JOURNAL OF CATALYSIS **122,** 271–279 (1990)

Olefin Oxidation by Zeolite-Encapsulated Mn(salen)$^+$ Complexes under Ambient Conditions

CHRIS BOWERS AND PRABIR K. DUTTA[1]

Department of Chemistry, Ohio State University, Columbus, Ohio 43210

Received June 26, 1989; revised September 18, 1989

Zeolite-encapsulated manganese complex of the salen ligand [*N,N'*-ethylenebis(salicylideneaminato)] was synthesized, and its catalytic activity toward various olefins was examined. Iodosylbenzene was chosen to be the terminal oxidant. Oxidation products, which included the epoxide, alcohol, and aldehyde, are formed from cyclohexene, styrene, and *trans-* and *cis*-stilbene. In comparison with catalysis by Mn(salen)$^+$ complexes in solution, encapsulation lowers the rate of reaction considerably, but provides for selective oxidation based on olefin size and ability to penetrate the zeolite cages. © 1990 Academic Press, Inc.

The catalytic properties of transition metal complexes encapsulated in zeolite cavities have recently become of considerable interest (*1*). These materials hold the promise of combining the advantage of homogeneous and heterogeneous catalytic systems. The active transition metal site differs from the solution species only by the constraints placed upon it by the zeolite, allowing reactions to occur under mild conditions. Also, as the catalyst is trapped inside the zeolite, the products can be readily separated. Other influences, arising primarily from the architecture of zeolites, include reactant and product selectivity due to size constraints in the zeolite cages (*2*). In addition, the lifetime of the catalyst can be influenced by its encapsulation, since degradation pathways involving reactions such as dimerization of catalysts can be prevented.

Previous work in the area of zeolite-encapsulated metal complexes has included the use of metal carbonyls for the water-gas shift reaction, carbonylation of methanol and aromatic compounds, and hydroformylation (*3–6*). Studies on oxidation catalysts have been more limited. These include the synthesis of iron phthalocyanine in zeolite Y and oxidation of saturated hydrocarbons. Certain alcohols and ketones were observed to be formed, based on their sizes relative to the complex in a homogeneous system (*7*).

In this preliminary study, we focus on a Mn^{III}(salen) [salen = *N,N'*-ethylenebis(salicylideneaminato)] complex encapsulated in zeolite Y cavities as an oxidation catalyst. Several studies have looked at the catalytic activity of manganese, chromium, and nickel complexes of salen in homogeneous medium (*8–10*). Also, the metal complexes of this ligand are of an appropriate size (~10–11 Å), so once formed in the supercages of zeolite Y (~13 Å), the complex cannot escape through the 7-Å ring openings (*11*). Iodosylbenzene (PhIO) was chosen to be the terminal oxidant over sodium hypochlorite, since the entire system could be in one organic solvent (*12*). Also, the insolubility of PhIO in the solvent allows it to be easily separated from the reaction products. In addition, quantitative analysis of the PhI formed allows for direct measurement of the oxygen transferred to reactants.

EXPERIMENTAL

Materials. Zeolite Y (NaY, Union Carbide) was ion exchanged with 0.1 M NaCl

---

[1] To whom correspondence should be addressed.

0021-9517/90 $3.00

for 16 h prior to its use. PhIO was prepared via literature methods from its diacetate (Aldrich) (*10*). Styrene (Gold Label), salen, *cis*-stilbene, *trans*-stilbene, styrene oxide, *cis*-stilbene oxide, *trans*-stilbene oxide, cyclohexene oxide, iodobenzene, and 1-octene were purchased from Aldrich and were used as received. Acetonitrile, chlorobenzene, cyclohexane, and cyclohexanol were from Mallinkrocdt and were used without further purification. Cyclohexane (E/M Science) and $MnCl_2 \cdot 4H_2O$ (Baker) were used as received. The hexafluorophosphate salt of ferrocenium was prepared from ferrocene (Strem) and $NaPF_6$ (Alfa).

Synthesis of Mn(salen) inside zeolite Y. One gram of NaY is shaken overnight in a aqueous solution containing the desired amount of manganous ion. At these low levels (~1 mM) it is approximated that all the manganese goes from solution into the zeolite. The zeolite is then filtered and washed with deionized water to remove any chloride ions present. Next, the Mn-NaY is heated to 400°C under vacuum or flowing dry nitrogen to dehydrate the zeolite. The zeolite is then cooled and ground with 0.1 g salen in an inert-atmosphere glove box; the solid is then sealed into a tube and heated to 120°C for ½ h. After heating, the solid is a bright yellow color which is indicative of a Mn^{II}(salen) complex. Treatment up to this point was identical for catalysts A,B, and C. Catalyst A was then Soxhlet extracted with CH_3CN and ion exchanged with 0.1 M NaCl for 12 h; upon filtering, the solid turned a brown color. Catalysts B and C were reacted with a solution of ferrocenium ions under an inert atmosphere. Upon addition of ferrocenium ions, the catalyst turns from bright yellow to brown. Catalyst B was then ion exchanged with 0.1 M NaCl for 1 h, and catalyst C was simply washed with acetonitrile.

Instrumentation. Gas chromatography analysis was done on a Varian Aerograph Series 1400 using a 2-m 10% Carbowax 1540 column. The apparatus was equipped with a flame ionization detector. Column temperature was programmed to go from 100 to 160°C at 6°C/min. Generally, 1-μl aliquots were injected. HPLC analysis was done on an Alltech Econosil column using a 75/25 mixture of methanol and water. Ultraviolet detection was used.

Elemental analysis was done on a Kevex 0700 X-ray fluorometer. The X-ray diffraction patterns were taken with a Rigaku D/Max 2B diffractometer. Diffuse reflectance UV–VIS spectra were recorded with a Shimadzu UV-265 equipped with a Harrick diffuse reflectance attachment. Infrared spectra were taken of self-supporting wafers of the catalyst samples with a Mattson Cygnus 25 FT-IR. All inert atmosphere manipulations were performed in a Vacuum Atmospheres glove box.

Oxidation and analysis of products. All oxidations were done in 5 ml CH_3CN with ~0.2 mmol of olefin, ~0.2 mmol chlorobenzene (internal standard), 25 mg PhIO, and 100 mg of catalyst. Unless otherwise noted the reaction time was 16 h. GC analysis was performed on the solution before the addition of PhIO and catalyst. After the desired reaction time, the solution was centrifuged and subjected to another GC analysis. Initial and final GC analyses were done three times and the peaks were ratioed to the internal standard. This procedure was used for all trials; however, for solutions containing *cis*- or *trans*-stilbene HPLC analysis was also necessary to quantitate the stilbenes. To obtain appropriate sample concentrations it was necessary to dilute a 10-μl aliquot to 2 ml. The relative reactivity experiments were done in a similar manner. Products were identified by comparison of retention times with those from authentic samples.

To determine the catalyst turnover number, cyclohexene oxidation was carried out as above, but with 400 mg PhIO and 0.5 mmol cyclohexene. After 60 h, production of PhI ceased, and the amount produced was used to calculate an average turnover number per catalyst molecule.

Relative reactivities of different olefins.

The relative reactivities of olefins in competition with each other were checked for catalysts A,B, and C with cyclohexene and styrene. In addition, for catalyst A *cis*-stilbene and *trans*-stilbene were compared to cyclohexene. The relative reactivity was calculated from the equation $k_x/k_y \cong \log(X_f/X_i)/\log(Y_f/Y_i)$, where X_i and Y_i are the initial concentrations of the olefins and X_f and Y_f are the final concentrations of these olefins (*10*).

Quantification of Mn in catalysts. The amounts of manganese in the various catalysts was determined by XRF. A calibration curve was set up by ion exchanging a known amount of manganese into a weighed amount of NaY. These samples were pressed into pellets as were the catalyst samples. The samples were analyzed with direct excitation for 300 s at 13 kV and 0.01 mA, in an evacuated sample chamber. The standard samples were used to set up a calibration curve which was used to determine the manganese content of the catalyst samples. The calibration curve could be set up using absolute manganese intensity or by ratioing the manganese peak to the silicon peak. Both methods gave straight lines for the calibration curve and the final results generally agreed within 5%. Figure 1 shows a typical calibration curve.

RESULTS

The reaction that is the focus of this investigation is

$$\text{hydrocarbon} + \text{PhIO} \xrightarrow{\text{zeolite catalyst}} \text{products} + \text{PhI}.$$

No reaction occurred if PhIO was excluded from the reaction system or if Na-exchange zeolite Y was used as the catalyst. It is clear that interaction of PhIO with the transition metal zeolite forms the active oxygenating species. The ratio of hydrocarbon that reacts to PhI formed provides a direct measure of the amount of hydrocarbon interacting with the catalyst.

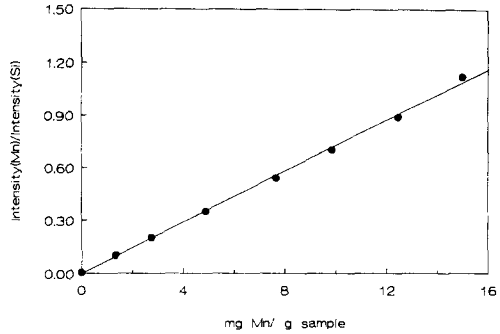


FIG. 1. Calibration curve for Mn in zeolite determined by energy-dispersive X-ray fluorescence.

Mn-Y. Mn^{2+}-exchanged zeolite Y (13 mg Mn/g zeolite, 1 Mn^{2+} per 2 supercages) exhibits catalytic activity in the oxidation of cyclohexene and styrene. The amount of manganese in the zeolite is 0.023 mmole. In both cyclohexene and styrene, about 60% of the PhIO reacts with the olefin. Cyclohexenol and phenylacetaldehyde are the major products, with selectivities of 16 and 27% as compared to the total olefin that has reacted. No epoxide was detected in the cyclohexene case, whereas only a small amount (4%) of styrene oxide was formed.

Mn(salen)–Y. Three catalyst preparations were examined. All of these were made starting from Mn^{II}(salen)–zeolite Y. This solid was a bright yellow, and its diffuse reflectance spectrum is shown in Fig. 2, with characteristic bands at 270 and 407 nm. Soxhlet extraction of this material with CH_3CN in an aerobic environment led to formation of a brown solid. Ion exchange with 0.1 M NaCl to remove unreacted Mn^{2+} ion led to preparation of the first catalyst sample (catalyst A). Catalyst A was found to contain 1.7 mg Mn/g of zeolite, while the starting MnNaY used to make this catalyst contained 7 mg Mn/g MnNaY. Diffuse reflectance and infrared spectra of catalyst A are shown in Fig. 3. The bands in the electronic spectrum at 231, 283, 314, 350, 382, and 500 nm are in fairly good agreement with a solution spectrum of $Mn(salen)^+$ PF_6^-. The IR spectra, with bands at

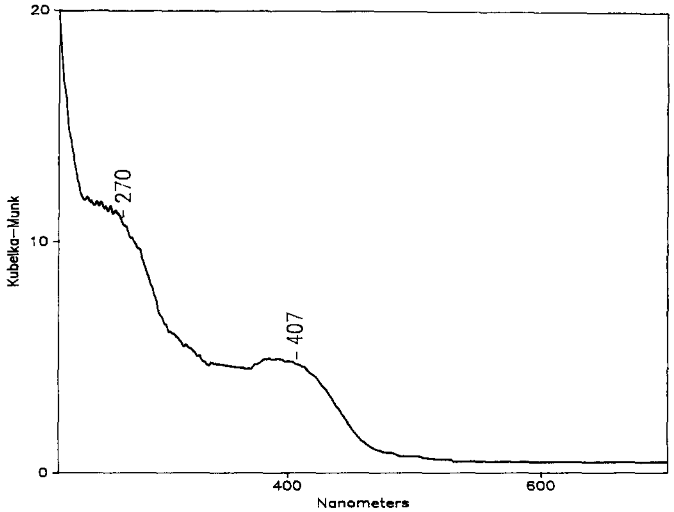
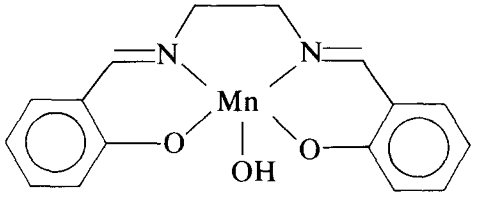


FIG. 2. Diffuse reflectance spectra of Mn^{II}(salen) encapsulated in zeolite Y (Kubelka-Munk with reference to NaY).

1609, 1583, 1512, 1468, 1448, 1414, 1396, 1290, 1232, and 1182 cm^{-1}, are also in fair agreement with the published data (*10*). Aerobic oxidation of Mn^{II}(salen) complexes in solution is very complicated (*13*). Based on magnetic measurements, a complex set of products has been proposed. These include Mn^{III}(salen)OH, as well as oxybridged structures and polymeric forms represented by [Mn(salen)O]$_n$ (*14, 15*). In the zeolite, there is no room in the supercages for polymerization of the Mn(salen) species. Also, the mobility of Mn(salen) through the zeolite is restricted because of the 7-Å ring openings of the supercage. We propose that the oxidation product is of the form Mn^{III} (salen)OH (Scheme I) on the basis of the spectroscopic properties and the constraints of the zeolite. It is important to point out that in contrast to solutions, in the zeolite, architecture is responsible for stabilizing the Mn^{III} monomeric complex.

Reactions of various olefins with catalyst A were examined and are shown in Table 1. The total amount of catalyst used in these experiments is 0.003 mmol of Mn^{III}(salen). In the case of cyclohexene, the amount of olefin that reacts is comparable to the amount of PhI formed. About 24% of the olefin could be accounted for in terms of the products cyclohexene oxide and cyclohexenol. A typical GC trace of the products is shown in Fig. 4. Styrene is also oxidized by this catalyst, forming two major products: styrene oxide and phenylacetaldehyde. Unlike cyclohexene, only about 60% of the styrene reacts with the oxygenated catalyst. It is possible that the initial products of the oxidation are reacting with the catalyst rather than styrene. To examine this possibility, styrene oxide and cyclohexene were reacted with the catalyst. It was found that while cyclohexene was oxidized, styrene oxide could be recovered quantitatively, indicating that the oxide is fairly inert to oxidation in the presence of olefin. A second possibility is that the ligand salen is being



SCHEME 1

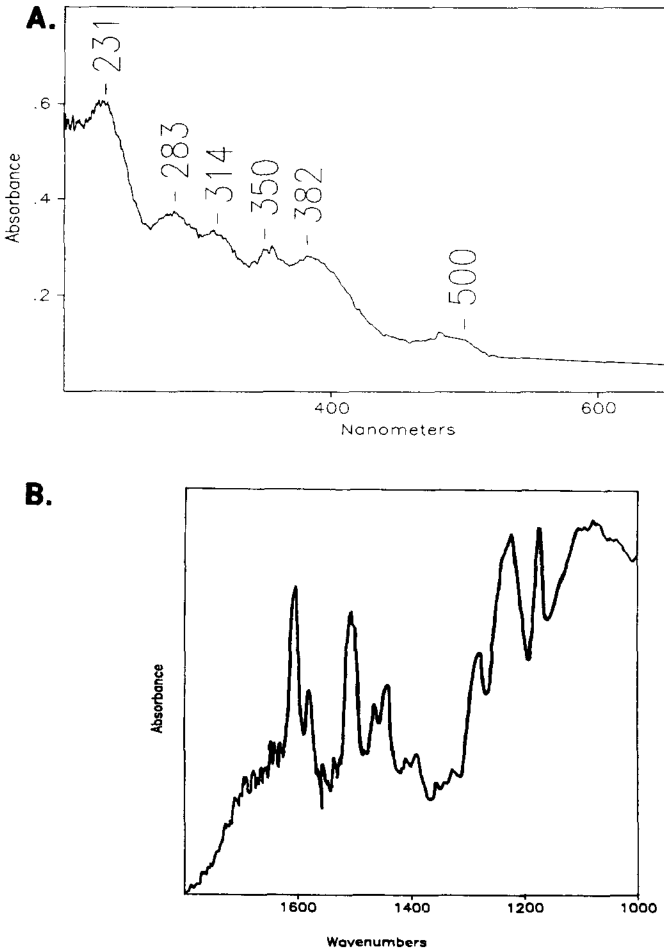


FIG. 3. (a) Diffuse reflectance spectra of Mn^{III}(salen)–Y. (b) Transmission infrared spectra of Mn^{III}(salen)–Y.

oxidized, especially since such effects have been observed with Cr(salen) in solutions (*8*). It is important to note, however, that due to encapsulation of Mn(salen) complexes in the zeolite supercages and the low loading levels, any direct interaction between Mn(salen) complexes in the zeolite is highly unlikely. There are 3.1×10^{-6} mole of Mn(salen) in a sample of catalyst A in a typical reaction. To fully account for the PhIO that does not react with styrene, each salen ligand would have to be oxidized 11 times on the average. The fact that some catalyst deactivation is occurring is evidenced by an ~20% decrease in the Mn content of the zeolite after the reaction. However, this would account only for a fraction of the PhIO consumed. Another possibility is that solvent molecules (acetonitrile) may be undergoing oxidation (*9*). The ability of the catalyst to oxidize unactivated C–H bonds was confirmed by the oxidation of cyclohexane to cyclohexanone and cyclohexanol. It was also found that PhI is formed in the catalytic system in the absence of any hydrocarbon. These data indicate that olefin molecules are competing with oxidation of the solvent. In the case of styrene, however, this electron-rich substrate is considerably more favored than

TABLE 1

Reactivity of Olefin

Catalyst	Olefin	Olefin reacted (mmol)	PhI formed[a] (mmol)	Ratio (olefin/PhI)	Product [mmol (%)[b]]
Mn–Y	Cyclohexene	0.058	0.096	0.6	0.009 (16) cyclohexenol
	Styrene	0.049	0.084	0.58	0.013 (27) $PhCH_2CHO$ 0.002 (4) styrene oxide
Mn(salen)-Y	Cyclohexene	0.11	0.11	1	0.015 (14) cyclohexene oxide
A					0.011 (10) cyclohexenol
	Styrene	0.057	0.092	0.6	0.011 (19) styrene oxide 0.015 (26) $PhCH_2CHO$
	trans-Stilbene	0.048	0.090	0.5	0.01 (20) *trans*-stilbene oxide
	cis-Stilbene	0.019	0.085	0.2	*cis*-Stilbene oxide
	1-Octene	0.009	0.082	0.1	No products were identified
	Cyclohexane	0.043	0.082	0.5	Cyclohexanone, cyclohexanol
	No olefin	—	0.10	—	—
B	Cyclohexane	0.066	0.095	0.7	0.007 (11) cyclohexene epoxide 0.004 (6) cyclohexenol
	Styrene	0.026	0.105	0.2	Styrene oxide
C	Cyclohexene	0.012	0.088		Products too small to be quantified
	Styrene	0.014	0.110	0.1	0.007 (50) styrene oxide 0.009 (60) $PhCH_2CHO$

[a] 0.110 mmol of PhIO.

[b] % relative to olefin reacted.

acetonitrile to undergo oxidation (*10*). The competition must arise from the restricted diffusion of styrene through the zeolite pore system and the considerably higher concentration of the solvent molecules. This is also confirmed by the study of larger olefins, such as 1-octene and *trans*- and *cis*-stilbene. In the case of the stilbenes, only 50 and 20% of PhIO molecules go toward the oxidation of *trans*- and *cis*- olefins, respectively. In both cases, formation of the oxides was noted from the HPLC traces. The yield for *cis*-stilbene oxide was too small to be measured accurately. From these data, however, it is clear that as the olefin increases in size (cyclohexene, 6.7 × 7.4 Å; styrene, 6.7 × 9.5 Å; *trans*-stilbene 6.7 × 13.9 Å; *cis*-stilbene, 8.0 × 10.3 Å), the competition with solvent oxidation rises. To further explore the size selectively of the oxidation catalyst, the relative reactivities (defined under Experimental) of the olefins were compared with that of cyclohexene. These data are shown in Table 2.

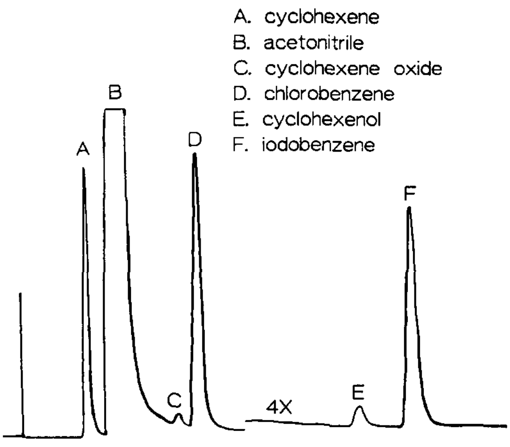


FIG. 4. GC trace of the products formed upon cyclohexene oxidation with catalyst A [Mn^{III}(salen)].

TABLE 2

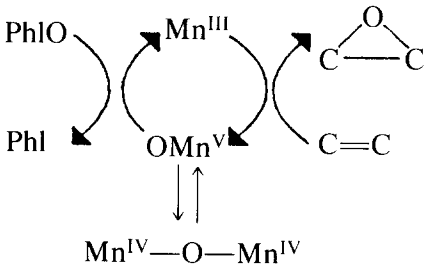
Relative Reactivity of Olefins versus Cyclohexene

Mn(salen)–Y	Amount (mmol)[a]		Relative reactivity
	Cyclohexene	Olefin	
A	0.247, 0.175	Styrene, 0.218, 0.184	0.50
	0.247, 0.180	*trans*-Stilbene, 0.286, 0.257	0.34
	0.247, 0.205	*cis*-Stilbene, 0.140, 0.132	0.31
B	0.247, 0.167	Styrene, 0.218, 0.179	0.50
C	0.247, 0.219	Styrene, 0.218, 0.193	0.83

[a] Initial, final.

The relative reactivities for styrene, *trans*-stilbene, and *cis*-stilbene were 0.5, 0.34, and 0.31 respectively.

Catalyst samples B and C were prepared from Mn^{II}(salen)–Y by oxidation with ferrocenium ion. This procedure was similar to that for homogeneous solutions (*10*). Catalysts B and C contained 6 and 12 mg Mn/g NaY, which corresponds to one ion per 4 and 2 supercages, respectively. In general, the reactivities of these catalysts were lower than that of catalyst A. Both these samples were not Soxhlet extracted to remove excess salen ligand, and only sample B was ion exchanged with 0.1 M NaCl to remove unreacted Mn^{2+} and ferrocenium cation. The lower reactivity of these systems could be due to pore plugging in the zeolite and the inability of olefin molecules to reach the active sites. The only point of interest appears to be the increase in the relative reactivity of styrene over cyclohexene from 0.5 for catalysts A and B to 0.83 for sample C. We proposed that this increase is due to the reaction in sample C on the zeolite surface, thereby leading to a lower discrimination in size selectivity.



SCHEME 2

DISCUSSION

Based on the oxidation of olefins by Mn (salen) complex in solution, Scheme 2 has been proposed (*10*). In the zeolite, the size of the supercage prevents formation of the μ-oxodimer. This is also supported by the lack of any spectral changes upon addition of PhIO to Mn^{III}(salen)–Y, in contrast to the appearance of the 530-nm band in solution.

It is useful to contrast the trends in reactivities of the encapsulated Mn(salen)–zeolite and the complex in solution (*10*). Reaction conditions are similar in both cases, except that the amount of catalyst in the zeolite sample was by a factor of 3.5 smaller than that in solution. Three features of the zeolite-encapsulated system will be discussed: (i) formation of PhI in the absence of olefin and a different product distribution; (ii) size-selective oxidative of olefins; and (iii) turnover number.

Greater than 90% of the PhIO was converted to PhI in the absence of olefin during the first 10 h of reaction. Similar observations have been made in homogeneous solution with both Mn(salen) and Co(II) complexes of bissalicylamide dianions (*10, 16*). In both cases, oxidation of the solvent, acetonitrile, has been proposed, though the products were not identified. The rate of generation of PhI is comparable in both homogeneous and zeolitic systems. Capillary GC traces of the product mixture exhibit only peaks due to CH_3CN and PhI. It is likely that some polymeric products form upon acetonitrile oxidation.

In the presence of olefin in the homogeneous system, the catalyst Mn(salen) preferentially reacts with the olefin rather than the solvent. Typically, this reaction is complete within 30 min. However, the reaction with the zeolite-encapsulated complex is considerably slower, being complete only after ~16 h of reaction. The slower overall rate for the zeolite system as compared to solution is similar to observations made for alkane oxidation by zeolite-encapsulated phthalocyanine (*7*). It appears that diffusion through the zeolite network may cause the overall lower reaction rate.

To quantify the role of diffusion inhibition in reaction rate, the Weisz–Prater criterion has often been used (*17, 18*). According to this criterion, if the modulus ϕ [$= k\,(R^2/D)$] exceeds 2, the reaction is diffusion inhibited. In this equation, $k\ (dn/dt)(1/C)$] is the observed rate constant, R is the radius of the catalyst particles, and D is the diffusion coefficient in the system. For the oxidation of cyclohexene, we calculated an initial first-order rate constant of 1.4×10^{-4} s^{-1} (for the first 2000 s) and estimate an average radius for the zeolite particles of 5×10^{-4} cm. So, for the reaction to be diffusion inhibited, the diffusion coefficient must be less than or equal to 1.75×10^{-11} cm^2/s.

The diffusion coefficients for the olefins used in this study could not be found in the literature. However, diffusitivities of similar-size molecules from the liquid phase into NaY has been reported (*19*). For example, cumene and 1,3,5-trimethyl-, triethyl-, and triisopropylbenzene with minimum molecular diameters of 6.8, 8.4, 9.2, and 9.4 Å have diffusion coefficients of 7×10^{-11}, 0.68×10^{-11}, 0.0065×10^{-11} and 0.00028×10^{-11} cm^2/s, respectively. The olefins used in this study include cyclohexene, styrene, and *trans*- and *cis*-stilbene. The comparability in size of these molecules and those described above indicates that the reaction is indeed operating in a region of diffusion-controlled rate inhibition. The diffusivity of cyclohexene is expected to be higher than the diffusivities of the other olefins and is probably comparable to that of cumene; therefore, its reactivity is on the borderline for diffusion inhibition. The relative rates for diffusion of cyclohexene, *p*-xylene, *o*-xylene, and mesitylene into zeolite Y have been reported by Chester and co-workers as 1, 0.25, 0.20, and 0.16 (*20*). This would indicate that for the olefins examined in this study, besides cyclohexene, the reaction rates are definitely in the diffusion-controlled inhibition regimes.

The total amount of olefins that react relative to the amount PhIO consumed is 100, 60, 50, and 20% for cyclohexene, styrene, and *trans*- and *cis*-stilbene. Clearly, with increasing size of the olefins, the competition with solvent oxidation increases, as the diffusivity of the olefin decreases. This is also reflected in the relative reactivities, if a mixture of olefins is allowed to react. As shown in Table 2, cyclohexene is twice as reactive as styrene and three times as reactive as *trans*-stilbene. In a similar study with the homogeneous system, styrene and cyclohexene exhibited similar reactivities, whereas *trans*-stilbene was 1½ times more reactive than cyclohexene (*10*). This reversal of reactivity is a reflection of reactant selectivity by virtue of size and diffusion through the zeolite pores.

The oxidation products formed from the olefins in the zeolite-encapsulated material were comparable to those formed in the homogeneous system, though the yields were different. The total products identified in homogeneous Mn(salen) reactions with cyclohexene, styrene, and *trans*-stilbene as reactants were 58, 48, and 47% of the total olefins reacted in each case (*10*). Analogous figures for the zeolite system were 24, 44, and 20% for cyclohexene, styrene, and *trans*-stilbene. The identity of the unrecovered products is unclear. In the homogeneous system, polymeric materials have been proposed as reaction products. Cyclohexene oxidation by the zeolite-encapsulated Mn(salen) resulted in formation of equal amounts of cyclohexene oxide and the allylic oxidation product cyclohexenol, whereas in the solution system, the epoxide was the dominant product (*10*). In the oxidation of styrene, the ratio of phenylacetaldehyde to styrene oxide was 1.36 in the zeolite system, as compared to 0.25 in the homogeneous phase. The oxidation reaction has been proposed to follow a radical pathway in the solution system (*10*). The different ratios of products in the zeolite as compared to the solution could result from several factors. The catalyst in the zeolite undergoes some degradation over the ~16-reaction period, as evidence by the 20% loss of Mn content of the zeolite. As indicated in Table 1, uncomplexed Mn–Y also catalyzes the oxidation of olefins, forming mainly cyclohexenol and phenylacetaldehyde. Part of the products in the zeolite system could arise from the Mn–Y formed by degradation of Mn(salen) complexes. The polar zeolitic environment may also promote the stabilization of charged species that are proposed to form from the radicals as intermediates in the formation of phenylacetaldehyde (*10*).

The encapsulated Mn(salen) exhibited catalytic activity for 60 h. From the amount of PhI formed, a turnover number of 60 was estimated. In addition to catalyst degradation, this decrease in catalytic activity could be due to plugging of zeolitic pores as was observed for the iron phthalcyanine–zeolite Y system (*7*). The long-term solution stability of Mn(salen) in the homogeneous system is unknown.

In conclusion, this study shows that Mn (salen) complexes encapsulated in zeolite Y cavities can promote the catalytic oxidation of olefins. The catalytic system shows selectivity based on substrate size and diffusivity through the pores. However, these factors also contributes to much lower rates of reaction as compared to homogeneous solution.

ACKNOWLEDGMENTS

We thank the National Science Foundation (CHE-8510614) for support of this work, and the reviewers for helpful comments.

REFERENCES

1. Naacache, C., and Taarit, Y. B., *Pure Appl. Chem.* **52,** 2175 (1980).
2. Csicsery, S. M., *Zeolite* **4,** 202 (1984).
3. Jacobs, P. A., Chantillon, R., DeLaet, P., Verdonck, J., and Tielem, M., *ACS Symp. Ser.* **218,** 439 (1983).
4. Auroux, A., Bolis, V., Wierzchowski, P. Gravelle, P., and Vedrine, J., *J. Chem. Soc. Faraday Trans. 2* **75,** 2544 (1979).
5. Iwamoto, M., Kusano, H., and Kagawa, S., *Inorg. Chem.* **22,** 3366 (1983).
6. Mantovani, E., Palladino, N., and Zarrobi, A., *J. Mol. Catal.* **3,** 285 (1977).
7. Herron, N., Stucky, G. D., and Tolman, C. A., *J. Chem. Soc. Chem. Commun.*, 1521 (1986).
8. Samsel, E. G., Srinivasan, K., and Kochi, J. K., *J. Amer. Chem. Soc.* **107,** 7606 (1985).
9. Koola, J. D., and Kochi, J. K., *Inorg. Chem.* **26,** 908 (1987).
10. Srinivasan, K., Michaud, P., and Kochi, J. K., *J. Amer. Chem. Soc.* **108,** 2309 (1986).
11. Herron, N., *Inorg. Chem.* **25,** 4714 (1986).
12. Muenier, B., Guilnet. E., DeCarvalho, M., and Poliblanc., R., *J. Amer. Chem. Soc.* **106,** 6668 (1984).
13. Hobday, M. D., and Smith, T. D., *Coord. Chem. Rev.* **9,** 311 (1973).
14. Earnshaw, A., King, E. A., and Larkworthy, L. F., *J. Chem. Soc. A,* 1048 (1968).
15. Lewis, J., Mables, F. E., and Weigold, H., *J. Chem. Soc. A*, 1699 (1968)
16. Koola, J. D., and Kochi, *J. K., J. Org. Chem.* **52,** 4545 (1987).
17. Weisz, P. B., and Prater, C. D., *Adv. Catal.* **6,** 143 (1954).
18. Miale, J. N., Chen, N. Y., and Weisz, P. B., *J. Catal.* **6,** 278 (1966).
19. Wu, E. L., Landolt, G. R., and Chester, A. W., "New Developments in Zeolite Science and Technology," Proceedings, 7th International Zeolite Conference Tokyo, p. 547. 1986.
20. Satterfield, C. N., and Cheng, C. S., *Amer. Inst. Chem. Eng. Symp. Ser.* **117,** 43 (1971).