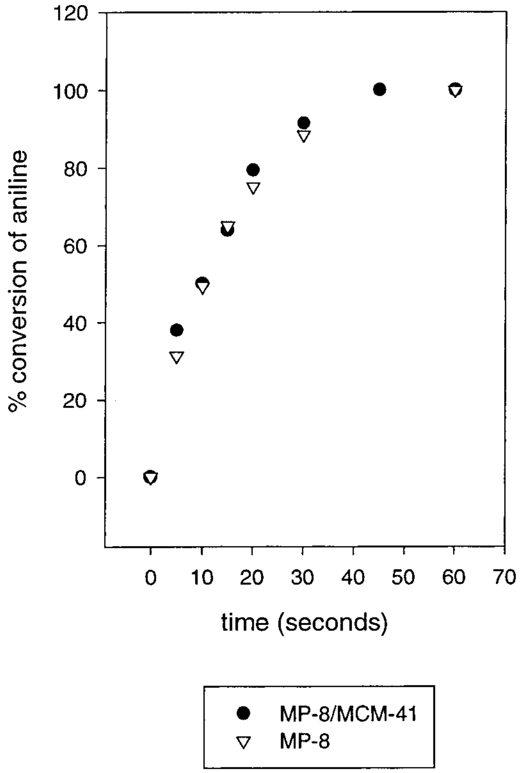

Figure 2. Comparison of the stability of MP-8 in MCM-41 and in solution. In both environments, MP-8 ceases to oxidize substrates after 1 min. Assay conditions detailed in text.

sizes, have led to a growing interest in the chemistry and catalytic activity of mesoporous molecular sieves, especially MCM-41, as hosts for transition metal catalysts.[30−32] We are reporting the first record of the catalytic activity of iron porphyrins embedded in MCM-41. (Note added in proof. For a recent report on the catalytic activity of iron porphyrins in metal-doped MCM-41, see: Zhang, L.; Sun, T.; Ying, J. Y. *Chem. Commun.* **1999**, 1103−1104.) However, a careful analysis of our work and the work of others suggests that using MCM-41 as a solid support for metalloporphyrins does not provide the significant advantages workers in the field had hoped for.[33]

Iron porphyrin/MCM-41 complexes catalyze the hydroxylation of aniline with catalytic activities similar to those reported for phthalocyanines in zeolites[2] and porphyrins on other inorganic supports.[26−28] The total number of nanomoles of aniline hydroxylated per nanomole of iron porphyrin range from 1 to 25 per assay. All materials that contained $\mathrm{Fe^{III}(TMP)(OH)}$ as the iron porphyrin showed undiminished catalytic activity when recovered and reused. Control experiments using MCM-41 alone and MCM-41 physically mixed with $\mathrm{Fe^{III}(TMP)(OH)}$ (solids were mixed in a 50:1 ratio and used as mixed in assay) were also performed. No catalytic activity was seen for MCM-41 alone, and only trace amounts of product were seen for the physically mixed samples, the latter emphasizing the need for solubilization of the water-insoluble $\mathrm{Fe^{III}(TMP)(OH)}$ before it can show catalytic activity in our water-soluble activity assay.

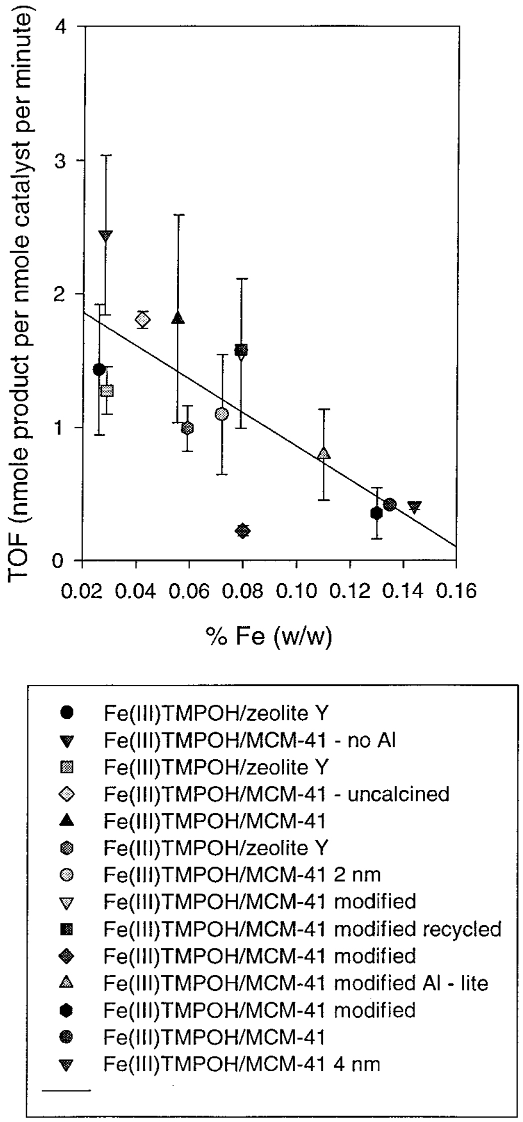

Figure 3. Catalytic activity of iron porphyrins on solid supports reported as turnover number vs amount of iron in sample.

Control experiments with MCM-41 to which $\mathrm{Fe(CO)_5}$ in $\mathrm{CH_2Cl_2}$ had been added to form Fe(III)/MCM-41 also showed only trace amounts of product, emphasizing the important role of iron porphyrins in the chemistry detected.

Since the synthetic iron porphyrins encapsulated in MCM-41 are not soluble under aqueous conditions, it is not possible to compare their reactivity in homogeneous solutions to that in the heterogeneous assay. However, it is possible to make this comparison for samples containing MP-8. There we see that turnover frequencies (nanomoles of product per nanomole of catalyst per second) for MP-8 in MCM-41 are slightly higher than they are for MP-8 alone (3.9 vs 1.5). No increase in the operational stability is seen for MP-8 in MCM-41 when compared to MP-8 in solution. In either case, MP-8 ceases to oxidize substrates after approximately 1 min (Figure 2). The observation that the embedding of MP-8 into the molecular sieve does not provide protection against its operational instability is noteworthy because recent data on microperoxidases with increasing lengths of the protein chains suggested improved shielding of the heme can protect against inactivation during catalytic turnover.[15] Thus the results presented in Figure 2 suggest that MCM-41 does not provide sufficient shielding of the porphyrin moiety of MP-8 to prevent its inactivation.

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We have compared the properties of iron porphyrin/MCM-41 materials prepared by two different methods in which MCM-41 is both calcined and uncalcined and contrasted these properties with those of iron porphyrin/zeolite Y materials prepared via the same two methods. We have also used MCM-41 with different pore sizes (2, 3.4, 4, and 4.3 nm). In all cases, the dominant variable affecting catalytic activity is the amount of iron loaded onto the solid support (Figure 3). Without exception, the higher the percentage of iron in the sample, the lower the turnover number. A few other groups have mentioned this finding in passing.[5,8,7] However, a careful analysis of over 200 individual catalytic assays shows this to be a dominant variable in our samples (Figure 3). At higher iron concentrations, the pores of the MCM-41 support may be blocked or the iron porphyrins may no longer be monodispersed. Either case would render some of the iron porphyrins catalytically inactive, leading to decreased turnover numbers.

Our results are consistent with a model in which the pores of MCM-41 do not play a dominant role in the catalytic properties of the hybrid materials. This assertion is further supported by the catalytic data reported for phthalocyanines in zeolites[2] or iron porphyrins supported on silica gel or clays,[26−28] which are similar to those reported for porphyrins in MCM-41.

Finally, our own comparison of iron porphyrins associated with zeolite Y, which has pores that are too small for a porphyrin to enter, and MCM-41 shows that there is no statistical advantage to using MCM-41 (Figure 3).

Additionally, studies in which we directly compare the catalytic activity of MP-8 in solution with MP-8 associated with MCM-41 indicate that MP-8 is not stabilized by association with MCM-41. Both show no catalytic activity after 1 min under the assay conditions reported here.

The fact that turnover frequencies diminish with iron loading effectively limits the moles of product produced per gram of catalyst. The precise mechanism that causes this effect is a subject of further study. One can speculate that nonpolar porphyrins with extended π systems may preferentially interact with electrophilic sites on the outer surface of MCM-41 and/or with other porphyrin molecules already attached to the surface. Preliminary studies in our laboratory have not provided any indication of porphyrin−porphyrin interactions, but more work will be required before we can propose and defend a mechanism for the diminution of catalytic activity with increased iron porphyrin loading. Thus, while mesoporous materials undoubtedly have much to offer the nanoscale and catalytic communities, issues remain to be resolved before they can be demonstrated to be an ideal scaffold for embedded catalysts.

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Supporting Information Available: EPR spectra and simulations for MP-8 in MCM-41. This material is available free of charge via the Internet at http://pubs.acs.org.

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