Shape Selectivity in Hydrocarbon Oxidations using Zeolite encapsulated Iron Phthalocyanine Catalysts

Norman Herron,* Galen D. Stucky, and Chadwick A. Tolman
Central Research and Development Department, E. I. du Pont de Nemours and Company, Experimental Station, Wilmington, DE 19898, U.S.A.

The oxidation of alkanes by iodosobenzene is catalysed by iron phthalocyanine encapsulated inside large pore zeolites NaX and NaY so that the product alcohols and ketones show an improved yield and altered selectivity as compared to the unencapsulated complex.

Our approach to the goal of selective partial oxidation of unactivated alkanes has been to design and synthesize an inorganic mimic of the remarkable enzymes: cytochromes P450.[1] A zeolite framework with an encapsulated metal catalyst has been prepared wherein the zeolite structure can impose sieving and orientating effects upon substrates approaching the otherwise non-selective metal active sites. The zeolite supercages[2] also provide 'reaction vessels' of molecular dimensions wherein the selective catalytic oxidations of current interest can take place. The catalytic system we have chosen to investigate follows the lead of the porphyrin literature[3] and uses an encapsulated phthalocyanine complex and iodosobenzene as the oxidizing system. The similarities to the natural enzymes are evident, and we report here results which indicate enhanced selectivities for these novel catalyst species.

A modified synthetic scheme, similar to that previously reported,[4] leads to iron phthalocyanine (FePc) inside the large pore zeolites NaX and NaY.† After synthesis it is essential that that portion of the metal complex which forms on the external surface of the zeolite particle be removed otherwise, because of diffusional considerations, this will tend to dominate the ensuing catalytic chemistry.[2] Such removal is accomplished by extended soxhlet extraction of the zeolite

with pyridine and α-chloronaphthalene. The resultant blue–green powders have good X-ray powder diffraction patterns (zeolite still crystalline, no pattern from crystalline phthalocyanine complexes), diffuse reflectance vis.–u.v. spectra consistent with phthalocyanine formation, analytical data in good agreement with the calculated Fe:C:N ratios for complete conversion of all iron atoms into FePc, X-ray photoelectron spectra showing no detectable surface iron, and a reduced sorption capacity of the zeolite for water since some of the internal pore volume is now occupied by FePc.

Oxidation of substrates was carried out with 30% by volume of substrate in CH_2Cl_2: 1 ml of this stock solution, 100 mg zeolite catalyst, and 100 mg iodosobenzene were sealed and stirred in air at room temperature overnight. Products were identified by capillary g.c. and all yields and selectivities are compared against the intrinsic selectivity of FePc itself under the same conditions.

Yields, expressed as turnovers on the iron complex present in the oxidation of methylcyclohexane, were: FePc, 1.1; FePc in zeolite NaX (2.4 wt% Fe), 0.5; FePc in zeolite NaX (0.24 wt% Fe), 4.1; FePc in zeolite NaY (0.13 wt% Fe), 5.6. The dramatic effect of the complex loading level on turnover may be explained by a pore blocking mechanism if one realizes that a loading of 2.4 wt% Fe corresponds to approximately 1 complex per supercage of the zeolite.[2] At this loading level most of the internal metal sites are blocked from substrate access by those complexes nearer the external surface of the zeolite particle; it follows that the turnover quoted (based on *all* iron sites present) is an underestimate based on those sites which are actually accessible. It is significant that the turnover in the lower loading cases considerably exceeds that for the native FePc itself, and this is due to an increased lifetime for

---

† Iron(ii) ion exchanged zeolite (2 g) is mixed with phthalonitrile (2 g) in an inert atmosphere glove box. The mixture is heated to *ca.* 200 °C and sealed. The molten slurry is stirred (4 h) and then cooled to room temperature. The originally pale green zeolite becomes deep blue–green during the reaction and is washed extensively with acetone and methanol to remove excess phthalonitrile prior to the soxhlet extractions.
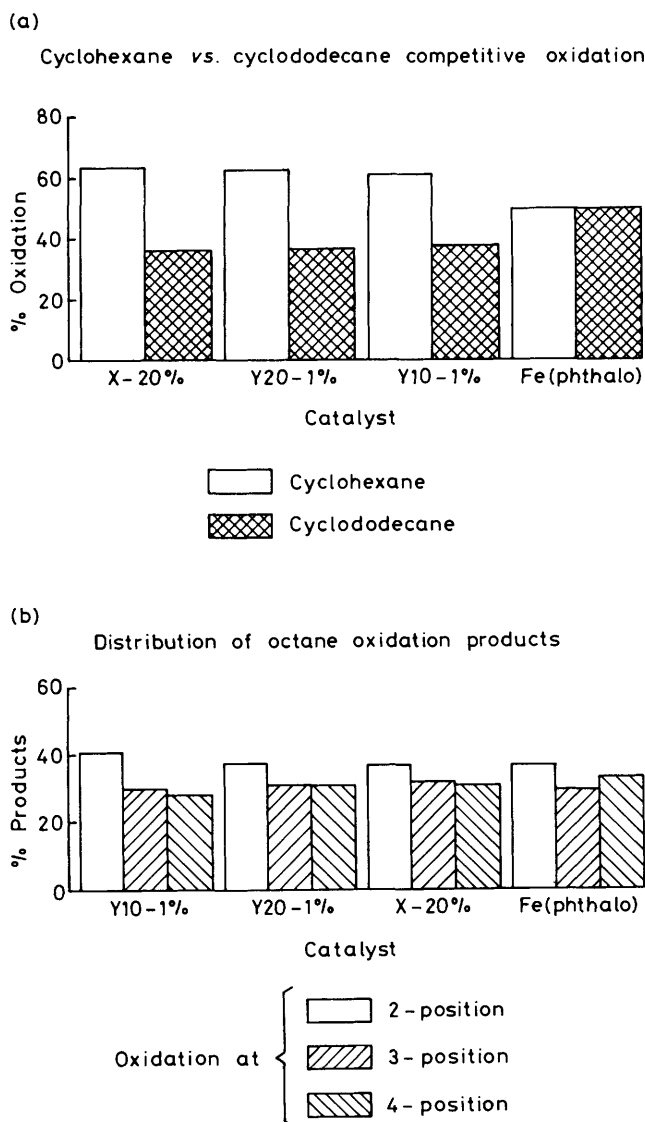
(a)

Cyclohexane vs. cyclododecane competitive oxidation

(b)

Distribution of octane oxidation products

Figure 1. Bar chart representation of (a) the competitive oxidation of cyclohexane and cyclododecane; (b) regioselectivity of n-octane oxidations. In both cases oxidation products are the sum of alcohols and ketones at each position. Catalyst designations are:

Y10-1% = Linde Zeolite ELZ-10 (Zeolite Y) containing 0.13 wt% iron (*ca.* 1% of exchange capacity).

Y20-1% = Linde Zeolite ELZ-20 (Zeolite Y) containing 0.13 wt% iron (*ca.* 1% of exchange capacity).

X-20% = Zeolite 13X containing 2.4 wt% iron (*ca.* 20% of exchange capacity).

the active catalyst inside the zeolite. It has been shown that a prominent mode of catalyst loss in this type of oxidizing system involves a bimolecular self destruction,[5] a process precluded in the zeolite entrapped systems by the restrictions of the internal zeolite structure. In support of this idea, the encapsulated FePc remains blue–green while the unsupported FePc turns dark brown as it is destroyed.‡

‡ The turnovers quoted for the zeolite entrapped catalysts do not represent an upper limit since we believe the catalytic reaction does not stop because of catalyst loss but rather because of zeolite plugging by reaction by-products. The used catalyst, if recovered, vacuum oven dried, and then reused, exhibits its initial catalytic activity. G.c. analysis of the organic products which are responsible for the plugging indicate that iodoso- or iodoxy-benzene is the culprit.

The expected substrate selectivity of the zeolite catalyst is shown in a competitive oxidation of cyclohexane and cyclododecane (Figure 1a). The zeolite entrapped catalysts show a clear preference for oxidation of the smaller of the two substrates, such selectivity presumably arising from the molecular sieving action of the zeolite support. Altering the zeolite pore size by exchanging the residual Na^+ ions for larger monovalent cations leads to greatly increased selectivity for the smaller substrate to a maximum 90:10 ratio with ammonium or Rb^+ ions.

In the oxidation of n-octane regioselectivity is apparent (Figure 1b). A small but reproducible change in selectivity for oxidation away from the 4-position and towards the 2-position of octane is observed. This shift towards oxidation nearer the ends of the long axis of the molecule is also observed with methylcyclohexane and is interpreted as an orientating influence of the zeolite framework upon the substrate as it approaches the iron-oxo active site. It follows therefore, that the octane molecule, for example, will tend to resemble a rod poked through the window which views the FeO unit so that the ends of the rod will be the first to approach this potent oxidant. This orientation of substrate and oxidant (reminiscent of enzyme/substrate orientation phenomena) leads to preferential oxidation near the terminus of the long axis of the substrate. Indeed, trace amounts of octan-1-ol are detectable with the zeolite systems whereas the FePc itself produces no detectable terminal hydroxylation.

Stereoselectivity is also observed with the zeolite entrapped catalysts. With methylcyclohexane as substrate the ratio of *trans* to *cis* alcohols produced at the 4-position (relative to the Me group) is close to 2 for the zeolite catalysts whereas FePc itself yields a ratio of 1.1. Likewise, with norbornane substrate, the *exo:endo* norborneol ratio using the zeolite catalysts is close to 6 whereas FePc has a ratio of 9. This increased preference for oxidation at one of two diastereotopic hydrogens is another consequence of the substrate/catalyst relative orientation imposed by the zeolite which may position one of the two H atoms closer to the active oxidant FeO.

In conclusion, we have shown that the concept of using a zeolite as a support for partial oxidation catalyst systems is viable, and that it leads to increased yields and selectivities as a result of the zeolite interior structure. While rates are slow, the increased control of partial oxidation with such systems warrants further investigation. High selectivities in olefin hydrogenation have already been demonstrated.[6]

References

1 I. C. Gunsalus and S. G. Sligar, *Adv. Enzymol.*, 1978, **47**, 1; R. E. White and M. J. Coon, *Ann. Rev. Biochem.*, 1980, **49**, 315.
2 D. W. Breck, 'Zeolite Molecular Sieves,' Krieger Publishing, Malabar, FL, 1984.
3 J. T. Groves and D. V. Subramanian, *J. Am. Chem. Soc.*, 1984, **106**, 2177; J. P. Collman, T. Kodadek, S. A. Raybuck, and B. Meunier, *Proc. Natl. Acad. Sci. USA*, 1983, **80**, 7039.
4 V. Y. Zakharov and B. V. Romanovsky, *Vestn. Mosk. Univ., Khim.*, 1979, **20**, 94; B. V. Romanovsky, Proceedings of the International Symposium on Zeolite Catalysis, May 1985, p. 215; G. Meyer, D. Wohrle, M. Mohl, and G. Schulz-Ekloff, *Zeolites*, 1984, **4**, 80.
5 M. J. Nappa and C. A. Tolman, *Inorg. Chem.*, 1985, **24**, 4711.
6 D. R. Corbin, W. C. Seidel, L. Abrams, N. Herron, G. D. Stucky, and C. A. Tolman, *Inorg. Chem.*, 1985, **24**, 1800.