JOURNAL OF CATALYSIS **170,** 244–253 (1997)
ARTICLE NO. CA971749

Oxyhalogenation of Aromatics over Copper Phthalocyanines Encapsulated in Zeolites

Robert Raja and Paul Ratnasamy[1]

National Chemical Laboratory, Pune 411 008, India

Received September 12, 1996; revised May 13, 1997; accepted May 14, 1997

The oxychlorination and oxybromination, under near-ambient conditions, of benzene, toluene, phenol, aniline, anisole, and resorcinol, using as catalysts the phthalocyanines of Cu, Fe, and Co encapsulated in zeolites X, Y, and L, are reported. Both H_2O_2 and O_2 have been used as oxidants. HCl and alkali chlorides/bromides have been used as sources of halogens. The metal phthalocyanines wherein the aromatic rings are substituted by −Cl or −NO_2 groups are more active. There is a dramatic increase in the turnover frequencies for substrate conversion when the complexes are encapsulated in the cavities of the zeolites X, Y, or L. The oxyhalogenation of both the aromatic nucleus and the alkyl side chains occur. Oxidation of the aromatic ring (to phenols or cresols, for example) does not occur. Alkyl side chains, however, are oxidized by the oxidant H_2O_2 or O_2 to alcohols, ketones, and acids. The performance of these novel catalyst systems as solid oxyhalogenation catalysts in utilizing O_2 and halide ions in the manufacture of halogenated aromatics holds promise in the organic chemicals industry. © 1997 Academic Press

1. INTRODUCTION

The oxidative liberation of halogens from hydrogen halides or their salts using H_2O_2 and suitable, homogeneous catalysts, has been known for more than 70 years (1). The halogen generated may be used for

$$2HX + H_2O_2 \rightarrow X_2 + 2H_2O \quad X = \text{Cl, Br, I}$$

halogenating organic substrates (2, 3). Dinesh *et al.* (3) from our group, for example, have recently shown that ammonium metavanadate efficiently catalyzes the oxyhalogenation of a variety of organic substrates in moderate to good yields, using dilute hydrogen peroxide (30%) as an oxidizing agent, exhibiting remarkable ortho selectivity with electron-rich aromatics. Similar results had been reported earlier by Conte *et al.* (4) and Rosa *et al.* (5). In the above studies (3–5) the authors' main goal was the development of functional mimics of the haloperoxidase marine enzymes. These enzymes oxyhalogenate aromatic substrates using H_2O_2 and halide ions present in the marine environment. The biosynthesis of the brominated compounds, for example, is likely to be mediated by vanadium bromoperoxidase through electrophilic bromination by oxidized bromine species. While oxyhalogenation using *in situ* generated halogens has many advantages (like fuller utilization of the halogen instead of only half of the available halogen, easier transport and handling of the aqueous hydrogen halides, and dilute H_2O_2 compared to halogens, etc.) the major disadvantages of the present day state-of-the-art processes in the liquid phase are (1) the high cost of H_2O_2 and (2) the disposal of the homogeneous metal catalysts used in the processes. The latter poses additional environmental problems. Very recently, a two-stage vapor phase process for the conversion of HCl to Cl_2 using solid catalysts has been reported (6). In the first stage, HCl is reacted over copper oxide at 473 K producing a copper chloride complex. In the second stage, the latter is reacted with O_2 at 633 K oxidizing the copper chloride to copper oxide and Cl_2. A solid-catalyzed, single-step process using H_2O_2 or preferably molecular dioxygen as the oxidant for the oxyhalogenation of aromatic substrates under near-ambient conditions using halide ions as the source of halogen will be advantageous. To our knowledge, oxyhalogenation of aromatic substrates using solid catalysts in the liquid phase at low temperature and using O_2 as the oxidizing agent has not been reported so far.

The present paper reports the oxychlorination and oxybromination, under ambient conditions, of aromatic compounds (like benzene, toluene, phenol, aniline, resorcinol, and anisole) using, as catalysts, the phthalocyanines of transition metals (like Fe, Co, Cu) encapsulated in zeolites X, Y, and L. Both H_2O_2 and O_2 have been used as oxidants. The performance of these novel catalyst systems as solid oxyhalogenation catalysts is quite promising.

2. EXPERIMENTAL

2.1. Materials

The *neat* $CuCl_{16}Pc$ (where Pc stands for phthalocyanine) complexes were synthesized according to the procedure

---

[1] To whom correspondence should be addressed. Fax: -91-212-330233. E-mail: prcat@ncl.ernet.in.

0021-9517/97 $25.00
Copyright © 1997 by Academic Press
All rights of reproduction in any form reserved.

reported by Birchall *et al.* (7). First, 2.8 mmol of $Cu(CH_3CO_2)_2$ (0.56 g, BDH) was mixed with 14.0 mmol (2.8 g, Aldrich) of tetrachlorophthalonitrile in 40 ml of 1-chloronaphthalene (Aldrich) in a Parr reactor under nitrogen (500 psi). The mixture was heated for 24 h, cooled to room temperature, and centrifuged. Then 200 ml of petroleum ether was added to the greenish blue filtrate that was then submerged in an ice bath. The dark greenish blue precipitate was recovered by centrifugation. The $CuCl_{16}Pc$ complex was recrystallized from sulfuric acid and isolated in 50.2% yield. CuPc, CoPc, $Cu(NO_2)_4Pc$, $FeCl_{16}Pc$, and $CoCl_{16}Pc$ complexes were obtained from M/s. Lona Industries, Bombay.

Before we describe the procedure for the encapsulation of these copper complexes in zeolites, we have to address the issue of solubility of these complexes in the zeolite synthesis medium. First, 0.6 g of $CuCl_{16}Pc$ (containing 3.5×10^{-2} g of Cu) was stirred in 100 g of an aqueous solution of fumed silica and NaOH (pH = 12.8) at room temperature for 24 h, before heating at 363 K for 12 h. This solution was identical to that used during synthesis of zeolites except that the Al source was not added. The latter precaution was taken to avoid the precipitation of an aluminosilicate solid. At the end of 12 h, 0.34 of the solid $CuCl_{16}Pc$ (equivalent to 1.9×10^{-2} g of Cu) was recovered by centrifugation (8000 rpm for 2 h) of the hot slurry. Chemical analysis of the clear solution (by atomic absorption spectroscopy) revealed the presence of 1.6×10^{-2} g of Cu in 100 g of the clear solution. In most of the encapsulation experiments, the yield of zeolite solid from 100 g of the solution was 5–7 wt.%. Since the copper content in most of the zeolite catalysts obtained by encapsulation was about 0.1 wt.%. (equivalent to about 0.5×10^{-2} g of Cu) it may be concluded that the zeolite synthesis medium contained enough *dissolved* phthalocyanine complex to lead to the encapsulation levels observed in Table 1. The synthesis of $CuCl_{16}Pc$, $Cu(NO_2)_4Pc$, $FeCl_{16}Pc$, and $CoCl_{16}Pc$ complexes encapsulated in zeolite NaX will now be described. Aluminium isopropoxide and NaOH (Aldrich) were used without further purification. In a typical synthesis, the silicate gel was prepared from 4.0 g fumed silica (Sigma); 3.2 g NaOH; 0.30 g $CuCl_{16}Pc$, $Cu(NO_2)_4Pc$, $FeCl_{16}Pc$, or $CoCl_{16}Pc$; and 8.0 ml H_2O. Addition of the aluminate solution (9.0 g Al $(iOPr)_3$, 3.2 g NaOH, 6.0 ml H_2O) resulted in a slurry with an intense greenish/blue colour. An additional 36 ml deionized water was added. The gel was then transferred to a polypropylene bottle. The mixture with a molar composition of $SiO_2 : Al_2O_3 : Na_2O : H_2O : CuCl_{16}Pc = 3 : 1 : 3.6 : 141 : 0.015$ was aged at room temperature with stirring for 24 h and then heated at 363 K for 15 h. It was then

TABLE 1

Oxyhalogenation of Toluene: Comparison of Catalysts

S. no.	Catalyst	TOF (h^{-1})	Products (wt.%) A	B	C	D	E	F	G
1	CuPc	0.32	—	100	—	—	—	—	—
2	CoPc	0.14	—	100	—	—	—	—	—
3	$Cu(NO_2)_4Pc$	2.19	21.2	47.0	8.3	5.5	18.0	—	—
4	$CuCl_{16}Pc$	8.92	45.0	17.0	15.7	10.7	2.6	9.0	—
5	$CoCl_{16}Pc$	6.96	52.0	13.5	11.5	3.3	2.2	17.5	—
6	$FeCl_{16}Pc$	7.31	63.5	3.8	5.7	11.0	—	16.0	—
7	$CuCl_2$–Na-Y(0.14) (exchanged)	42.44	60.0	12.1	4.2	3.7	10.3	—	9.7
8	$CuCl_{16}Pc$–Na-Y (0.32) (impregnated)	52.25	50.0	19.7	8.6	9.1	2.5	10.1	—
9	$CuCl_{16}Pc$ + Na-Y (Phys. mix.; Cu = 0.11 wt.%)	47.15	48.5	16.1	9.2	9.7	3.1	13.4	—
10	$Cu(NO_2)_4Pc$–Na-X (0.14)	99.4	18.0	58.5	5.0	1.5	17.0	—	—
11	$CuCl_{16}Pc$–Na-X (0.27)	161.32	46.5	31.5	14.3	6.3	1.4	—	—
12	$CuCl_{16}Pc$–Na-Y (0.11)	309.3	40.4	30.3	17.4	9.6	2.3	—	—
13	$CuCl_{16}Pc$–K-L (0.10)	382.1	8.5	21.0	18.7	23.5	3.5	24.8	—
14	$CoCl_{16}Pc$–Na-X (0.27)	106.7	45.0	9.0	18.2	7.5	2.2	18.1	—
15	$FeCl_{16}Pc$–Na-X (0.16)	210.28	49.5	9.5	8.5	15.2	—	17.3	—

Note. Temperature = 338 K; halide, HCl; toluene: H_2O_2, 3 mole; TOF, turnover frequency; moles of substrate converted per mole of copper per hour. The TOF and selectivity values are reproducible to about ±10%. A, benzaldehyde; B, benzyl alcohol; C, orthochlorotoluene; D, parachlorotoluene; E, benzyl halide; F, di- (mainly ortho- and para-) and trichlorotoluenes; G, benzoic acid. Sample $CuCl_2$–Na-Y (0.14) (exchanged) was prepared by ion exchanging 0.14 wt.% of copper from aqueous $CuCl_2$ solution into Na-Y. Sample $CuCl_{16}Pc$–Na-Y (0.32) (impregnated) was prepared by impregnating Na-Y with a pyridine-acetic acid (glacial) solution of $CuCl_{16}Pc$ to get 0.32 wt.% of copper in the final catalyst. Sample ($CuCl_{16}Pc$ + Na-Y) (phys. mix.; Cu = 0.11 wt.%) was a physical mixture of 1.017 g Na-Y and 17.5 mg $CuCl_{16}Pc$.

allowed to cool to room temperature and was diluted with copious amounts of deionized water. The solid crystals were isolated by centrifugation at 8000 rpm for 2 h. The light, greenish/blue solid was dried at 363 K for 24 h in air and extracted (soxhlet) first with acetone, then with pyridine, acetonitrile, and finally again with acetone for 72 h. It was finally dried at 363 K under vacuum (10^{-3} Torr) for 15 h. The X-ray diffraction pattern of the material confirmed it to be the zeolite Na-X. Na-X with varying loadings of $CuCl_{16}Pc$, $Cu(NO_2)_4Pc$, $FeCl_{16}Pc$, or $CoCl_{16}Pc$ was prepared similarly. The synthesis of $CuCl_{16}Pc$ and $Cu(NO_2)_4Pc$ encapsulated in Na-Y was also similar to the synthesis procedure described above for Na-X. The silica source was sodium silicate (Lona) and aluminium sulfate (Aldrich) was used as the alumina source. The SiO_2/Al_2O_3 molar ratio was 2.6. $CuCl_{16}Pc$ was encapsulated in K-L by the following procedure. First, 12.44 g of fumed silica (Aldrich) was stirred in 17 ml of distilled, deionised water for 30 min. Then, 0.15 g of $CuCl_{16}Pc$ was added to the silica-sol and the mixture was stirred for another 30 min at 333 K. In a separate polypropylene beaker 8.96 g KOH (A.R. Grade, S.D. Fine Chemicals), 1.55 g hydrated alumina (Catapal B, Sigma), and 17 ml distilled, deionized water were stirred for 60 min at 333 K. The silica solution containing the metal complex was gradually added to the alumina solution over a period of 45 min. An additional 10 ml distilled deionized water was added to get a uniform gel. The contents were stirred for a further 60 min and then transferred to an autoclave reactor (Parr). The autoclave was maintained at 414 K, for 4.5 days under stirring (rpm = 300). The SiO_2/Al_2O_3 ratio of the final zeolite L was 6.8. Zeolites containing impregnated Pc (Table 1, No. 8; Fig. 1B) were prepared by dissolving the Pc in a pyridine-acetic acid (glacial) solution and "dry-impregnating" the zeolite with the solution. The catalysts are designated by the following notation [(Complex)-(Zeolite) (metal content in the zeolite, wt.%)]. Thus $CuCl_{16}Pc$–Na-X (0.27) designates a Na-X zeolite containing 0.27 wt.% copper in the form of a hexa decachloro copper phthalocyanine complex encapsulated, most probably, in the supercages of the faujasite structure.

2.2. Procedures

2.2.1. Catalytic reactions. In a typical oxyhalogenation reaction, the solid catalyst (0.2 to 0.75 g) was added to the substrate in a suitable solvent (for example, a 1 : 2 volume mixture of water : acetonitrile) where the halide source K*X* or H*X* ($X = Cl, Br, I$) was previously dissolved. When HCl was used as the halide source the pH of the mixture was adjusted to 5.0 using phosphate buffer. Aqueous H_2O_2 (25 wt.%) was added after the desired temperature was attained. The catalytic runs were carried out in a three-necked flask (100 ml capacity) fitted with a condenser (circulating chilled water) and magnetic stirring. The temperature of the reaction vessel was maintained using an oil bath. Periodically, samples were removed and centrifuged to remove the solid catalyst. Copper was not detected (by atomic absorption spectroscopy, Hitachi Model Z-8000) in the colorless reaction product when using any of the solid catalysts used in the present study. In the case of oxyhalogenation reactions using molecular O_2 as the oxidant, tertiary butyl hydroperoxide (TBHP, 70% aqueous solution, Aldrich, equivalent to 1% by weight of the substrate) was added to the reaction mixture before air was admitted to the Parr autoclave (300 ml). The substrates chosen were toluene, phenol (A.R. grade, S.D. Fine Chemicals, India), aniline, resorcinol (B.D.H.), anisole, and benzene (Aldrich, USA).

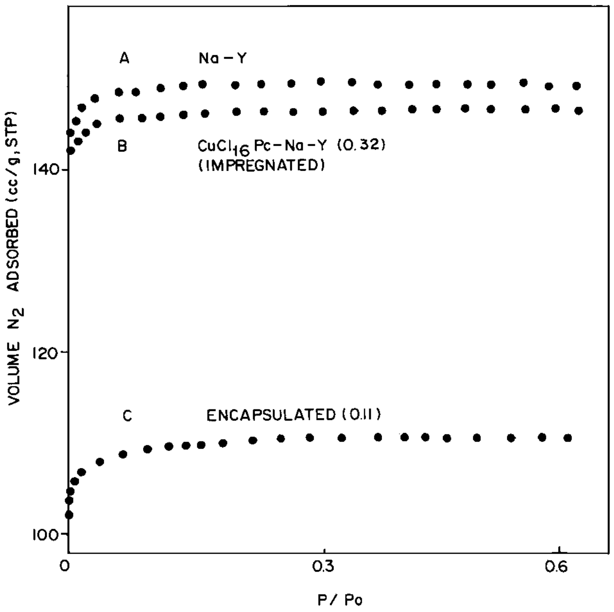

FIG. 1. N_2 adsorption isotherms at liquid N_2 temperature of Na-Y (A), $CuCl_{16}Pc$–Na-Y (0.32) (impregnated) (B), and $CuCl_{16}Pc$–Na-Y (0.17) (encapsulated) (C).

2.2.2. Product analysis. The products of the oxyhalogenation reaction were analyzed by gas chromatography (Hewlett–Packard, 5880 A), employing a FID detector and equipped with a capillary column (50 m × 0.25 mm crosslinked methyl silicone gum). At the end of the reaction, the halogenated aromatics were extracted with diethyl ether and saturated with sodium hydrogen carbonate prior to analysis. In some cases, the products were isolated by column chromatography, after appropriate work-up to establish yields. The identity of the products was further confirmed by GC–MS (Shimadzu QCMC-QP2000A).

2.3 Catalyst Characterization

The copper content and chemical analysis were measured by atomic absorption spectroscopy (Hitachi Model Z-8000), EDS (Kevex), and X-ray fluorescence spectroscopy (Rigaku-3070, X-ray spectrometer). Omnisorb

100 CX (Coulter Corporation, USA) was used for the measurement of nitrogen adsorption. Prior to the adsorption measurements, the samples were activated at 373 K for 4 h in high vacuum (1.33×10^{-6} Pa.) The ESR spectra of the solid catalysts were measured at room and liquid N_2 temperatures using a Bruker ESR spectrometer (200 D). X-ray diffractograms of the solid catalysts were recorded using a Rigaku D-max III, X-ray diffractometer with a Cu$K\alpha$ target. IR and diffuse reflectance UV spectroscopy of the solid catalysts were recorded using a Perkin–Elmer 1600 FTIR and a Shimadzu UV-2101 UV–VIS spectrophotometer, respectively. The IR spectra of the solid catalysts were recorded in nujol media (Perkin–Elmer). $BaSO_4$ was used as the reference material for recording the diffuse reflectance spectra in the 200- to 900-nm region. UV spectra of liquid samples were measured in the 200- to 400-nm region. XPS of the solid catalysts were recorded with a VG Scientific ESCA III Mark (II) with Mg$K\alpha$ (1253.6 Å) as the excitation source. Scanning electron micrographs of the solid catalysts were recorded on a Leica, Stereoscan-440, Cambridge, instrument. The samples were dusted on alumina and coated with a thin film of gold to prevent surface charging and to protect the surface material from thermal damage by the electron beam. In all analyses a uniform thickness of about 0.1 mm was maintained. Molecular modeling studies were carried out on a Silicon Graphics, Indigo-2 workstation, using the Insight II software supplied by Biosym, Inc. (8). The computer models of Pc and $Cl_{14}Pc$ were generated and their geometries optimized with respect to their strain energy using molecular mechanics and energy minimization procedures (9). As a first approximation, it was assumed that CuPc and $CuCl_{14}Pc$ will have geometric strains similar to Pc and $Cl_{14}Pc$, respectively. This assumption is justified in view of the small volume occupied by the Cu^{2+} ion in the phthalocyanine complex. The interaction potentials of Cu^{2+} and the other atoms of the complex have not, so far, been reported in literature.

3. RESULTS AND DISCUSSION

3.1. *Catalyst Characterization*

The X-ray diffractograms of the catalysts containing the copper complexes did not reveal any significant difference from those of the pure zeolites. The encapsulation of the copper complexes inside the zeolite cavities is indicated by the absence of extraneous material by scanning electron microscopy. The SEM photographs indicate the presence of well-defined zeolite crystals without any patches of phthalocyanine complexes overlaid on their external surface. N_2 adsorption data (Fig. 1) confirm the presence of the copper complex inside the zeolite cavities. When $CuCl_{16}Pc$ was merely impregnated on the external surface of Na-Y (Fig. 1B), there was no significant reduction in the volume of N_2 adsorbed, indicating that the large internal pore volume is still accessible to N_2. However, there was a drastic reduction in the pore volume in the case of samples containing the encapsulated copper complex, wherein the zeolite was synthesized in the presence of the $CuCl_{16}Pc$ complex (Fig. 1C), providing direct evidence for the presence of the copper complex inside the zeolite cavities and not on the external surface of the crystals. Similar results were also observed in the case of other encapsulated complexes. The structural integrity of the encapsulated complexes was indicated by the XPS, FTIR, and diffuse reflectance UV spectral data (10–12). However, there was a red shift in the UV–VIS electronic spectra of the copper complexes on encapsulation. Thus, the absorption maxima for $CuCl_{16}Pc$ shifted from 665.5 and 374.0 nm to 681.0 and 384.0 nm, respectively. These spectra are due to ligand-based electronic ($\pi \rightarrow \pi^*$) transitions. There was no similar spectral shift when the $CuCl_{16}Pc$ complex was merely impregnated into the zeolite (Table 1, S. no. 8). Balkus *et al.* (13) had also observed a similar phenomenon in the case of Cobalt (II) and Copper (II) perfluorophthalocyanines encapsulated in Na-X zeolites and attributed it to the distortion of the phthalocyanine ligand in the supercage of the zeolite. This hypothesis (applicable to the encapsulated $CuCl_{16}Pc$ in our case) is further supported by computer modeling and molecular strain energy minimization calculations (see Experimental). The latter indicate that the geometric environment around the copper is distorted from the square planar symmetry (of the free complex) when encapsulated in the supercage of the faujasite (Fig. 2). The copper atom is now at the bottom of a *hydrophobic bowl.* The red shift observed in the UV–VIS spectra provides experimental evidence for this molecular distortion. The additional strain energy required for this distortion (3.6 K cal/mol) is available to the system during the synthesis of the encapsulated catalyst. Substituted phthalocyanines are known to be quite rugged and stable up to about 773 K. Such distortions of the symmetry of the complex from square planarity to quasi-tetrahedral symmetry will admix the d_{xy} orbital with d_{z^2} orbital, leading to a lower electron density on the metal ion and thereby enhancing the reactivity of the complex toward molecular O_2 (14) in general and in oxidation reactions in particular.

3.2. *Catalytic Activity*

Experimental evidence that the oxyhalogenations investigated in the present study are indeed catalyzed by the solid zeolite containing the encapsulated complex is presented in Fig. 3. In one of a set of two identical experiments, the solid catalyst was removed by filtration at a reaction time of 4 h (Fig. 3B). While conversion of toluene to oxyhalogenated products continued in the presence of the catalyst (Fig. 3A), there was no further conversion of toluene when the catalyst was removed from the reaction system (Fig. 3B). This indicates that (1) the solid catalyst

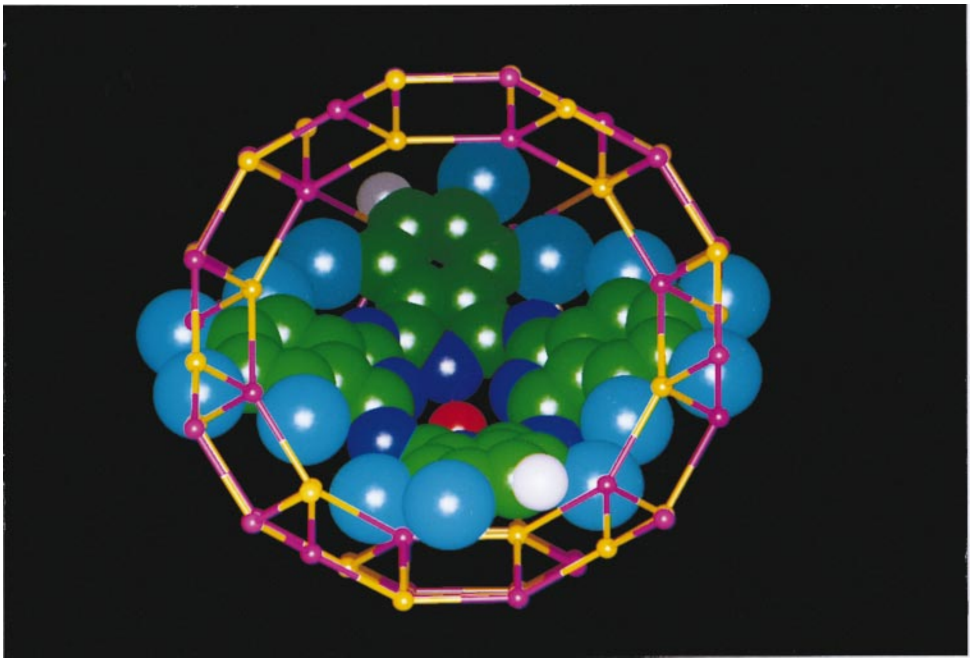

FIG. 2. Energy minimized structure of $CuCl_{14}Pc$ encapsulated inside the supercage of the faujasite structure red, copper; dark blue, nitrogen; green, carbon; white, hydrogen; light blue, chlorine.

is essential for the oxyhalogenation reaction to occur—this phenomenon was also observed with the other substrates used in this study; (2) oxyhalogenations of the substrate by dissolved copper complexes leached out from the solid material is negligible—this conclusion was independently confirmed by the absence of copper in the filtrate (atomic absorption spectroscopy); and (3) in the absence of the catalyst, H_2O_2 alone is unable to oxyhalogenate the substrate to any significant extent. In independent experiments carried out in the absence of the catalyst, the conversion of toluene under otherwise identical experimental conditions of Fig. 3 was about 1.1 wt.%. When molecular O_2 with TBHP as the initiator was used as the oxidant under the same reaction conditions, the toluene conversion in the absence of the catalyst was only 2.1 wt.%. The zeolites alone were also catalytically inactive in oxyhalogenation. Thus, we may conclude that the oxyhalogenations reported in the present study are indeed catalyzed by the metal complexes encapsulated in the zeolite matrix.

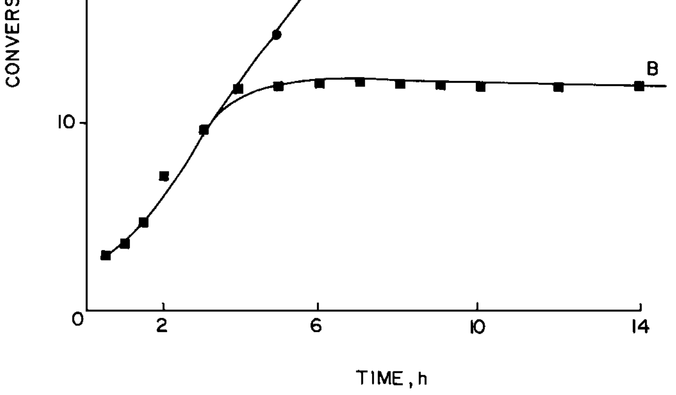

FIG. 3. Kinetics of toluene oxybromination in the presence of the solid catalyst $CuCl_{16}Pc$–Na-X (0.27) (A) and when the catalyst is removed from the reaction mixture at 4 h reaction time (B).

The results of the oxychlorination of toluene, using aqueous HCl as the halogenating agent and H_2O_2 as the oxidant, at 333 K, over the various copper, cobalt, and iron phthalocyanine complexes, in both the neat and the encapsulated states, are presented in Table 1. The following points may be noted:

(1) The unsubstituted metal phthalocyanines have a low activity; only oxidation reactions by H_2O_2 are observed. Halogenated products are not formed.

(2) The intrinsic catalytic activities (turnover frequencies, TOF) of the neat copper, cobalt, and iron complexes are of the same order of magnitude.

(3) When the copper ion is exchanged into the zeolite without the Pc ligand ($CuCl_2$–Na-Y (0.14), No. 7), even

though the TOF is relatively higher (TOF = 42.44) than that of the neat Pc complexes (TOF = 8.92), it is still much lower than that of the encapsulated complexes (TOF = 160–380). More importantly, significant differences in selectivity are seen: Benzoic acid, which is not formed over the Pc catalysts is seen among the products; on the other hand, the formation of mono- and dichlorotoluenes (columns C, D, and F), typical products of electrophilic chlorination, is much lower than over the Pc catalysts.

(4) When $CuCl_{16}Pc$ is impregnated on Na-Y (No. 8, $CuCl_{16}Pc$–Na-Y (0.32) (impregnated), although the TOF (52.25) is higher than that of the neat complexes, it is still lower than that of the encapsulated Pc complexes. More interestingly, the ratio of (dichlorotoluenes + trichlorotoluenes)/monochlorotoluenes is higher over the impregnated catalysts compared to the encapsulated catalysts (compare catalysts 8 and 12, for example). This difference in selectivity provides additional evidence for the encapsulation of the complexes inside the cavities of the zeolites.

(5) A physical mixture of $CuCl_{16}Pc$ and Na-Y (catalyst 9, Table 1) behaves in a manner similar to that of catalyst 8 ($CuCl_{16}Pc$ impregnated on Na-Y).

(6) There is a dramatic increase in the turnover frequency (by more than an order of magnitude) when the halogenated or nitrated complexes are encapsulated in the cavities of zeolites. Further, the TOF increases with site isolation of encapsulated complexes. A probable explanation is that at higher occupancy levels of the supercages of the zeolite by the phthalocyanine complexes, the diffusional resistance encountered by the substrate toluene molecules in reaching the active sites will be higher, leading to lower TOF values at higher loading levels of the metal complex.

(7) Both oxidation (of the side chain) and oxyhalogenation (of both the aromatic nucleus and the side chain) occur. Oxidation of the aromatic ring to cresols, however, does not occur.

(8) Oxychlorination was more dominant than oxidation only when the complexes were encapsulated in K-L zeolite (No. 13, Table 1). Side-chain oxidation by H_2O_2 was predominant in the case of Na-X. This is the first report of zeolite L-containing phthalocyanine complexes. While the high content of parachlorotoluene (23.5%) in the products compared to Na-X and Na-Y (6.3 and 9.6%, respectively) may suggest the location of the complex in a shape selective environment, the simultaneous formation of rather large quantities of di- and trichlorotoluenes (24.8%) is intriguing. Perhaps, in the case of zeolite L whose channels are too narrow to accommodate a perchlorophthalocyanine complex, the latter resides in a mesopore formed during the synthesis of the zeolite “around” the metal complex. Indeed, this is a distinct possibility in the synthesis of various metal complexes encapsulated in other zeolites also. We are, at present, developing techniques to distinguish, by various physicochemical and structural measurements, metal complexes in such mesopores from those encapsulated inside the channels/cavities of zeolites or chemisorbed on the external surface of the zeolite crystals. The relatively higher activity of zeolite L (compared to Na-X and Na-Y) in oxyhalogenation is not surprising in view of the generation and involvement of molecular halogen during oxyhalogenation reaction (see later). Our earlier studies with various zeolites had clearly established that zeolite L is the most active zeolite for the halogenation of aromatics using molecular halogen (15). While the uniqueness of K-L zeolites in catalyzing halogenation reactions using molecular halogen over zeolites is well known (15), further studies are necessary to delineate the role of the zeolite matrix in K-L, if any, in oxyhalogenation reactions using halide ions. In addition to the above points, it may be mentioned that the central transition metal of the phthalocyanine complex is the seat of catalytic activity. $Cl_{14}Pc$ or phthalocyanines of nontransition metals (like Al) had negligible oxidation or oxyhalogenation activity. While there is a loss of zeolite crystallinity and catalytic activity when using HCl or HBr as the source of halogen, no significant changes were noticed (at least upto 3 cycles) when alkali halides were substituted for HCl/HBr.

The possibility of benzyl alcohol and benzaldehyde arising from side chain halogenation of toluene followed by hydrolysis was investigated. Benzyl chloride, under the operating conditions of oxyhalogenation is not converted to benzyl alcohol/benzaldehyde. The experiment of Table 1, S. no. 12 was repeated using benzyl chloride instead of toluene as the substrate. The conversion of benzyl chloride after 24 h was 2.2 wt.% (TOF = 21.6). Benzyl alcohol and benzaldehyde were the only products. Hence, we conclude that most, if not all, of the benzyl alcohol/benzaldehyde in our product are formed by the direct oxidation of toluene and NOT by chlorination followed by hydrolysis.

The oxyhalogenation of benzene and toluene over $CuCl_{16}Pc$–Na-X (0.27) using both H_2O_2 and O_2 as oxidants is shown in Tables 2 and 3, respectively. Both hydrogen and alkali halides were used as the sources of halide ions. The absence of di- and trihalogenated products in Table 2 when using O_2 as the oxidant is due to the low levels of conversion of benzene. The dihalobenzenes were mainly the ortho and para dihaloproducts with the former being predominant. Oxidation products of benzene (like phenol) were not observed under the reaction conditions mentioned in Table 2. Similarly, cresols were absent in the products from the toluene experiments indicating that oxidation/hydroxylation of the aromatic ring (by H_2O_2) was negligible. On the other hand, the oxidation of the methyl side chain leading to benzyl alcohol and benzaldehyde was significant. Benzoic acid was not observed at these conversion levels. The absence of nuclear hydroxylation products (like phenols and cresols) is interesting since, in the absence

TABLE 2

Oxyhalogenation of Benzene over $CuCl_{16}Pc$–Na-X (0.27)

				Halogenated products (wt.%)		
Oxidant	Initiator	Halide	Conv. (%)	Mono-	Di-	Tri-
H_2O_2	—	KCl	9.7	47.5	37	15.5
H_2O_2	—	KBr	11.5	58	34	8
O_2	—	KCl	3.2	100	—	—
O_2	—	KBr	4.1	100	—	—
O_2	TBHP	KCl	5.5	100	—	—
O_2	TBHP	KBr	6.2	100	—	—

Note. Temperature = 338 K; duration = 10 h. Oxidations with O_2 (air) were carried out at 400 psig. Tertiary butyl hydroperoxide (70% in H_2O) was used as the initiator. The concentration of TBHP was 2% of the substrate. The dihalobenzenes were mainly ortho-/para dihalo products. The molar ratio of H_2O_2 : substrate was 1 : 3.

TABLE 3

Oxyhalogenation of Toluene over $CuCl_{16}Pc$–Na-X (0.27)

				Halogenated products (wt.%)				
Oxidant	Initiator	Halide	Conv. (%)	A	B	C	D	E
H_2O_2	—	HCl	31.5	14.5	6.5	—	1.0	78.0
H_2O_2	—	KCl	19.2	20.5	15.0	7.0	6.0	51.5
H_2O_2	—	KBr	26.6	19.0	18.0	15.5	4.5	43.0
O_2	—	HCl	13.5	15.0	27.5	4.5	4.0	49.0
O_2	TBHP	HCl	15.4	9.5	4.5	—	1.5	84.5
O_2	—	KCl	8.2	35.5	20.5	14.5	5.0	24.5
O_2	TBHP	KCl	14.0	30.5	23.0	23.0	4.0	19.5
O_2	—	KBr	11.7	30.5	26.5	9.5	16.0	17.5
O_2	TBHP	KBr	16.8	30.5	26.5	5.5	12.5	25.0

Note. Temperature = 338 K; duration = 10 h; Toluene: H_2O_2 = 3 mole. Oxidation with O_2 (air) was carried out at 300 psig. A, orthohalotoluene; B, parahalotoluene; C, di- and trihalotoluenes; D, benzyl halide; E, benzyl alcohol + benzaldehyde. See footnote to Table 2 for other details.

of the halide ions, they are formed in significant quantities (11). Apparently the nucleophilic halide ions, when present, coordinate with the copper ions and suppress the formation of intermediates (like dioxygen complexes) that lead to nuclear hydroxylation. As was to be expected from the large pore character of zeolite X, there was no pronounced shape selectivity favoring parahalotoluenes. In order to investigate the oxybromination of toluene in more detail, the kinetics of the reaction using H_2O_2 as the oxidant was studied (Fig. 4). Oxidation was the predominant reaction in the initial stages (curve 3, Fig. 4A). There is an induction period in the formation of brominated products (curve 2, Fig. 4A). After the significant onset of the oxybromination reaction (about 4 h), the further formation of oxidation products (like benzyl alcohol and benzaldehyde) ceased and toluene was converted mainly to its brominated products. Among the brominated products, the bromotoluenes were formed at a much faster rate than benzyl bromide (Fig. 4B), suggesting that the brominating species is not a radical. The latter usually leads to significant yields of benzyl bromide (15). Since the liberation of Br_2 from KBr by H_2O_2 in the presence of homogeneous and enzyme catalysts is well known, it was expected that the same situation may prevail in the present case also. If Br_2 is formed from KBr in our system, it can be detected spectrophotometrically through its complex Br_3^- which has an absorption maximum at 267 nm. The tribromide ion is formed according to the equilibrium

$$Br_2 + Br^- \rightleftharpoons Br_3^-$$

$$K_e = \frac{[Br_3^-]}{[Br_2][Br^-]}$$

Literature values for K_e vary from 15 to 20 M^{-1} and are dependent on reaction conditions (16). We analyzed for

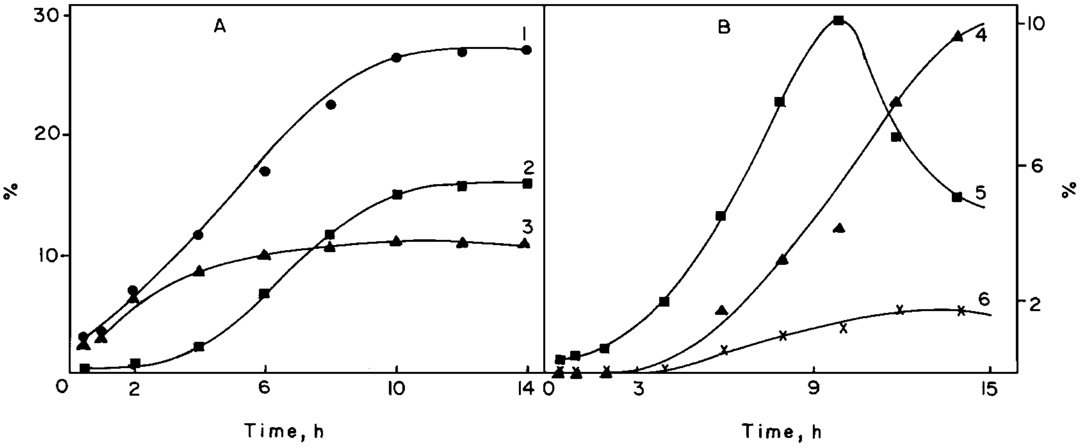

FIG. 4. Kinetic plots for the oxybromination of toluene over $CuCl_{16}Pc$–Na-X (0.27). (A) Curves 1–3 indicate toluene conversion (1), and formation of halogenated (2) and oxidation (3) products respectively. (B) Curves 4–6 indicate distribution of monobromotoluenes (4), di + tribromotoluenes (5) and benzyl bromide (6), respectively.

TABLE 4

Oxyhalogenation of Phenol over $CuCl_{16}Pc$–Na-X (0.27)

Oxidant	Initiator	Halide	Conv. (%)	Halogenated products (wt.%) Mono-	Di-	Tri-
H_2O_2	—	KCl	21.2	42.0	32.0	26.0
H_2O_2	—	KBr	24.1	40.0	33.5	26.5
O_2	—	KCl	7.9	64.5	26.5	9.0
O_2	—	KBr	8.8	62.5	33.0	4.5
O_2	TBHP	KBr	18.1	62.0	25.0	13.0

Note. Temperature = 323 K; duration = 10 h; phenol: H_2O_2 = 3 mole. Oxidations with O_2 (air) were carried out at 300 psig. For other details see footnote to Table 2.

TABLE 5

Oxyhalogenation of Aniline over $CuCl_{16}Pc$–Na-X (0.27)

Halide	Conv. (%)	Halogenated products (wt.%) Mono-	Di-	Tri-
KCl	9.7	64.0	30.0	6.0
KBr	10.3	63.0	15.5	21.5

Note. Temperature = 338 K; duration = 10 h; oxidant, O_2 (Air) = 400 psig. TBHP was used as the initiator. Orthohaloaniline was the major monohalogenated product. See footnote to Table 2 for other details.

the presence of Br_3^- by measuring the absorption at 267 nm spectrophotometrically during the course of oxybromination of toluene (Fig. 5A). In the presence of catalyst but absence of toluene substantial formation of Br_3^- (and hence Br_2^-) is detected (curve 1, Fig. 5B). Only a trace amount of Br_3^- is detected in the absence of both catalyst and toluene (curve 2, Fig. 5B). When toluene is present, the concentration of Br_3^- (and hence Br_2) is suppressed (curves 3 and 4, Fig. 5B), presumably because the Br_2 formed is immediately consumed in the bromination of toluene and hence no free Br_2 is available to form Br_3^-. Hence, our studies suggest that Br_2, formed by oxidation from Br^-, may be the brominating agent. In agreement with this hypothesis, when Br_2 is used to brominate toluene over K-L zeolites, the product pattern (nuclear vs side-chain bromination) was similar (15) to that observed in the present study; products of nuclear halogenation (like chlorotoluenes) predominated over those like benzyl chloride arising from chlorination of the methyl side chain.

The oxyhalogenation of phenol, aniline, anisole, and resorcinol are shown in Tables 4, 5, 6, and 7, respectively. The halogenated derivatives of these aromatics are of significant economic value in the fine chemicals industry. The monohalogenated derivatives were ortho/para products with the ortho products in slight excess. Metahalogenated products were not observed. Even though Tables 4–7 present results with KCl and KBr as halogenating agents, similar results were also obtained with NaCl and NaBr, respectively. Dinesh *et al.* (3), reported the oxybromination of phenol and resorcinol with KBr and H_2O_2 using ammonium metavanadate dissolved in acetonitrile–H_2O as solvent. While phenol could not be brominated by KBr, resorcinol was converted to an extent of about 40% during 20 h of reaction at room temperature (entries 10 and 8 in Table 1 of Ref. 3). The major product obtained by the bromination

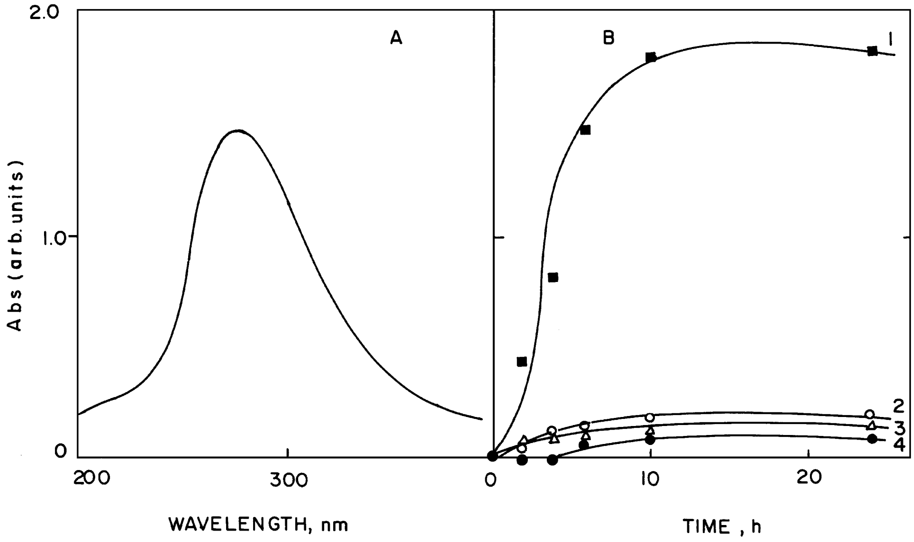

FIG. 5. (A) UV spectrum of Br_3^- in the reaction mixture during oxybromination of toluene by KBr and H_2O_2 using $CuCl_{16}Pc$–Na-X (0.27) as catalyst. (B) Variation in the intensity of the 267 nm band in the presence of catalyst but absence of toluene (curve 1), in the absence of both catalyst and toluene (curve 2), in the presence of both catalyst and toluene (curve 3), and in the presence of toluene but absence of catalyst (curve 4).

TABLE 6

Oxyhalogenation of Anisole over $CuCl_{16}Pc$–Na-X (0.27)

			Halogenated products (wt.%)			
			Monohalo			
Oxidant	Halide	Conv. (%)	ortho	para	2.4. di	2.4.6. tri
H_2O_2	KBr	13.8	27.0	21.0	13.0	39.0
O_2	KBr	6.7	18.0	7.5	55.0	19.5
O_2	KCl	4.8	18.5	6.5	60.5	14.5

Note. Temperature = 338 K; duration = 10 h. TBHP was used as an initiator in oxidation with O_2 (air). For other details see footnote to Table 2.

of resorcinol was the 2-bromo derivative. Similar results are also observed over our solid catalysts with *both* H_2O_2 and O_2 as oxidizing agents. An advantage in the use of O_2 during oxychlorination of resorcinol is the higher selectivity for the desired monochloro product (Table 7). Conte *et al.* (4) had earlier reported the oxybromination of anisole with H_2O_2 and KBr using dissolved NH_4VO_3 as catalyst. Parabromoanisole was the major monohalogenated product. Our results with the solid catalyst $CuCl_{16}Pc$–Na-X (0.27) (Table 6) are different; both the ortho and the para derivatives are formed in significant quantities. Perhaps, as suggested by the authors themselves (4), the two phase, $H_2O/CHCl_3$ solvent system, facilitates the selective formation of the para derivative. The use of solid catalysts in conjunction with O_2 as the oxidizing agent at low temperatures is a significant advance in the technology of oxyhalogenation of aromatic compounds.

The influence of pH on the selectivity for halogenated products in the oxybromination of resorcinol with KBr and H_2O_2 is shown in Fig. 6. The pH was adjusted with a phosphate buffer. The optimal performance of our catalyst system in the pH range 5.0–6.0 is similar to that of the enzyme vanadium bromoperoxidase but differs from dioxovanadium (V) catalysts which require significantly greater acid concentration (≥ 0.001 MH^+) (5). While the reaction mechanism of oxyhalogenation catalyzed by enzymes is not yet clear in all detail, it seems to involve a halogenium ion (X^+) or hypohalous acid (HO^-X^+) as an intermediate of the reaction (17, 18). Bromine, for example, is known to be in equilibrium with the tribromide ion and hypobromous acid in aqueous systems, the position of the equilibrium being

TABLE 7

Oxyhalogenation of Resorcinol

Catalyst	Oxidant	Halide	Conv. (%)	Halogenated products (wt.%) Mono-	Di-	Tri-
$CuCl_{14}Pc$–Na-X	H_2O_2	KBr	31.6	54.5	26.5	19.0
$CuCl_{14}Pc$–Na-X	H_2O_2	KCl	28.5	59.0	30.5	10.5
$CuCl_{14}Pc$–Na-X	O_2	KCl	16.5	85.5	14.5	—
$CuCl_{14}Pc$–Na-X	O_2	KBr	18.2	100	—	—
$CuCl_{14}Pc$–K-L	O_2	KBr	14.9	90.0	10.0	—
$Cu(NO_2)_4Pc$–Na-Y	O_2	KBr	7.5	100	—	—

Note. Temperature = 323 K; duration = 10 h. Oxidations with O_2 (air) were done at 300 psig. No initiator was used. 2-halo resorcinol was the major monohalogenated product. For other details see footnote to Table 2.

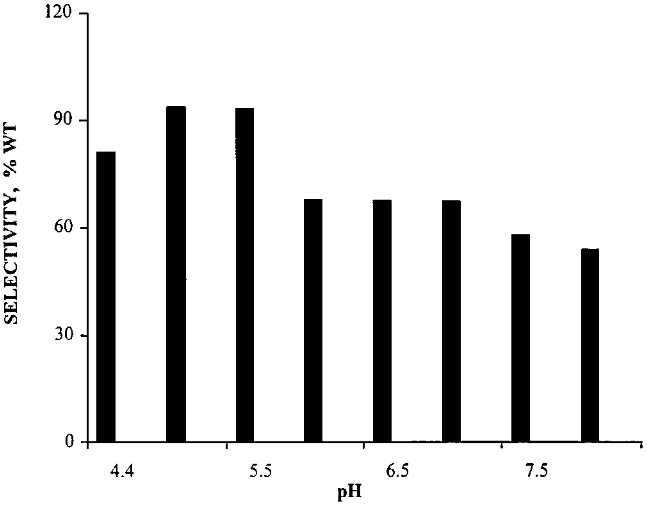

FIG. 6. The influence of pH on the selectivity for brominated products in the oxybromination of resorcinol using $CuCl_{16}Pc$–Na-X (0.27), KBr, and H_2O_2 at 333 K.

$$Br_2 \xrightleftharpoons{Br^-, H_2O} Br_3^- + HOBr$$

dependent on the pH of the medium. The observation of Br_2 in our system (Fig. 5A), the ortho–para orientation among the nuclear halogenated products (Table 3, for example) and the pH dependence of the conversion (Fig. 6) suggest that the halogenating agent is an electrophilic species.

4. CONCLUSIONS

We have developed a novel, solid, catalyst system for the oxychlorination and oxybromination of aromatics. The catalysts comprise of the chloro- or nitrophthalocyanines of Cu, Fe, and Co encapsulated in zeolites. They use H_2O_2 or O_2 as the oxidants and the halides of hydrogen or alkali metals as the halogenating agents under ambient or near-ambient conditions. We envisage their application, especially in the fine chemicals industry, for the manufacture of halogenated aromatics in an environmentally *clean* manner using low value halogenating agents like HCl rather than more expensive halogens, like Cl_2.

ACKNOWLEDGMENTS

We thank Dr. R. Vetrivel for the molecular modeling work and the members of the Catalysis Division for experimental assistance. We also thank the European Commission (Contract C11-CT93-0361) for partial financial support. R.R. thanks CSIR for a research fellowship.

REFERENCES

1. Leulier, A., *Bull. Soc. Chim. Fr.* **35**, 1325 (1924).
2. Johnson, R., and Reeve, K., *Spec. Chem.* 32 (Oct. 1992).
3. Dinesh, C. U., Kumar, R., Pandey, B., and Kumar, P., *J. Chem. Soc. Chem. Commun.*, 611 (1995).
4. Conte, V., Furia, F. D., and Moro, S., *Tetr. Lett.* **35**, 7429 (1994).
5. de la Rosa, R. I., Clague, M. J., and Butler, A., *J. Am. Chem. Soc.* **114**, 760 (1992).
6. Westervelt, R., *Chem. Week*, 26 (Aug. 14, 1996).
7. Birchall, J. M., Hazeldine, R. N., and Morley, O. J., *J. Chem. Soc. C*, 2667 (1970).
8. “Insight II User Guide, Version 2.3.5,” Biosym. Technologies, SanDiego, 1994.
9. Ermer, O., *Structure Bonding* **27**, 161 (1976).
10. Raja, R., and Ratnasamy, P., *Stud. Surf. Catal. A* **101**, 181 (1996).
11. Raja, R., and Ratnasamy, P., *Stud. Surf. Catal. B* **103**, 1037 (1996).
12. Raja, R., and Ratnasamy, P., *Appl. Catal. A: General* **143**, l45 (1996).
13. Balkus, K. J., Jr. Gabrielov, A. G., Bell, S. L., Bedioui, F., Roue, L., and Devynck, J., *Inorg. Chem.* **33**, 67 (1994).
14. Bhadbhade, M. M., and Srinivas, D., *Inorg. Chem.* **32**, 5458 (1993).
15. Ratnasamy, P., Singh, A. P., and Sharma, S., *Appl. Catal. A: General* **135**, 25 (1996).
16. Popov, I. A., *in* “Halogen Chemistry,” Vol. 1, p. 225. Academic Press, New York, 225, 1967.
17. Yamada, H., Itoh, N., and Izumi, Y., *J. Biol. Chem.* **260**, 11962 (1985).
18. Itoh, N., Izumi, Y., and Yamada, H., *Biochem.* **26**, 282 (1987).