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Oxidation of Alkanes Catalyzed by Zeolite-Encapsulated Perfluorinated Ruthenium Phthalocyanines

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The oxidation of alkanes catalyzed by metal complexes is often hampered by oxidative degradation of the catalyst and/or deactivation by irreversible dimerization of the complexes. In the case of porphyrin- or phthalocyanine-based catalysts, halogenation of the macrocycle periphery has proven to be effective at enhancing the complex stability as well as the activity.[1−8] The halogen substituents replace abstractable hydrogens and render the ligand less susceptible to electrophilic attack. Additionally, the central metal ion becomes easier to reduce via inductive effects. The electron-withdrawing substituents also destabilize normally unreactive μ-oxo dimers. In spite of such improvements, these systems eventually degrade.

An alternative strategy to enhance the lifetime and activity of such catalysts involves site isolation of the metal complexes within the micropores of zeolites. Both porphyrins and phthalocyanines have been encapsulated in the supercages of X- and Y-type zeolites via a variety of synthetic methods.[9] Intrazeolite iron(II) phthalocyanines have shown promise as catalysts for the oxidation of alkanes, exhibiting activity as much as 3 orders of magnitude greater than that of the homogeneous catalysts. Generally, peroxides or iodosylbenzene are employed as oxidants. However, iodosylbenzene leads to zeolite pore blockage, and peroxides can bleach the catalyst unless added slowly in a controlled fashion. Parton et al. recently circumvented the problem with peroxides by incorporating the zeolite-encapsulated FePc complex in a polymer matrix.[10] The polymer serves to inhibit the preferable adsorption of peroxide over alkane and therefore enhances the catalyst stability. We have examined the encapsulation of a perfluorinated iron(II) phthalocyanine in NaX and NaY zeolites as a strategy toward a more stable oxidation catalyst. However, we found the $FeF_{16}Pc$ intrazeolite complex to be equally as sensitive to high concentrations of peroxide as FePc. We thus turned our attentions to the preparation of the isoelectronic ruthenium complexes. Recent studies of ruthenium porphyrin[11] and phthalocyanine[12] complexes indicate they can function as oxidation catalysts. In this paper, we report the preparation of $RuF_{16}Pc$ and zeolite NaX-encapsulated $RuF_{16}Pc$. Preliminary results indicate that the intrazeolite $RuF_{16}Pc$ is an effective oxidation catalyst and apparently is more stable than the iron(II) analogs.

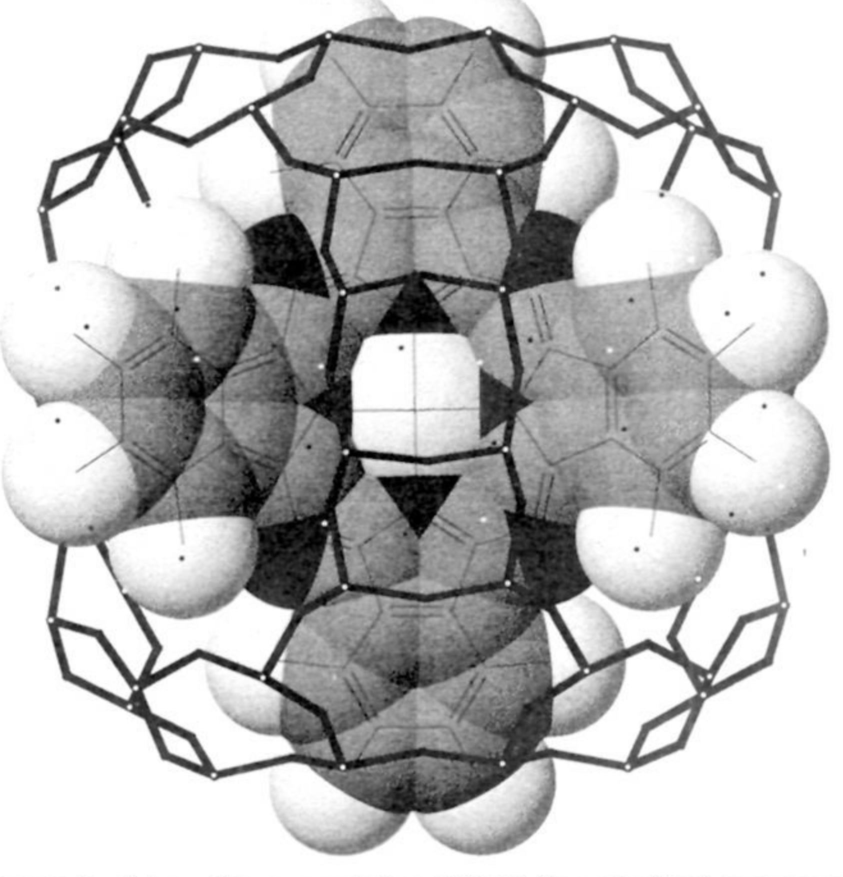

Figure 1. Schematic representation of $RuF_{16}Pc$ and a NaX supercage containing $RuF_{16}Pc$ calculated using MM2 parameters and CAChe molecular modeling.

The $RuF_{16}Pc$ complex was prepared by the reaction of tetrafluorophthalonitrile and $Ru_3(CO)_{12}$ in chloronapthalene at 280 °C under a stream of N_2. The resulting royal blue $RuF_{16}Pc$ complex was purified by column chromatography and characterized by elemental analysis and mass spectrometry as well as FT-IR and UV−vis spectroscopy.[13] The $RuF_{16}Pc$ complex can be readily isolated without contamination from the CO adduct, which is in contrast to the non-fluorinated phthalocyanine, which forms only the stable RuPc(CO) complex. $RuF_{16}Pc$ was encapsulated inside the supercages of zeolite NaX following a procedure similar to that previously described for the preparation of NaX-$FeF_{16}Pc$[14] or NaX-$CoF_{16}Pc$.[15] This involved the synthesis of zeolite NaX around the $RuF_{16}Pc$ complex. This approach provides many advantages over in situ or template methods of inclusion, where free metal ions or uncomplexed ligand often result.[9] The highly crystalline zeolites containing metal complexes were solvent extracted with acetone and pyridine to remove surface species and characterized by XRD, FT-IR, and UV−vis spectroscopy as well as elemental analysis. $RuF_{16}Pc$ is physically trapped in the supercages of NaX, as illustrated by the calculated structure shown in Figure 1. The intact $RuF_{16}Pc$ complex can be recovered only after partial digestion of the zeolite with H_2SO_4. Elemental analysis reveals metal complex loadings on the order of ~1 complex per 125 NaX supercages. This corresponds to an encapsulation efficiency of ~25% from the crystallization gel. This relatively low loading is important in maintaining diffusion pathways

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(13) $RuF_{16}Pc$ was isolated as a royal blue powder. Elemental analysis for $RuF_{16}C_{32}N_8$ was calculated: Ru/F = 0.062, Ru/C = 0.030, Ru/N = 0.12. Found: Ru/F = 0.061, Ru/C = 0.026, Ru/N = 0.11. FABMS: *m/e* = 902. UV−vis, λ nm (ϵ): 323 (3.9×10^4), 352 (1.8×10^4), 562 (1.3×10^4), 615 (5.6×10^4). FT-IR (cm^{-1}): 612 (mw), 839 (mw), 966 (vs), 1169 (s), 1271 (m), 1311 (m), 1459 (m), 1493 (vs), 1553 (s).

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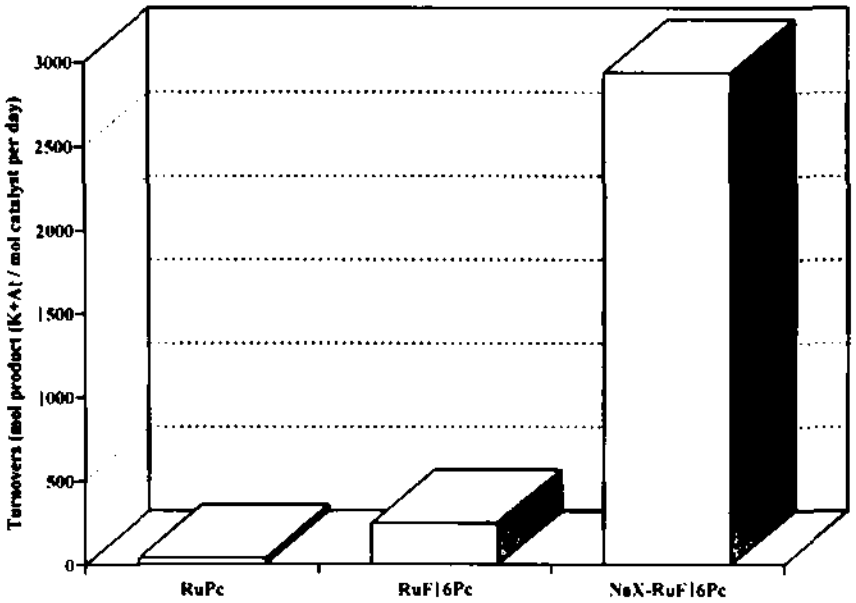

Figure 2. Plot of turnovers (moles of ketone + alcohol/moles of catalyst) per day for the oxidation of cyclohexane catalyzed by RuPc, $RuF_{16}Pc$, and NaX-$RuF_{16}Pc$.

during catalysis. The UV−vis spectra show that the characteristic Q band for the intrazeolite complex is red-shifted 644 nm from the outer surface physisorbed complex (622 nm) or the solution $RuF_{16}Pc$ complex (616 nm, acetone). This shift to lower energy has been ascribed to a slight distortion of the macrocycle inside the supercage[9] but may also arise from other interactions between the complex and the zeolite lattice.

Both the free $RuF_{16}Pc$ complex and the intrazeolite NaX-$RuF_{16}Pc$ complex were found to be catalysts for the oxidation of cyclohexane to the corresponding cyclohexanone (K) and cyclohexanol (A) at room temperature using *tert*-butyl hydroperoxide (*t*-BOOH) as the oxidant. The oxidation reactions were carried out in sealed vials containing a mixture of 0.3 mL (2.4 mmol) of *t*-BOOH, 0.66 mL (6 mmol) of cyclohexane, 0.1 g (0.0002 mmol of complex) of NaX-$RuF_{16}Pc$ or 0.004 g (0.0044 mmol) of $RuF_{16}Pc$, and 1.5 mL of acetone as solvent. The peroxide can be added to the reaction through a septum as needed. The amount or rate of peroxide addition does not appear to significantly affect the catalytic activity. If we assume that 1 mol of ketone product is formed for every 2 mol of peroxide, then a molar excess of *t*-BOOH greater than 2 times the concentration of substrate would ultimately have to be added to ensure complete conversion. Products were quantified by gas chromatography and verified by mass spectroscopy. The oxidation reactions were performed under nitrogen.

Figure 2 shows a plot of the number of millimoles of product (K + A) per millimole of $RuF_{16}Pc$ per day for the RuPc-, RuF_{16}-Pc- and NaX-$RuF_{16}Pc$-catalyzed oxidation of cyclohexane. The RuPc is a poor catalyst and is completely deactivated after a few hours. This is evidenced by a bleaching of the blue RuPc to form a yellow-brown solid. As anticipated, perfluorination of the phthalocyanine ligand results in a more stable and active catalyst. Cyclohexane is oxidized in the presence of $RuF_{16}Pc$ at a rate of ~250 turnovers/day with no signs of deactivation after 1 week. Unfortunately, the activity is slower than one would like because of rapid dimerization of the complexes. Formation of the $F_{16}PcRu{-}O{-}RuF_{16}Pc$ (νRu−O, 721 and 731 cm^{-1}) is accompanied by a change in color from blue to green and a shift in the Q band to 663 nm. Since this complex is still catalytically active, the dimer must be in equilibrium with monomeric species as a result of the electron-withdrawing effect of the fluorine substituents. Similar behavior has been noted before in the case of fluorinated iron porphyrin oxo dimers,[1,2] which are also catalytically active. Encapsulation of $RuF_{16}Pc$ complexes with in the supercages of NaX precludes dimerization, and Figure 2 clearly illustrates the enhanced catalytic activity that results. Even though the zeolite-catalyzed reactions contain less metal complex, they are >10 times more active than the homogeneous catalyst, which is an effect of site isolation. Cyclohexane is oxidized to primarily the ketone at a rate of nearly 3000 turnovers/day, and there is no sign of deactivation after >20 000 turnovers (~70% conversion of cyclohexane). Incorporation of the complex inside the zeolite increases the selectivity toward cyclohexanone (98.4% vs 67%) compared with the homogeneous complex. Additionally, the peroxide efficiency improves from 55% for $RuF_{16}Pc$ to a maximum of 97% for NaX-$RuF_{16}Pc$.

The intrazeolite $RuF_{16}Pc$ complex also exhibits shape selectivity in the oxidation of cycloalkanes, providing further evidence for the location of the active sites. For example, RuF_{16}-Pc exhibits very little difference in activity for the oxidation of cyclododecane versus cyclohexane (243 vs 258 turnovers/day). However, NaX-$RuF_{16}Pc$ demonstrates a clear preference for the smaller cyclohexane (2933 vs 295 turnovers/day), which is a consequence of the steric constraints imposed by the zeolite channels.

Detectable products are observed for a catalyst/substrate ratio of 3×10^{-5} after 8 h. However, the addition of AIBN (2,2′-azobis[isobutyronitrile]), a radical initiator accelerates the reaction. The addition of hydroquinone to the mixture completely inhibits the reaction, suggesting that the oxidation of cyclohexane is radical in nature. Further mechanistic studies are in progress.

We have shown that $RuF_{16}Pc$ is an effective catalyst for the room temperature oxidation of cycloalkanes. Site isolation of the $RuF_{16}Pc$ complex in zeolite NaX clearly enhances the catalytic activity and selectivity. In terms of activity and stability, this system holds promise as one of the best low-temperature peroxide-based oxidation catalysts of its kind.

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