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Synthesis and Catalytic Capability of Zeolite-Encapsulated Iron and Manganese Tetramethylporphine Complexes

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Synopsis. Iron and manganese tetramethylporphine (TMP) complexes were synthesized within the cages in NaY zeolite. The ligation of porphine to the metals enhanced the capability of ion-exchanged zeolite to oxidize saturated hydrocarbons with hydrogen peroxide.

The development of efficient oxidation catalysts which mimic the mono-oxygenase cytochrome P-450 has recently received a lot of attention.[1-3] Supporting metalloporphyrins onto a rigid support has been found to provide an ideal catalyst which imitates the high specificity and activity of the enzyme.[4-6] Site isolation of the active center created by bonding to the support is thought to prevent the formation of less reactive dimers, e.g. (μ-oxo)metalloporphyrin dimers and affect the catalytic activity favorably.

Herron and his co-workers synthesized zeolite-encapsulated iron phthalocyanine complex, and used it with iodosobenzene as the oxidizing system.[7] They showed that the concept of using a zeolite as a support for partial oxidation catalyst system is viable. Since the complex synthesized within the supercages of faujasite type zeolites is too large to pass through the ehannels of the zeolite, the dimer formation leading to deactivation would be prevented. We present here the synthesis of metalloporphyrin complexes in zeolite micropores and their activity in the oxidation of saturated hydrocarbons using hydrogen peroxide as an oxidizing agent.

Although 5,10,15,20-tetraphenylporphine is most commonly used as the ligand of model compounds of cytochrome P-450 and is easily synthesized in good yield, the molecule seems too large to be accomodated within the large pore zeolites NaX and NaY. We thought 5,10,15,20-tetramethylporphine (TMP) might be constructed within the supercages of NaY, applying the Rothemund method in the presence of Fe(II) or Mn(II) ion which had been introduced into the zeolite micropores by the ion exchange method.

Experimental

Ion-Exchanged Zeolite. NaY zeolite (20 g) with Si/Al=9.6 was suspended in distilled water (500 cm^3), and the mixture was degassed by bubbling nitrogen for 2 h at room temperature. $Fe_2SO_4\cdot 7H_2O$ (1 g) was dissolved in degassed distilled water (50 cm^3) under nitrogen atmosphere, and the solution was added to the NaY suspension. The resultant mixture was stirred at 80—90 °C for 2 h, and was allowed to stand for 24 h at room temperature under nitrogen atmosphere. Filtration and drying were carried out under nitrogen.

Porphyrin Synthesis. Methanol was degassed by bubbling nitrogen for 3 h. Pyrrole and acetaldehyde were degassed by means of the repeated freezing-pumping method. Pyrrole (15 cm^3) and acetaldehyde (20 cm^3) were added to a suspension of Fe(II)-Y zeolite (5.0 g) in methanol (500 cm^3) and the mixture was refluxed under nitrogen atmosphere for 2 h. The resulting mixture was allowed to stand for 12 h at room temperature. Filtration, washing with methanol and drying were carried out under nitrogen.

Characterization. Ion-exchanged zeolite was dissolved with hydrofluoric acid and the solution was subjected to atomic absorption analysis to determine the metal loadings. Diffuse reflectance visible spectra of the catalyst powders were recorded on a Hitachi 340 spectrophotometer.

Hydrocarbon Oxidation. A typical oxidation run used 1.0 g of a catalyst in cyclohexane (10 cm^3) in a round-bottom flask, to which was added 30% aqueous solution of hydrogen peroxide (10 cm^3). The resulting mixture was stirred for 1 h at 50 °C. Catalysts were filterd off, and both the organic and aqueous phases were subjected to gas chromatographic analysis with a Shimadzu Model GC-14A equipped with a flame ionization detector and a 3 m PEG-20M/KOH column.

Results and Discussion

Rothemund found that TMP was formed by refluxing pyrrole and acetaldehyde in methanol for 15—25 h.[8] An increase in porphyrin yield in the presence of metallic cations has been noted in a variety of porphyrin condensation reactions.[9] We anticipated

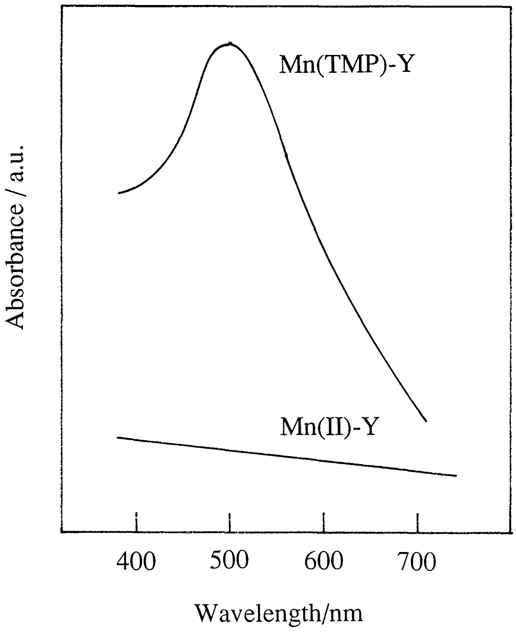

Fig. 1. Diffuse reflectance spectra of the Mn(II) exchanged zeolite: Effect of tetramethylporphine ligation to metal.

Table 1. Cyclohexane Oxidation Catalyzed by Ion-Exchanged Y-Zeolite and TMP Ligated Ion-Exchanged Y-Zeolite[a)]

Exchanged ion	TMP ligation	Metal loading	Yield/mol (mol-metal)$^{-1}$	
		%	Cyclohexanol	Cyclohexanone
Mn(II)	No	6.6	0.002	n.d.[b)]
Fe(II)	No	0.94	0.09	0.19
Fe(III)	No	5.7	n.d.[b)]	n.d.[b)]
Mn(II)	Yes	6.6	0.27	0.13
Fe(II)	Yes	0.94	0.16	0.59
Fe(III)	Yes	5.7	0.11	0.31

a) Catalyst 1.0 g, cyclohexane 93 mmol, hydrogen peroxide 88 mmol, 50 °C, 1 h. b) Not detected.

that Fe(II) or Mn(II) ion introduced in advance could promote the rate-limiting ring closure reaction by chelation of the intermediate species into a favorable steric configuration.[10)] Figure 1 shows a marked difference in the diffuse reflectance visible spectra between the TMP ligated and unligated Mn(II)-exchanged Y-zeolite. Absorption band centered at 500 nm should be assigned to the Soret band of the porphyrin ring and is a strong evidence of porphine ring formation in the zeolite.[11)] Absorption around Q-band region was not observed, suggesting that the conjugated plane of tetramethylporphine is considerably distorted owing to the limited free space inside the NaY cage.[12)]

The simplest over-all formation reaction in the presence of metallic cation might be

$$4\ \text{pyrrole} + 4\ \text{acetaldehyde} + 3[\text{O}] + \text{M}^{2+} \longrightarrow \text{M-TMP} + 4\text{H}_2\text{O} + 3\text{H}_2[\text{O}] + 2\text{H}^+$$

where [O] represents 2 oxidizing equivalents of any suitable oxidant and might be identified with either acetaldehyde or $1/2\text{O}_2$.[10)] Although the condensation reaction was carried out under nitrogen in the case of Fe(II)-Y and Mn(II)-Y, there might remain some adventituous molecular oxygen in methanol, causing the conversion of chlorin to porphyrin.

Catalytic activities of Mn(II)- and Fe(II)- exchanged Y-zeolites and that of TMP ligated Mn(II)- and Fe(II)-Y-zeolites are compared in Table 1. TMP ligation to Mn(II) greatly improved the oxidation activity of Mn(II)-Y zeolite which otherwise gave trace amount of cyclohexanol. TMP ligation to Fe(II) also significantly increased the yields of cyclohexanol and cyclohexanone. In all cases, the reaction did not proceed catalytically. In this regard it is to be mentioned that most of internal metal sites might be blocked from substrate access by those complexes nearer the external surface of the zeolite particle, resulting in an underestimate of the turnover. It is also to be noted that the catalytic turnover number of Fe(TMP)-Y is comparable with that of FePc-Y (zeolite encapsulated iron phthalocyanine) which we applied to the same oxidation reaction as a control, giving an oxygenate yield of 1.0 mol/mol-Fe.

While Fe(III)-Y was completely inactive in cyclohexane oxidation, TMP ligated Fe(III)-Y gives some oxidized products, suggesting that TMP enhanced the interaction between Fe(III) and oxygen atom. Another possibility is the reduction of Fe(III) to Fe(II) by acetaldehyde on preparation.

Neither Cu(I)- nor Cu(II)- exchanged Y-zeolite yielded oxygenated products, indicating that the cyclohexane oxidation should not proceed through Haber–Weiss type reaction mechanism.[13)] If the active species of the reaction was the hydroxyl radical generated from hydrogen peroxide, Cu(I)- exchanged Y-zeolite would exhibit activity comparable with Fe(II)- exchanged Y-zeolite. This finding together with the activity enhancement by TMP ligation suggests the active species is an oxygen adduct of the exchanged metal ion, which has been acknowledged as the active center of biomimetic systems of cytochrome P-450.

Fe(II) ion was also introduced by means of the ion exchange method into other zeolites with different pore sizes such as ZSM-5 (5.4×5.6 Å), mordenite (6.7×7.0 Å) and dealuminated Y-zeolite (7.4 Å). On cyclohexane oxidation the dealuminated Y-zeolite gave the highest yield (4.0 mol/mol-Fe) of cyclohexanol and cyclohexanone, while ZSM-5 and mordenite showed little activity probably because the micropores of the latter zeolites are too small for substrate molecules to diffuse. Fe(II)- exchanged dealuminated Y-zeolite exhibited less activity in heptane oxidation (0.39 mol of total oxygenates/mol-Fe) than in cyclohexane oxidation, indicating that no reactant shape selectivity was observed in contrast with the titanosilicate catalyzed oxidation of hydrocarbon with hydrogen peroxide.[14,15)]

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