

A novel 'build-bottle-around-ship' method to encapsulate metalloporphyrins in zeolite-Y. An efficient biomimetic catalyst

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Electrostatic interaction is introduced between the host and guest in the synthesis of faujasite-Y confined metallotetrakis(*N,N,N*-trimethylanilinium) porphyrin cations (MTMAnP⁴⁺); the synthesized composites display high catalytic activity in the oxidation of cyclohexene.

One of the most attractive properties of zeolites are their well organized nanopores and nanochannels which serve readily as supporting hosts for various molecules. Encapsulation of catalytically active transition metal complexes inside the nanopores of zeolites, often referred to as 'ship-in-a-bottle' systems,¹ has been believed to be one of the most promising strategies in the development of viable industrial catalysts.^{1–6} Extensive effort has been devoted to the synthesis and catalytic properties of zeolite entrapped metallocomplexes with such ligands as bipyridine, salen, polyamines and phthalocyanines.^{1–6} In most of these syntheses, a so-called 'assemble-ship-inside-bottle' approach has usually been adopted in which the desired catalytic metallocomplex is synthesized inside the nanopores/channels of the zeolite in the presence of an excess of ligand or its synthetic precursors. As a consequence, what was usually obtained is a mixture of the desired complex with unreacted free ligand as well as side-products. For example, the synthesis of metalloporphyrin (MP) inside zeolites often leads to a significant portion of undesired polymerization product and the unmetallated free base porphyrin ligand.^{7–9}

We report here a novel, efficient and quantitative method to synthesize high purity MPs incorporated in faujasite-Y at a controllable loading concentration. The novel aspect of this method is that an electrostatic interaction was introduced between the host (anionic aluminosilicate species) and the guest (cationic peripheral substituents on MPs) in a 'build-bottle-around-ship' approach, namely to synthesize the nanocages of zeolite around the high purity cationic MPs. The selected guest molecules have excellent solubility in aluminosilicate gel. In a typical synthesis, 240 mg of MTMAnPCL₅ was added into an aluminosilicate gel, freshly prepared by mixing silicate and aluminate solutions containing 4.6 g of silica, 6.2 g of NaOH, 3.2 g of NaAlO₂ and 80 ml of H₂O. The gel was then crystallized at 95 ± 2 °C under static and autogeneous conditions in a stainless steel bomb (250 ml) for 48 h. After cooling to room temp., a solid product was recovered by filtration. The complexes adsorbed on the exterior surfaces were removed by a thorough extraction with distilled water, methanol, pyridine (2%)–methanol, and methanol again, respectively. The removed complexes can be fully recovered for the next round of synthesis. The crystals were then dried at 60 °C for 24 h. Thermogravimetry (TG) of the composite indicates that 1.51 mass% is attributable to the confined guest, corresponding to *ca.* one MP complex for every forty supercages or a supercage occupancy of 2.5%.

The loading concentration of MTMAnP⁴⁺ is adjustable by controlling its concentration in the aluminosilicate gel before crystallization. The largest loading of *ca.* 5 mass% of the guest molecule can be achieved if 800 mg of MTMAnPCL₅ is added to *ca.* 94 g of aluminosilicate gel. We speculate that the main driving force for the very successful nano-inclusion of

MTMAnP⁴⁺ cations in the zeolitic supercages in such a readily controllable manner is the electrostatic interaction between the anionic aluminosilicate species and the cationic peripheral substituents on the porphyrin macrocycle. The excellent aqueous solubility of the cationic MP may contribute to the enhanced loading concentration in the zeolite, but this factor alone does not guarantee successful encapsulation. This assertion is supported by the following experimental facts: (a) in addition to MTMAnP⁴⁺, we have also successfully encapsulated other metalloporphyrins with cationic peripheral substituents into zeolitic cages such as metallo-tetrakis(*N*-methyl-4-pyridyl)porphyrins (M = transition metal ion); (b) metalloporphyrins with anionic peripheral substituents, such as metallo-tetra(4-sulfonatophenyl)porphyrin (MTPPS⁴⁻), could not be entrapped into the supercages of zeolite by this method; and (c) metalloporphyrins with neutral peripheral substituents, such as metallo-tetraphenylporphyrin (MTPP), could only be incorporated into the zeolite in trace amounts independent of the initial concentration of the porphyrin in the gel. On the other hand, it is believed that the first step in the construction of the zeolitic framework is the formation of anionic aluminosilicate species.

X-Ray powder diffraction (XRD) patterns of the unloaded zeolite and zeolite entrapped FeTMAnP⁴⁺ and MnTMAnP⁴⁺ are in excellent agreement with the calculated simulation of the XRD pattern for faujasite zeolite.¹⁰ The excellent signal to noise ratio in the XRD indicates that our synthesized faujasite crystals are of high quality. X-Ray induced fluorescence (XIF) analysis indicates that all the samples have a Si/Al ratio of *ca.* 1.6. This suggests that the framework around the guest molecule MTMAnP⁴⁺ is faujasite-Y (denoted MTMAnP@NaY) (M = Fe^{III}, Mn^{III} *etc.*). The encapsulation of the cationic MP inside the zeolite nanopores is also supported by TG, UV–VIS DRS, surface area measurements, and resonance microRaman spectroscopy (μ RR, *vide infra*). This observation suggests that the occluded MTMAnP⁴⁺ cations fit well into the supercages of faujasite-Y. In view of the 13 Å diameter of supercage of faujasite, *ca.* 18 Å MTMAnP⁴⁺ cation [across two opposite trimethylanilinium (TMan) substituents assuming a planar macrocycle] must distort itself somewhat in order to fit into a supercage. The most plausible distortion is that each of the four peripheral TMan groups swings toward one of the four channel windows (*ca.* 7 Å in diameter) tetrahedrally located in a supercage, leading to an overall ruffling of the macrocycle, a distortion commonly observed in the X-ray structures of similar MPs.¹¹

Resonance Raman techniques are very powerful in the study of heme proteins and zeolite confined molecules.^{12,13} Here, we applied μ RR to study the synthesized zeolite–porphyrin composites. Laser excitation at 632.8 nm, in close resonance with the Q₀ absorption band of MTMAnPCL₅, was used. Fig. 1 shows the μ RR spectra of MnTMAnPCL₅ and its faujasite-Y confined composite MnTMAnP@NaY. The normal modes of MnTMAnPCL₅ and other similar compounds have been thoroughly studied and assigned.¹³ Fig. 1 clearly shows that the basic RR features of MnTMAnPCL₅ are all retained in the spectrum of MnTMAnP@NaY, indicating that neither decom-

Table 1 Catalytic oxidation of cyclohexene with *t*-BHP over MnTMANP@NaY

No	Catalyst	Product distribution (%)				<i>t</i> ^a /h	Conv. (%)	TOF ^b /h ⁻¹
		Oxide	Diol	Acid	Others			
1	MnTMANP@NaY	18.9	77.4	1.4	2.3	24	5.0	2.1
2		15.7	75.7	5.8	2.8	48	28.6	6.1
3	MnTMANP@NaY ^c	12.4	87.6	Trace	Trace	24	24.5	10.2
4		12.4	69.5	18.1	Trace	48	45.1	10.3
5	H ₂ TMANP@NaY ^c	12.8	59.8	15.7	11.7	24	3.5	1.5

^a Reaction time. ^b Based on the efficiency of the inserted 'oxygen' into substrate. ^c 30 mg of pyridine was added into the reaction mixture (see text).

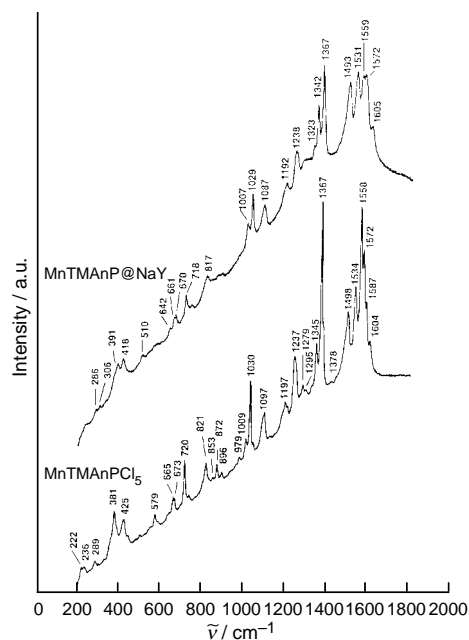


Fig. 1 Resonance microRaman spectra of MnTMANPCL₅ (blank) and MnTMANP@NaY; 632.8 nm excitation

position nor dimerization occurred during the process of hydrothermal crystallization. It is noticeable that (a) several structure sensitive bands located in the region 1300–1600 cm⁻¹, corresponding to the vibrations of $\nu(\text{C}_\alpha\text{-N})$, $\nu(\text{C}_\alpha\text{-C}_\beta)$, $\nu(\text{C}_\beta\text{-C}_\beta)$, and $\nu(\text{C}_\alpha\text{-C}_m)$ of the MP macrocycle,^{11–13} display some changes in their relative intensity but their frequencies remain more or less the same as that in the spectrum of MnTMANPCL₅; (b) the anilinium distortion modes located at 810–900 cm⁻¹ become broader and weaker in the spectrum of entrapped MP; and (c) the frequency of the Mn–N stretching mode at ca. 400 cm⁻¹ shifted markedly by ca. 10 cm⁻¹. All these changes of vibrational signatures of the entrapped MP indicate that the entrapped complex is indeed distorted in the cavity of faujasite-Y.

The catalytic oxidation of cyclohexene over zeolite confined metalloporphyrins (MnAnP@NaY) with *tert*-butyl hydroperoxide (*t*-BHP) was performed in a glass tube with a stopper in a standard manner. At 50 °C, using a ratio of 1:1.5 for cyclohexene to *t*-BHP, and a mole ratio of 12 000:1000:1 for solvent:reactant:catalyst, we obtained a 28.6% conversion of cyclohexene with an average of 6.1 h⁻¹ turnover frequency (TOF) in 48 h when MnTMANP@NaY was used as the catalyst. Of particular interest is that the catalytic activity of MnTMANP@NaY is enhanced ca. fivefold in the presence of pyridine in the first 24 h (Table 1, entries 1 and 3). Everything else being the same as above, a blank experiment using H₂TMPyP@NaY gave a conversion of 3.5%, much lower than that of 24.5% for

MnTMANP@NaY (entries 3 and 5). This shows clearly that the encapsulated MP is indeed involved in the oxidation process. Longer reaction time leads to >90% conversion of cyclohexene and gives adipic acid as the main product. To the best of our knowledge, this is the highest catalytic activity ever achieved in cyclohexene oxidation using a zeolite confined transition metal complex as catalyst. No significant loss of activity was detected in the reaction process. The mixture of the final products is colourless and no leaching of MPs into the reaction solution was detected according to atomic absorption spectroscopy. The catalytic activity of our catalyst was completely recovered by filtration of the reaction solution and washing of the catalyst with acetone at room temperature.

In conclusion, we have developed a novel, efficient and quantitative method to synthesize high purity metallo-tetrakis(*N,N,N*-trimethylanilinium) porphyrin encapsulated in the supercages of faujasite-Y. This method introduced an electrostatic interaction between the host (zeolite) and the guest (cationic MPs) in a 'built-bottle-around-ship' approach. The loading of the guest molecules can be adjusted easily by controlling the initial concentration of cationic MPs in aluminosilicate gel. In our preliminary study of the catalytic oxidation of cyclohexene by *t*-BHP, MnTMANP@NaY gives very high activity and epoxidation selectivity. Its activity was enhanced ca. fivefold when pyridine was added to the reaction mixture.

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Notes and References

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