Oxidation of cyclohexane over copper phthalocyanines encapsulated in zeolites

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The oxidation of cyclohexane to cyclohexanol, cyclohexanone and adipic acid has been studied using phthalocyanines and substituted (chloro- and nitro-) phthalocyanines of copper, cobalt and iron encapsulated in zeolites X and Y, at ambient conditions and using molecular oxygen as well as alkyl (tertiary butyl, cyclohexyl and cumyl) hydroperoxides as the oxidants. The catalytic efficiencies of the encapsulated materials are much higher than those of the neat complexes. The rate of oxidation of cyclohexane using copper hexadecachloro phthalocyanine-encapsulated Y zeolite catalysts is quite high (TOF = 400 h^{-1}) with TBHP efficiencies which can reach upto 90%. The isolated encapsulated metal complex is the active site. Solvents exert a major influence on product distribution (cyclohexanol, cyclohexanone and adipic acid are the major products). Byproducts like succinic and glutaric acids are not formed when using acetonitrile as the solvent. Rates of oxidation when using the alkyl hydroperoxides as oxidants decrease with an increase in their molecular cross-section (cyclohexyl > *t*-butyl > cumyl) confirming that the active site is indeed located inside the zeolitic cavities and not on the external surface.

Keywords: cyclohexane oxidation, copper catalysts, selective oxidation, zeolite catalysts, copper phthalocyanine, adipic acid

1. Introduction

The oxidation of cyclohexane to cyclohexanol and cyclohexanone, under mild conditions has an important industrial significance. More than 10^6 tonnes of cyclohexanol and cyclohexanone are made worldwide per year for the production of Nylon-6 and Nylon-6-6. Industrially, cyclohexane is oxidized at 423–433 K and 0.9 M Pa air, in the presence of cobalt naphthenate, or metaboric acid to form a mixture of cyclohexanol and cyclohexanone [1] (the so-called K-A oil). Enzymes are capable of oxidizing cyclohexane to cyclohexanol at room temperature with high selectivity [2–8]. The ability of cytochrome P-450 to activate oxygen for hydrocarbon oxidation has motivated many studies involving metalloporphyrin catalysts [9–11]. In the Gif system of Barton et al. [12], which oxidizes saturated hydrocarbons at ambient conditions, the hydrocarbon in pyridine–acetic acid solvent is oxidized in the presence of an iron-based catalyst and an electron source. Gif systems were designed to emulate the non-heme enzymatic oxidations of alkanes. A major drawback of the Gif system is that during the oxidation, radical reactions become more important causing over-oxidation and coupling of the products with pyridine [13]. Moreover, the water formed during the oxidation causes hydrolysis of the catalyst and phase separation, thereby leading to its deactivation. An interesting feature of the Gif system is that the iron salt can be substituted by a copper salt [14]. This system was less efficient than the iron system, although more selective for oxidation of cyclohexane to cyclohexanone.

Encapsulated Fe(II) and Ru(II) phthalocyanines have also shown promise as catalysts for the oxidation of cyclohexane, using alkyl peroxides or iodosyl benzene as the oxidants [15–19]. Iodosyl benzene, however, leads to zeolite pore blockage and alkyl peroxides can bleach the catalyst. Parton et al. [18] circumvented the above problem by incorporating the zeolite encapsulated FePc complex in a polymer matrix. The polymer serves to inhibit the preferential adsorption of the peroxide over the alkane, and thereby enhances catalyst stability. Parton et al. [16] found that iron-phthalocyanine-Y catalysts are more active and regenerable than the homogeneous complexes which are oxidatively destroyed under reaction conditions and are therefore not regenerable.

In view of the role of copper in the Gif system mentioned above [14], it is of interest to investigate the catalytic properties of copper in other enzyme-mimicking systems. The present paper reports the oxidation of cyclohexane over phthalocyanines and substituted phthalocyanines of copper encapsulated in zeolites X and Y at ambient conditions and using molecular oxygen as well as alkyl hydroperoxides as the oxidants. Apart from the intrinsic scientific merits, the quest for a solid catalyst for the oxidation of cyclohexane, if successful, can have a significant industrial impact in (1) replacing the homogeneous metal catalysts in the preparation of

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K-A oil and (2) replacing HNO_3 in the oxidation of K-A oil to adipic acid. Moreover, the direct oxidation of cyclohexane to adipic acid, in significant yields, over a solid catalyst has not been reported so far in the open literature.

2. Experimental

2.1. Materials

The *neat* $CuCl_{16}Pc$, $CoCl_{16}Pc$, $FeCl_{16}Pc$ (where Pc stands for phthalocyanine) complexes were synthesized according to the procedure reported by Birchall et al. [20]. 2.8 mmol of Cu(II), Co(III) or Fe(II) acetate (0.56 g, BDH) was mixed with 14.0 mmol (2.8 g, Aldrich) of tetrachlorophthalonitrile in 55 ml of 1-chloronaphthalene (Aldrich) in a Parr reactor under nitrogen (500 psi). The mixture was refluxed for 24 h, cooled to room temperature and centrifuged. Then 200 ml of petroleum ether was added to the greenish blue/ brown/ bluish grey filtrate that was then submerged in an ice bath. The dark greenish blue/ brown/ bluish grey precipitate was recovered by centrifugation. The $CuCl_{16}Pc$, $CoCl_{16}Pc$, $FeCl_{16}Pc$ complexes were recrystallized from sulfuric acid and isolated in 50–60% yield.

Copper(II) tetra nitro phthalocyanines ($Cu(NO_2)_4$ Pc) were synthesized as described below: 0.63 g copper(II) acetate (BDH) was mixed with 3.75 g of 4-nitrophthalonitrile (Aldrich) in 60 ml of 1-chloronaphthalene (Aldrich) in a Parr reactor under nitrogen (500 psi) with constant stirring (300 rpm). The mixture was refluxed for 24 h, cooled to room temperature and centrifuged. Then 200 ml of petroleum ether was added to the bluish grey filtrate that was then submerged in an ice bath. The dark blue precipitate was recovered by centrifugation. The $Cu(NO_2)_4Pc$ complex was recrystallized from sulfuric acid and isolated in 45% yield. CuPc and CoPc 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. 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 $CuCl_{16}Pc$, $Cu(NO_2)_4Pc$, $FeCl_{16}Pc$ or $CoCl_{16}Pc$ 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 of fumed silica (Sigma), 3.2 g NaOH, 0.30 g of $CuCl_{16}Pc$, $Cu(NO_2)_4Pc$, $FeCl_{16}Pc$ or $CoCl_{16}Pc$ and 8.0 ml of H_2O. Addition of the aluminate solution (9.0 g of 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 of 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 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. The synthesis of $CuCl_{16}Pc$, $CoCl_{16}Pc$, $FeCl_{16}Pc$ 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. Zeolite Y was synthesized using seeds of an alumino-silicate gel. 12 g of homogeneous seed slurry (aged for 24 h at room temperature) was added to a mixture containing 21.7 g of sodium silicate. 0.30 g of the metal complex ($CuCl_{16}Pc$, $CuCl_{14}Pc$, $FeCl_{16}Pc$, $CoCl_{14}Pc$ or $Cu(NO_2)_4Pc$) was homogeneously blended with the silicate solution. The aluminate solution (1.4 g of sodium aluminate and 2.1 g of aluminium sulphate) was added dropwise to the silicate solution and this resulted in a slurry with an intense green colour. The gel was aged at room temperature with stirring for 24 h and then heated at 373 K for 12 h. Na-X and Na-Y with varying loadings of $CuCl_{16}Pc$, $Cu(NO_2)_4Pc$, $FeCl_{16}Pc$ or $CoCl_{16}Pc$ were prepared similarly. Zeolites containing impregnated Pc (table 1, No. 10; figure 1, curve B) were prepared by dissolving the Pc in a pyridine–acetic acid 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(0.11) designates a Na-X zeolite containing 0.11 wt% copper in the form of a hexa decachloro copper phthalo-

Table 1
Oxidation of cyclohexane with O_2 over phthalocyanines [a]

S. No.	Catalyst	Total conv. (wt%)	TOF [b] (h^{-1})	Products [c] (%)					
				A	B	C	D	E	F
1	CuPc	1.1	0.005	70.0	30.0	–	–	–	–
2	CoPc	1.5	0.006	41.6	58.4	–	–	–	–
3	$CuCl_{16}Pc$	17.2	0.14	37.7	44.2	6.9	7.2	4.0	–
4	$Cu(NO_2)_4Pc$	6.5	0.04	46.1	53.9	–	–	–	–
5	$FeCl_{16}Pc$	13.4	0.13	38.5	41.0	5.0	13.4	2.1	–
6	$CoCl_{16}Pc$	18.0	0.16	13.5	53.6	6.0	23.9	3.0	–
7	$NiCl_{16}Pc$	2.1	0.02	47.6	–	–	–	52.4	–
8	$AlCl_{16}Pc$	0.6	0.01	–	–	–	–	100	–
9	$CuCl_2$-Na-Y(0.14) (exchanged) [d]	0.1	1.7	80.2	8.5	–	–	4.1	7.2
10	$CuCl_{16}Pc$-Na-Y(0.32) (impregnated) [e]	2.0	19.2	38.3	33.5	5.5	7.9	14.8	–
11	$CuCl_{16}Pc$ + Na-Y (phys. mix., Cu = 0.11 wt%) [f]	0.7	17.5	35.5	35.2	6.7	8.6	14.0	–
12	$CuCl_{16}Pc$-Na-X(0.28)	14.9	167.8	28.1	48.5	7.0	16.4	–	–
13	$CuCl_{16}Pc$-Na-Y(0.11)	13.7	405.8	30.2	48.3	12.7	8.8	–	–
14	$Cu(NO_2)_4Pc$-Na-X(0.14)	5.7	132	78.9	21.2	–	–	–	–
15	$FeCl_{16}Pc$-Na-X(0.16)	11.3	196.1	33.0	47.8	7.8	11.4	–	–
16	$CoCl_{16}Pc$-Na-X(0.27)	17.6	184	19.4	51.1	8.8	20.7	–	–
17	no catalyst	0.5	≈0	–	–	–	–	100	–

[a] Cyclohexane = 25 g; catalyst weight = 0.75 g; reaction time = 8 h; temperature = 343 K; solvent = acetonitrile = 45 g; air = 800 psi; TBHP = 0.40 g.
[b] TOF = turnover frequency; moles of cyclohexane converted per mole of copper in the catalyst per hour.
[c] A = cyclohexanol; B = cyclohexanone; C = valeraldehyde; D = adipic acid; E = succinic plus glutaric acids; F = valeric acid.
[d] 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.
[e] 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.
[f] Sample $CuCl_{16}Pc$ + Na-Y (phys. mix., Cu = 0.11wt%) was a physical mixture of 1.017 g of Na-Y and 17.5 mg of $CuCl_{16}Pc$.

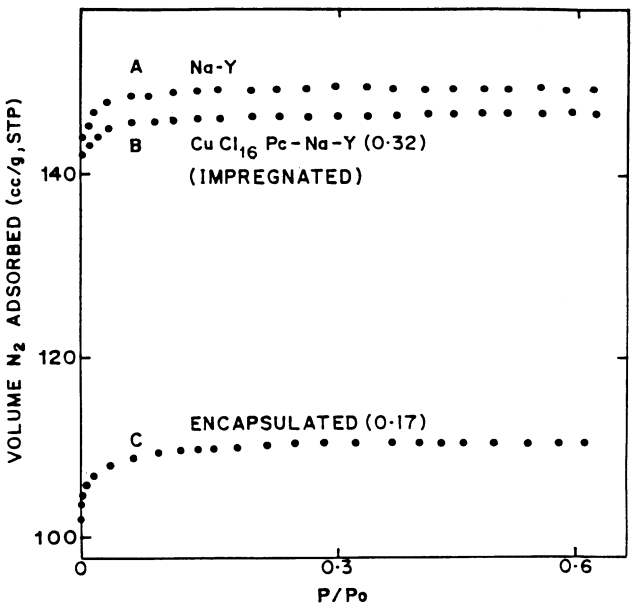

Figure 1. N_2 adsorption isotherms at liquid N_2 temperature of Na-Y (A); $CuCl_{16}Pc$-Na-Y(0.32) (impregnated) (B); and $CuCl_{16}Pc$-Na-Y(0.17) (encapsulated) (C).

cyanine complex encapsulated, most probably, in the supercages of the faujasite structure.

2.2. Procedures

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. In a typical oxidation reaction, the solid catalyst (0.2–0.75 g) was added to the substrate in the specified solvent (acetonitrile, acetone, etc.). Aqueous H_2O_2 (25 wt%) was added after the desired temperature was attained. In the case of oxidations using O_2 as the oxidant, tertiary butyl hydroperoxide (70% aqueous solution (Aldrich)) equivalent to 1–3% by weight of the substrate was added to the reaction mixture before air was admitted into the Parr autoclave (300 ml capacity). Periodically, samples were removed and centrifuged to remove the solid catalyst. The gas from the Parr reactor was collected in a gas bulb fitted with a three-way valve. Copper, iron or cobalt were not detected (by atomic absorption spectroscopy, Hitachi model Z-8000) in the colourless reaction product when using any of the solid catalysts used in the present study. The products of the oxidation reactions were analyzed by gas chromatogra-

phy (Hewlett Packard, 5890) equipped with a FFAP column (30 m × 0.25 mm). The analyses for CO_2 and water were carried out using a Shimadzu GC-15-A equipped with a TCD detector and a Porapak N column. The liquid products were extracted with diethyl ether. In some cases, the products were isolated by column chromatography, after appropriate work-up to establish yields. The acids formed (formic, adipic, succinic, valeric and glutaric acids) were esterified and analyzed as methyl esters by the procedure given below: 300 μl of the sample was taken in a glass vial. 2 ml of 14% boron trifluoride (BF_3) in methanol was added to the glass vial which was stoppered with a teflon lined stopper and heated for 1 h at 353 K. The sample was cooled to room temperature and 2 ml of Milli-Q reagent water was added with mild shaking. 2 ml of HPLC grade dichloromethane (S.D. Fine Chemicals) was added before the GC analysis. The identity of the products was further confirmed by GC-MS (Shimadzu QCMC-QP 2000A).

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 Kα 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 200–900 nm region. UV spectra of liquid samples were measured in the 200–400 nm region. XPS of the solid catalysts were recorded with a VG Scientific ESCA III Mark (II) with Mg Kα (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 an 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. [21]. 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 [22]. 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. 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 confirm the presence of the copper complex inside the zeolite cavities (figure 1). When $CuCl_{16}Pc$ was merely impregnated on the external surface of Na-Y (curve B, figure 1) 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 (curve C, figure 1), wherein the zeolite was synthesized in the presence of the $CuCl_{16}Pc$ complex 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 [23–25]. 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 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, sample No. 10). Balkus et al. [26] 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. 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 kcal/mol), is available to the system during the synthesis of the encapsulated catalyst. Substituted phthalocyanines are known to be quite rugged and stable upto 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 thereby enhancing the reactivity of the complex towards molecular O_2 [27] in general and in oxidation reactions, in particular.

3.2. Catalytic activity

Experimental evidence to show that the oxidation of cyclohexane is indeed catalyzed by the solid zeolite catalyst containing the encapsulated metal complex and not by the free complex dissolved in solution is presented in figure 2. In one set of two identical experiments, the solid catalyst ($CuCl_{16}$Pc-Na-X(0.28)) was removed by centrifugation after a reaction time of 6 h (curve B, figure 2). While the conversion of cyclohexane proceeded further in the presence of the solid catalyst (curve A, figure 2), there was no further conversion of cyclohexane when the catalyst was removed from the reaction system (curve B, figure 2). This indicates that: (1) The solid catalyst is essential for the oxidation of cyclohexane. (2) Oxidation of cyclohexane by free metal complex or dissolved copper complexes leached out from the zeolite matrix is negligible. This conclusion was independently confirmed by the analysis of the reaction products for copper (by atomic absorption spectroscopy). (3) In the absence of the catalyst, molecular oxygen as well as TBHP are unable to oxidize cyclohexane to any significant extent. In independent experiments carried out in the absence of the catalyst, the conversion of cyclohexane under otherwise identical experimental conditions to those of figure 2, was about 0.6 mol%. When TBHP was used as the oxidant, the cyclohexane conversion in the absence of the catalyst was only 0.5 mol%. The zeolites alone, without the encapsulated metal complexes, were also catalytically inactive. Thus, we may conclude, that the oxidation of cyclohexane reported in the present study, is indeed catalyzed by the metal complexes encapsulated in the zeolite matrix.

The results of the oxidation of cyclohexane using O_2 as the oxidant, TBHP as the initiator (2% by weight) and acetonitrile as the solvent at 343 K over the various copper, iron, cobalt, nickel and aluminium phthalocyanines both in the neat and in the encapsulated states are presented in table 1. The following points may be noted:

(1) The unsubstituted metal phthalocyanines have a low activity; only cyclohexanol and cyclohexanone are formed.

(2) Copper, cobalt and iron phthalocyanines containing electron-withdrawing groups (like –Cl or $–NO_2$) were more active, by an order of magnitude, than their non-substituted analogs. The electron-withdrawing groups enhance the electrophilic character of the active oxygen species and consequently its reactivity. This is comparable with what is reported in literature for porphyrins [28].

(3) The intrinsic catalytic activity (TOF = turnover frequency; moles of cyclohexane converted per mole of catalyst per hour) of the neat chloro complexes of iron, copper and cobalt are of similar magnitude.

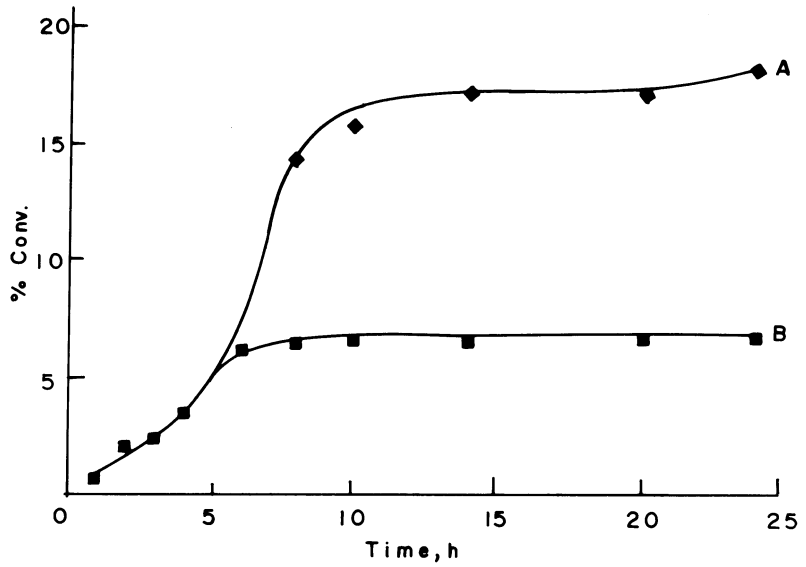

Figure 2. Kinetics of cyclohexane oxidation in the presence of $CuCl_{16}$Pc-Na-X(0.28) (curve A) and when the catalyst is removed from the reaction mixture at 6 h reaction time (curve B).

(4) When the copper ion is exchanged into the zeolite without the Pc ligand ($CuCl_2$-Na-Y(0.14), No. 9), even though the TOF is relatively higher (TOF = 1.7) than that of the neat Pc complexes (TOF = 0.14), it is still much lower than that of the encapsulated complexes (TOF = 130–400). More importantly, significant differences in selectivity are seen: The major product is cyclohexanol. Valeraldehyde and adipic acid, which are normally produced by the further reaction of the cyclohexanol and cyclohexanone, are absent, and valeric acid, which is not observed over the Pc catalysts, is seen amongst the products.

(5) When $CuCl_{16}Pc$ is impregnated on Na-Y (No. 10, $CuCl_{16}Pc$-Na-Y(0.32) (impregnated)), though the TOF (19.2) is higher than that of the neat complexes, it is still lower than that of the encapsulated Pc complexes. More interestingly, glutaric and succinic acids, which are absent in the case of the encapsulated catalysts, are seen in the products (compare catalysts 10 and 13, for example). This difference in selectivity is an additional evidence for the encapsulation of the complexes in the cavities of the zeolites.

(6) A physical mixture of $CuCl_{16}Pc$ and Na-Y (catalyst 11, table 1) behaves in a manner similar to that of catalyst 10 ($CuCl_{16}Pc$ impregnated on Na-Y).

(7) It may be noted that though the neat complexes are more active than their encapsulated analogs (for, e.g., the cyclohexane conversions using $CuCl_{16}Pc$ and $CuCl_{16}Pc$-Na-X(0.28) were 17.2 and 14.9 wt%; and using $Cu(NO_2)_4Pc$ and $Cu(NO_2)_4Pc$-Na-X(0.14) were 6.5 and 5.7 wt%) on a weight basis, the catalytic efficiency of the encapsulated catalysts (in terms of activity per copper atom per hour) is higher than that of the neat complexes by more than an order of magnitude. This is, probably, due to the isolation of the copper sites in the zeolite cavities. 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 cyclohexane molecules in reaching the active sites will be higher leading to lower TOF values at higher loading levels of the metal complex (catalysts 12 and 13, for example).

(8) The central transition metal of the phthalocyanine complex is the seat of the catalytic activity. $Cl_{16}Pc$ or phthalocyanines of non-transition metals (like Al) had negligible oxidation activity (the conversion of cyclohexane using $Cl_{16}Pc$ as the catalyst was 0.5 wt%).

Even though cyclohexane could be oxidized over the above catalysts (table 1) using air alone, the conversion levels were below 3%. There is, hence, a synergistic enhancement in TOF when both O_2 and TBHP were used as the oxidants. The synergistic role of TBHP (along with O_2) in enhancing the rate of oxidation reactions has been reported very recently [29,30], though the mechanism is not very clear. Since there is a direct correlation between the presence of TBHP and cyclohexane conversion levels, the reaction is probably of a radical nature. When cyclohexane is reacted over $CuCl_{16}Pc$-Na-X(0.28) in the absence of O_2, substituting N_2 for air under otherwise identical conditions of table 1, the TOF was 1.2 instead of 167.8 (table 1, No. 12). The concentration of cyclohexanol and cyclohexanone in the products was 57.1 and 42.9 wt%, respectively.

The kinetics of oxidation of cyclohexane using $CuCl_{16}Pc$-Na-X(0.28) as the catalyst is illustrated in figure 3. Cyclohexanol and cyclohexanone were the

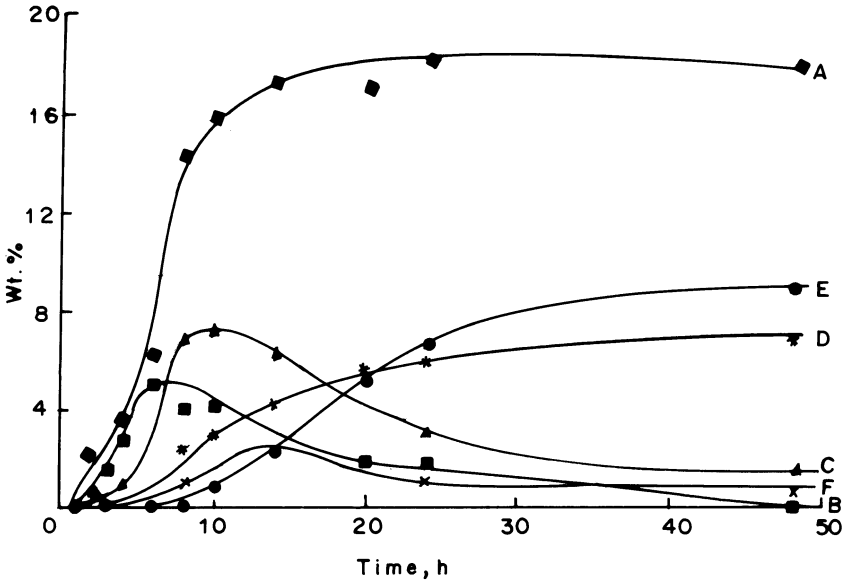

Figure 3. Kinetic plots for the oxidation of cyclohexane using $CuCl_{16}Pc$-Na-X(0.28) as the catalyst; cyclohexane = 25 g; catalyst weight = 0.75 g; temperature = 343 K; solvent = acetonitrile = 45 g; air = 800 psi; TBHP = 0.40 g. Curves A–F indicate cyclohexane conversion (A), and the yields of cyclohexanol (B), cyclohexanone (C), adipic acid (D), glutaric plus succinic acids (E) and valeraldehyde (F).

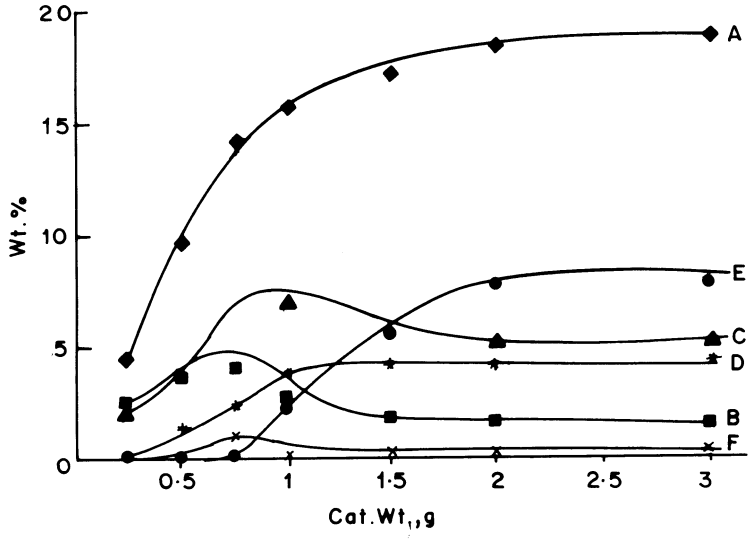

Figure 4. Influence of catalyst weight on cyclohexane conversion (A) and formation of cyclohexanol, cyclohexanone, adipic acid, glutaric plus succinic acids, and valeraldehyde (mol%, curves B–F, respectively). Cyclohexane = 25 g; reaction time = 8 h; temperature = 343 K; solvent = acetonitrile = 45 g; air = 800 psi; TBHP = 0.40 g.

major products at lower conversion levels and residence times. When the reaction is continued beyond 14 h significant amounts of adipic, glutaric and succinic acids start appearing in the reaction mixture. At 48 h, there is almost complete conversion of the cyclohexanol and cyclohexanone to adipic and other acids. In independent experiments carried out, where cyclohexanol or cyclohexanone were taken as the substrates, there was conversion of the above substrates to acids.

The catalytic nature of the reaction is confirmed by the data in figure 4, which illustrates the influence of catalyst weight on cyclohexane conversion and product distribution. Cyclohexane conversion is negligible in the absence of any catalyst and no oxidation products are formed. The conversion increases linearly with increase in catalyst concentration (figure 4) and levels off beyond 2 g. This phenomenon is quite common in heterogeneous catalysis and may arise due to a variety of reasons including thermodynamic limitations, poisoning of the catalyst by one of the secondary solid products formed (adipic, glutaric and succinic acids, for example), mass transfer limitations at high reaction rates, etc. A combination of such reasons is, probably, responsible for the leveling off in conversion observed in figure 4. The presence of acids is also negligible at lower conversion levels.

The influence of temperature on the rate and product distribution (in the oxidation of cyclohexane) is shown

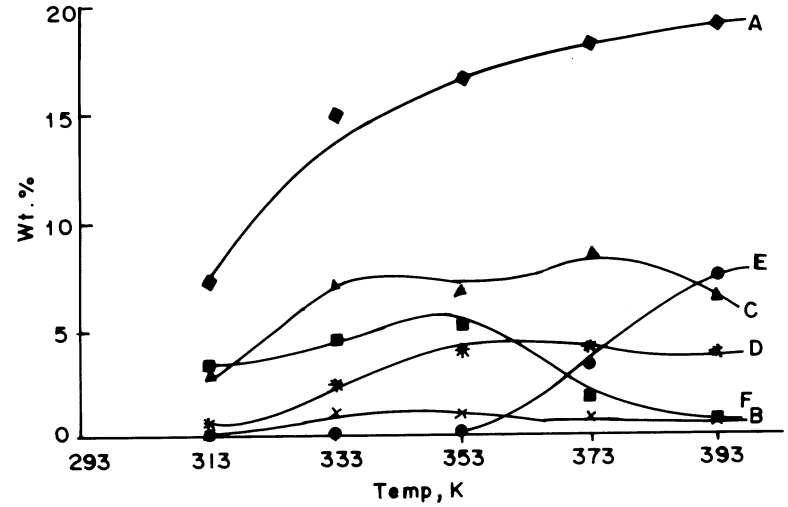

Figure 5. Influence of temperature on cyclohexane conversion (A), and formation of cyclohexanol, cyclohexanone, adipic acid, glutaric plus succinic acids and valeraldehyde (mol%, curves B–F, respectively); catalyst weight = 0.75 g. Cyclohexane = 25 g; reaction time = 8 h; solvent = acetonitrile = 45 g; air = 800 psi; TBHP = 0.40 g.

Table 2
Influence of cyclohexane : TBHP ratio [a]

Cyclohexane : TBHB ratio (mol)	TBHP efficiency (%)	Total conv. (wt%)	TOF [b] (h^{-1})	Products [c] (mol%)				
				A	B	C	D	E
1 : 5	35.6	35.6	401.1	1.9	18.5	5.3	32.3	42.0
1 : 2	34.7	34.7	390.3	1.5	25.6	4.6	33.1	35.2
1 : 1	29.5	29.5	332.1	3.0	31.2	2.7	30.1	33.0
2 : 1	52.8	26.4	297.3	7.5	33.7	18.1	19.6	21.1
3 : 1	64.5	21.5	242	22.3	41.8	12.1	18.1	5.7
5 : 1	91.0	18.2	205	23.0	41.2	12.0	22.0	1.8

[a] Cyclohexane = 25 g; catalyst weight, $CuCl_{16}$Pc-Na-X(0.28) = 0.75 g; reaction time = 8 h; temperature = 343 K; solvent = acetonitrile = 45 g. The cyclohexane : TBHP ratio was varied by changing [TBHP].
[b] TOF = turnover frequency; moles of cyclohexane converted per mole of copper in the catalyst per hour.
[c] A = cyclohexanol; B = cyclohexanone; C = valeraldehyde; D = adipic acid; E = mainly succinic and glutaric acids.

in figure 5. At high temperatures large amounts of adipic, glutaric and succinic acids are produced, probably due to the further oxidation of the cyclohexanol formed. Beyond 80°C, there is a gradual decrease in quantity of cyclohexanol in the reaction mixture, but an increase in the concentration of acids in the products. The presence of acids was confirmed *only* on esterification of the reaction mixture.

The influence of concentration of the oxidant, TBHP, on cyclohexane conversion and product formation over $CuCl_{16}$Pc-Na-X(0.28) is given in table 2. The results indicate that for maximum utilization of TBHP in the conversion of cyclohexane (to cyclohexanol, cyclohexanone and adipic acid) and minimum formation of succinic and glutaric acids, the cyclohexane : TBHP (mole) ratio should be kept as high as possible. The formation of acids increased with increasing the concentration of TBHP. At the end of the oxidation reaction, TBHP was converted to tert-butanol. Other oxygen sources like H_2O_2, cyclohexyl hydroperoxide or cumene hydroperoxide readily oxidized cyclohexane even in the complete absence of molecular oxygen as can be seen from table 3. The rates of oxidation of cyclohexane (TOF) by alkyl hydroperoxides decrease with an increase in their molecular cross section (cyclohexyl > *t*-butyl > cumyl) confirming that the active copper site is indeed located (as an encapsulated complex) deep within the zeolite cavities and not on the external surface of the zeolite particles. Large amounts of acids are formed, even at low conversion levels, when H_2O_2 was used as the oxidant. Large amounts of byproducts such as glutaric and succinic acids were formed when cumene hydroperoxide, H_2O_2 or cyclohexyl hydroperoxide were used as the oxidants.

The effect of solvents on the oxidation of cyclohexane using O_2 or TBHP as the oxidants is illustrated in tables 4 and 5, respectively. The conversion was the highest when pyridine or acetic acid was used as the solvent. However, large amounts of succinic and glutaric acids were formed when using these solvents. When acetonitrile was used as the solvent, there was negligible formation of succinic and glutaric acids. The conversion dropped when water was used as the solvent. Valeraldehyde was not detected when methanol, ethanol, methyl ethyl ketone or water were used as the solvents in the presence of O_2. Irrespective of the type of solvent, higher turnover frequencies were observed, when TBHP was used as the oxidant (table 5). Solvents may be expected to influence the reaction rates through competitive sorption/adsorption in the zeolite cavities. The polarity, hydrophilicity and size of the solvent molecule will be major factors.

The influence of site isolation of the copper complexes $CuCl_{16}$Pc (figure 6A) and $Cu(NO_2)_4$Pc (figure 6B)

Table 3
Influence of oxidant [a]

Oxidant	Total conv. (wt%)	TOF [b] (h^{-1})	Products [c] (mol%)				
			A	B	C	D	E
TBHP	21.5	242	22.3	41.8	12.1	18.1	5.7
cumene hydroperoxide	16.6	187	13.2	19.2	7.2	29.5	30.9
H_2O_2	9.1	102.2	13.2	20.8	21.9	3.3	40.8
cyclohexyl hydroperoxide	27.3	307	7.0	44.8	3.3	18.4	26.5

[a] Catalyst weight, $CuCl_{16}$Pc-Na-X(0.28) = 0.75 g; reaction time = 8 h; temperature = 343 K; solvent = acetonitrile = 45 g; cyclohexane : oxidant = 3 : 1. Air was not used as the oxidant.
[b] TOF = turnover frequency; moles of cyclohexane converted per mole of copper in the catalyst per hour.
[c] A = cyclohexanol; B = cyclohexanone; C = valeraldehyde; D = adipic acid; E = mainly succinic and glutaric acids.

Table 4
Effect of solvent using $CuCl_{16}Pc$-Na-X(0.28) and O_2 [a]

Solvent	Total conv. (wt%)	TOF [b] (h^{-1})	Products [c] (mol%)				
			A	B	C	D	E
pyridine	17.9	201.5	7.8	44.1	1.1	16.7	30.3
acetic acid	17.3	195	17.9	20.2	11.5	15.6	34.8
acetonitrile	14.9	167.8	28.1	48.5	7.0	16.4	–
methanol	12.7	143.2	18.1	32.2	–	41.1	8.6
ethanol	9.8	110.2	56.1	25.5	–	–	18.4
methyl ethyl ketone	9.7	109.5	61.8	7.2	–	21.6	9.4
water	7.2	81.4	38.8	26.3	–	9.7	25.2

[a] Cyclohexane = 25 g; catalyst weight, $CuCl_{16}Pc$-Na-X(0.28) = 0.75 g; reaction time = 8 h; temperature = 343 K; solvent = 45 g; air = 800 psi; TBHP = 0.40 g.
[b] TOF = turnover frequency; moles of cyclohexane converted per mole of copper in the catalyst per hour.
[c] A = cyclohexanol; B = cyclohexanone; C = valeraldehyde; D = adipic acid; E = mainly succinic and glutaric acids.

encapsulated in the faujasite structure on the TOF of oxidation of cyclohexane using O_2 as the oxidant clearly indicates that the isolated metal complex is the active site in the oxidation reactions.

The probable reaction sequence for the oxidation of cyclohexane is given in figure 7. Cyclohexane is first oxidized to cyclohexanol and cyclohexanone. Cyclohexanone is further oxidized to a di-ketone which is the reaction intermediate, before the cyclohexanone cleaves to give adipic acid. The rate of oxidation of this di-ketone to adipic acid is very fast and therefore not observed in the reaction products. Adipic acid cleaves, on further oxidation, to glutaric and succinic acids.

4. Conclusions

The selective oxidation, with molecular dioxygen as well as TBHP, of cyclohexane to cyclohexanol, cyclohexanone and adipic acid at near-ambient conditions has been studied. Phthalocyanines of Fe, Cu and Co, wherein all or most of the ring hydrogens have been substituted by electron-withdrawing groups like the halogens or nitro groups, when encapsulated in zeolites X and Y possess high catalytic activity and stability. The integrity of the copper complexes in the cavities of the molecular sieves was confirmed by IR, UV-Vis, ESCA and ESR spectroscopic techniques. There is a considerable increase in turnover numbers for cyclohexane conversion and turnover numbers as high as 3200 have been obtained when the complexes are encapsulated in the cavities of zeolites. Significant differences in activity and selectivity are observed when the copper complexes are

Table 5
Effect of solvent using $CuCl_{16}Pc$-Na-X(0.28) and TBHP [a]

Solvent	Total conv. (wt%)	TOF [b] (h^{-1})	Products [c] (mol%)				
			A	B	C	D	E
acetic acid	27.7	312.1	5.8	17.6	17.6	22.7	36.3
acetonitrile	21.5	242	22.3	41.8	12.1	18.1	5.7
MEK	20.0	225.4	10.0	12.0	37.5	19.5	21.0
water	15.5	174.6	11.0	11.0	18.7	27.0	32.3

[a] Catalyst weight, $CuCl_{16}Pc$-Na-X(0.28) = 0.75 g; reaction time = 8 h; temperature = 343 K; solvent = 45 g; cyclohexane : TBHP = 3 (mol).
[b] TOF = turnover frequency; moles of cyclohexane converted per mole of copper in the catalyst per hour.
[c] A = cyclohexanol; B = cyclohexanone; C = valeraldehyde; D = adipic acid; E = mainly succinic and glutaric acids.

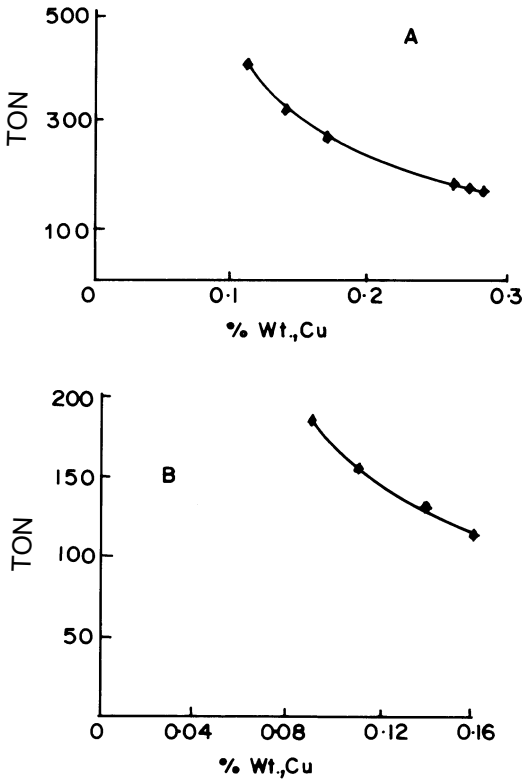

Figure 6. Influence of site isolation of the copper complexes $CuCl_{16}Pc$ (A) and $Cu(NO_2)_4Pc$ (B) encapsulated in the faujasite structure on the TON of oxidation of cyclohexane.

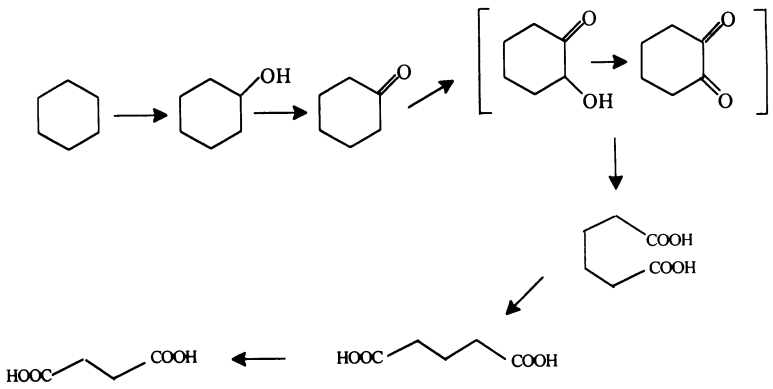

Figure 7. Reaction sequence for the oxidation of cyclohexane.

merely impregnated on the zeolite surface and not encapsulated in the zeolite cavities. A linear correlation was obtained between the TOF and metal loading in the zeolite suggesting that the isolated metal complex is the active site in the oxidation reaction. One distinguishing and unique feature of all the phthalocyanine-based catalyst systems studied is that the catalyst remains in the solid phase during the entire course of the reaction and can be easily filtered off after the reaction is over, thereby providing significant processing advantages in their large scale application.

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