Immobilization and characterization of copper chlorophthalocyanine on alumina-pillared montmorillonite

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Abstract

Alumina-pillared montmorillonite (Al-PILC) has been used as the host material for the immobilization of copper-tetra decachlorophthalocyanine ($Cu-Cl_{14}Pc$) complex using ultrasonic technique. Thermogravimetric (TG)/DTG analysis, BET surface area, XRD, FT-IR and UV–VIS spectroscopic techniques have been used to characterize samples containing different concentrations of copper (0.104–0.152 wt.%) in Al-PILC. The studies reveal that $Cu-Cl_{14}Pc$ is present in the porous structure of Al-PILC and that the immobilized samples prepared by ultrasonication contain better-dispersed $Cu-Cl_{14}Pc$ compared to the sample prepared by normal agitation method. The catalytic activity for the hydroxylation of phenol to catechol and hydroquinone using the immobilized $Cu-Cl_{14}Pc$ and H_2O_2 is reported. The immobilized copper is the active center in the hydroxylation. The method of preparation and dispersion of $Cu-Cl_{14}Pc$ influence the catalytic activity. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Among the inorganic mimics of enzymes, metal complexes containing porphyrin, salen and phthalocyanine ligands have been investigated as possible alternative catalysts in many oxidation and hydroxylation reactions [1–4]. One approach is to stabilize and isolate the transition metal complexes by encapsulation inside the cages and super cages of a zeolite or zeolite-like materials [5–7]. There are different procedures such as ligand synthesis, template synthesis and zeolite synthesis methods for the encapsulation of metal complexes inside a zeolite cage [1,5–7]. The porous inorganic mantle is supposed to provide the right steric configuration of the metal complexes and orient in a way that the access to the active site (the metal center) by the substrate molecule is regulated. Many porous materials have been used to encapsulate or anchor these metal complexes and the most popular systems have been the large pore X and Y zeolites, which have a large α-cage with about ∼1.2 nm diameter. The bulkier metal complexes, particularly the metal phthalocyanines, which have molecular dimensions of >1.2 nm do not fit easily inside the zeolite cages and are reported to be distorted after encapsulation [2,8]. These complexes also tend to adsorb strongly on the external surface of the zeolite. Pillared clays (PILC) have not been extensively studied as hosts for such metal complexes. Pillaring or intercalation of clays by alumina, for example, is known

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to transform the unstable clay structures into highly porous and stable structures. The robust oxide particles, which form the pillars in between the clay layers, prevent the collapse of the expanded layers and simultaneously lead to the formation of large pores with dimensions of >2.0 nm, depending upon the extent of pillaring and the pillared material [9,10]. The presence of such large pores in PILC is expected to facilitate the introduction and stabilization of the metal complexes.

In this presentation, we have attempted to use alumina-pillared montmorillonite (Al-PILC) as the host material for immobilization of Cu-phthalocyanine (Cu-Pc) substituted by chloro-groups (copper-tetradecachlorophthalocyanine (Cu-Cl_{14}Pc)). We have earlier reported on the rapid and effective intercalation of montmorillonite type of clays with Al_{13} oligomers by the use of ultrasonic technique [11,12]. Such an Al-PILC is used to immobilize Cu-Cl_{14}Pc under ultrasonic conditions. The resulting materials are characterized by different techniques and tested for selective hydroxylation of phenol using aqueous H_2O_2 as oxidant.

2. Experimental

2.1. Preparation of clay-complex catalysts

The Na-form of montmorillonite (procured from Kunipia F, Kunimine, Japan) was exchanged for Ca^{2+} ions and then used for pillaring with Al_{13} ions (chlorohydrol) under ultrasonic conditions. The details of the preparation of alumina-pillared montmorillonite (Al-PILC) samples and their characterization are described elsewhere [11]. In a typical preparation involving immobilization of the Cu-Cl_{14}Pc complex, 1 g of Al-PILC were suspended in 20 ml pyridine (S.D. Fine Chemicals). A solution of 25 mg of Cl-Pc ($CuC_{32}H_2Cl_{14}N_8$, Lona Industries, Mumbai) in 20 ml of pyridine was added and agitated for 20 min at 300 K in an ultrasonicator (38 kHz). The suspension was then centrifuged and washed repeatedly with pyridine followed by acetonitrile. The sample was then subjected to Soxhlet extraction using pyridine as the first solvent for 12 h, followed by acetonitrile for another 6 h, which removed all the Cu-Cl_{14}Pc that were loosely bound to the surface. Finally, the sample was washed several times with acetone and dried at 473 K for 2 h. Samples containing 50 and 75 mg of Cu-Cl_{14}Pc/g of Al-PILC were similarly prepared. The samples are labeled accordingly as Cu-Al-PILC-25(US) (indicating that 25 mg Cu-Cl_{14}Pc has been loaded by ultrasonication), Cu-Al-PILC-50(US) and Cu-Al-PILC-75(US), respectively. A schematic representation of the process of pillaring of the clay material by alumina and further immobilization of the Cu-complex is given in Scheme 1. For comparison, a sample (25 mg Cu-Cl_{14}Pc/g of Al-PILC) was prepared by normal stirring of Al-PILC with Cu-Cl_{14}Pc (without
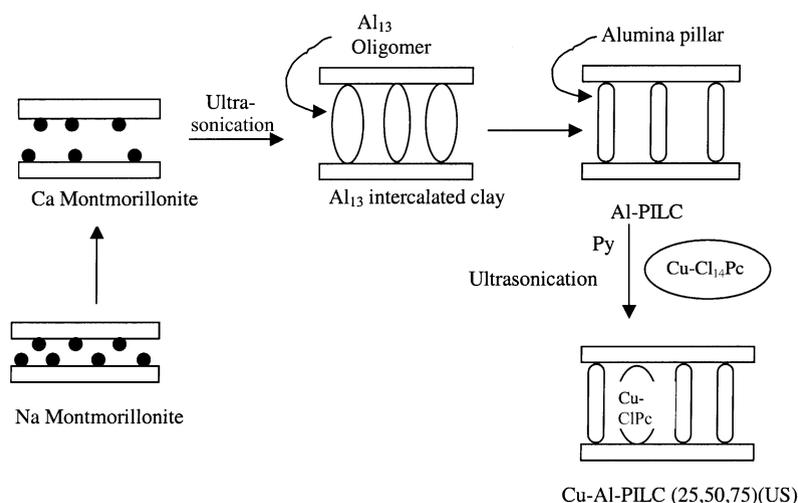
Scheme 1.

ultrasonication) for 20 min in pyridine and treated as above and labeled as Cu-Al-PILC-25(S).

2.2. Catalyst characterization

The X-ray diffraction patterns of the samples were recorded using a Rigaku miniflex X-ray diffractometer with a Cu Kα target. The FT-IR spectra of the samples were recorded in fluorolube and nujol medium using Shimadzu model 8300 FT-IR instrument. The UV–VIS diffuse reflectance spectra were recorded in the 200–800 nm region (Shimadzu UV-2101 model) and $BaSO_4$ was used as the reference material. The samples were subjected to thermal analysis in a simultaneous thermogravimetric (TG)/DTA instrument (Setaram, TG/DTA 92 model) in a flow of air from room temperature to 823 K at 10 K/min ramp rate. The chemical composition of the samples was estimated from XRF analysis of the solid samples (Rigaku model 3070) and was referenced to the original montmorillonite clay.

2.3. Hyrdoxylation of phenol

The hydroxylation of phenol was carried out in a batch reactor (100 ml capacity, fitted with a condenser and a magnetic stirrer) using water as solvent. To an aqueous solution of phenol, 50 mg of the Cu-Al-PILC sample was added and the temperature was raised to 353 K under agitation. Aqueous H_2O_2 (25 wt.%), corresponding to phenol to H_2O_2 mole ratio of 3, was added in one lot. Periodically, several aliquots of samples were removed, centrifuged to remove the solid particles and analyzed in a GC (HP-5880) equipped with a 50 m × 0.25 mm cross-linked methyl silicon gum capillary column and a flame ionization detector.

The catalytic activity is expressed as turn over numbers (TON, moles of phenol converted/g of Cu).

3. Results and discussion

3.1. Chemical and thermal analysis

The chemical compositions of the samples, starting from the original Na-form of the montmorillonite clay and after immobilization of the Cu-Cl$_{14}$Pc in Al-PILC at different concentrations are summarized in Table 1. As expected, the pillaring of the Ca-montmorillonite changes the SiO_2 to Al_2O_3 ratio with a corresponding decrease in CaO content. The introduction of Cu-Cl$_{14}$Pc at different levels under ultrasonication into Al-PILC does not change the overall composition of the pillared clay either. The amount of Cu in the final samples is very small, ranging from 0.13 to 0.19% as CuO by XRF analysis for the three Cu-Al-PILC-25(US) to Cu-Al-PILC-75(US) samples. This is lower than the input Cu concentration, as only a part of initial Cu-Cl$_{14}$Pc is finally retained inside the pores of the Al-PILC. It may be noted that the sample prepared under normal agitation (Cu-Al-PILC-25(S)) has a lower Cu content compared to the samples prepared under ultrasonic conditions (Table 1).

TG and DTG plots of the samples are shown in Fig. 1. The main decomposition of the neat Cu-Cl$_{14}$Pc begins around 723 K (curve a). A minor loss noticed at 623 K (DTG) might be due to some impurity present in the neat complex. As seen from the DTG plots (curves b–d), the decomposition of the organics is shifted to higher temperatures on immobilization of the complex in Al-PILC. This shift is also due to the difference in the concentration of the complex in the

Table 1
Chemical composition of samples prepared from Ca-montmorillonite clay

Samples	Chemical composition (wt.%)							
	SiO_2	Al_2O_3	MgO	Fe_2O_3	Na_2O	CaO	K_2O	CuO
Ca-montmorillonite	66.07	24.85	5.39	1.42	0.17	2.04	0.07	–
Al-PILC	53.26	40.23	5.08	1.15	0.16	0.06	0.06	–
Cu-Al-PILC-25(US)	53.59	39.65	5.07	1.20	0.21	0.06	0.09	0.13
Cu-Al-PILC-50(US)	53.99	39.33	5.06	1.10	0.20	0.06	0.09	0.16
Cu-Al-PILC-75(US)	54.46	38.94	5.04	1.06	0.20	0.07	0.09	0.19
Cu-Al-PILC-25(S)	48.99	43.69	4.89	1.01	0.19	0.06	0.09	0.08
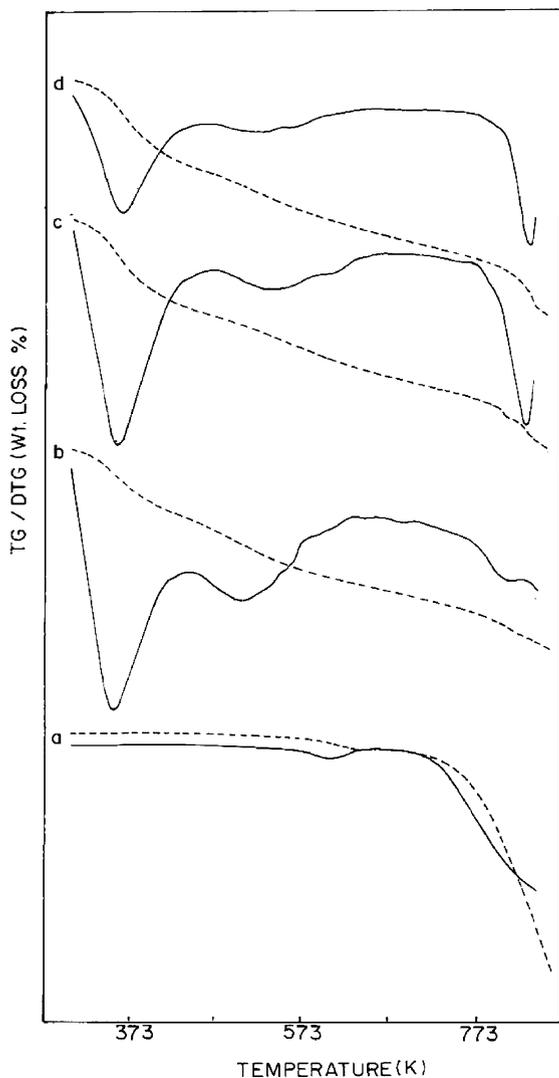
Fig. 1. Thermogravimetric (TG) (- - -) and DTG (——) plots of samples: (a) Cu-Cl$_{14}$Pc (neat complex); (b) Cu-Al-PILC-25(US); (c) Cu-Al-PILC-50(US); (d) Cu-Al-PILC-75(US).

two sets. The greater difficulty in the decomposition of the organics in the Cu-Al-PILC samples indicates that the Cu-Cl$_{14}$Pc is located inside the pores/voids of the Al-PILC and not adsorbed on the external surface of the pillared clay. The DTA plots of the samples given in Fig. 2 lend additional support to the above. It is seen that the exotherm is progressively shifted to higher temperatures from the neat to immobilized Cu-Cl$_{14}$Pc (curves a–d) (Fig. 2). On a rough estimate, the

enthalpy of decomposition of the complex in Al-PILC increases from 19.89 to 128.07 kJ/mg, in agreement with the increased concentration of Cu in samples, Cu-Al-PILC-25 to Cu-Al-PILC-75(US).

3.2. Structural and textural properties

The powder X-ray diffractograms of the Cu-Cl$_{14}$Pc immobilized clay samples (Fig. 3) did not have any significant differences from that of parent Al-PILC. The *d*-values of the 0 0 1 reflection of all the catalysts remained as 19.3 Å indicating the existence of the same layer distance in all the samples as in the case of Al-PILC. This indicates that ultrasonication or stirring of Al-PILC does not damage the pillared structure, and that the structure is retained even after loading of the Cu-Cl$_{14}$Pc complex. The BET surface areas of the samples, calculated from the N$_2$ adsorption isotherms are included in Table 2. There is a progressive decrease in the surface area of Al-PILC due to the introduction of the complex inside the pore structure of the clay (from 221 to 116 m^2/g), for the three concentrations of the Cu-Cl$_{14}$Pc in them. Even a small increase in Cu concentration causes a larger decrease in BET area. The sample Cu-Al-PILC-25(S), prepared under normal agitation, has a low surface area, indicating that the pores of Al-PILC are probably blocked by the complex. It indicates that the preparation method plays a significant role. The super cages in Y zeolite can accommodate only one such Cu-Cl$_{14}$Pc per cage. The smaller pore mouths prevent them from agglomeration. In our samples, even though the concentration of Cu is low, the Cu-Cl$_{14}$Pc molecules tend to be present as agglomerates due to larger interlayer separation and pore widths due to pillaring (>2.2 nm). The size of the agglomeration is small in samples prepared by ultrasonication compared to that prepared by normal agitation.

3.3. Spectral analysis of the samples

The FT-IR spectra of the samples are given in Fig. 4. It is seen that the bands due to Cl$_{14}$Pc at 1568, 1391 and 1096 cm^{-1} for $\nu_{C=N}$, $\nu_{C=C}$ and ν_{C-N}, respectively, and the skeletal vibrations at 1497 cm^{-1} are present in the samples. The presence of these bands in samples Cu-Al-PILC-25(US) and Cu-Al-PILC-75(US) and their absence in the Al-PILC
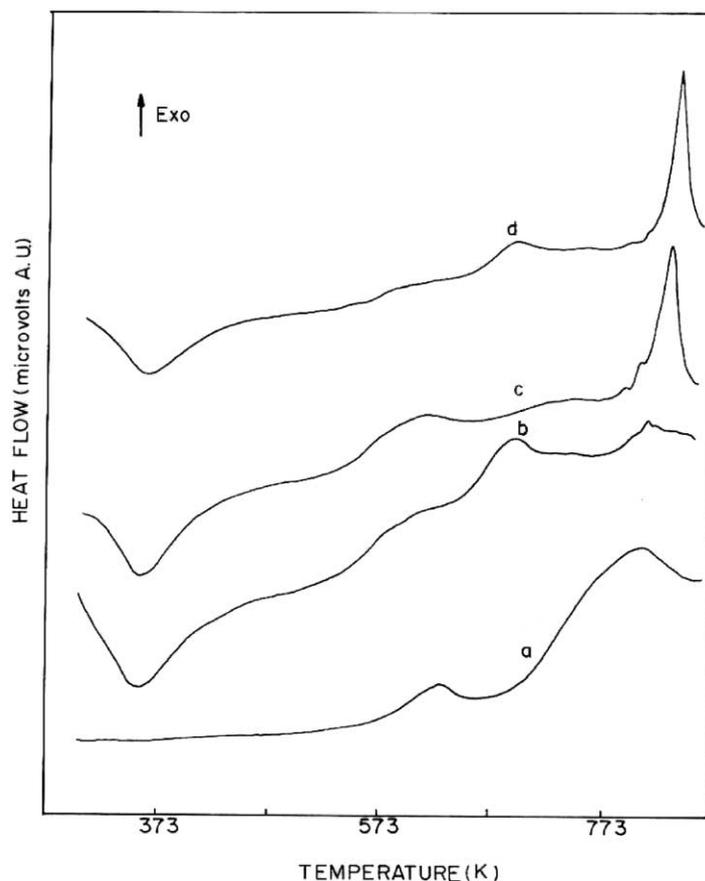
Fig. 2. DTA plot of samples: (a) Cu-Cl$_{14}$Pc (neat complex); (b) Cu-Al-PILC-25(US); (c) Cu-Al-PILC-50(US); (d) Cu-Al-PILC-75(US).

ascertains that Cu-Cl$_{14}$Pc has been immobilized in the catalysts. Further, the bands due to Al-PILC are also present in the catalysts without any change. The aromatic C=C stretching vibration band (normally seen at around 1595 cm^{-1}) is absent in the neat complex due to its symmetry (Fig. 4, curve a), but its presence at 1596 cm^{-1} in the two samples, Cu-Al-PILC-25(US), Cu-Al-PILC-75(US) prepared under ultrasonic agitation and a shoulder at 1595 cm^{-1} in the sample Cu-Al-PILC-25(S) (spectra c–e) indicates a change in

Table 2
TG/DTA analysis of clay immobilized Cu-tetradecachlorophthalocyanine samples

Samples	TG/DTA data			
	BET surface area (m^2/g)	Total weight loss (wt.%)[a]	T_{max} exotherm (K)	Intensity exotherm (kJ/mg)
Al-PILC	221	5.8	–	–
Cu-Al-PILC-25(US)	157	13.6	814	19.89
Cu-Al-PILC-50(US)	135	16.4	837	124.22
Cu-Al-PILC-75(US)	116	16.7	840	128.07
Cu-Al-PILC-25(S)	16	11.9	814	29.26
Cu-Cl$_{14}$Pc	–	81.0	798	647.34

[a] Upto 863 K.
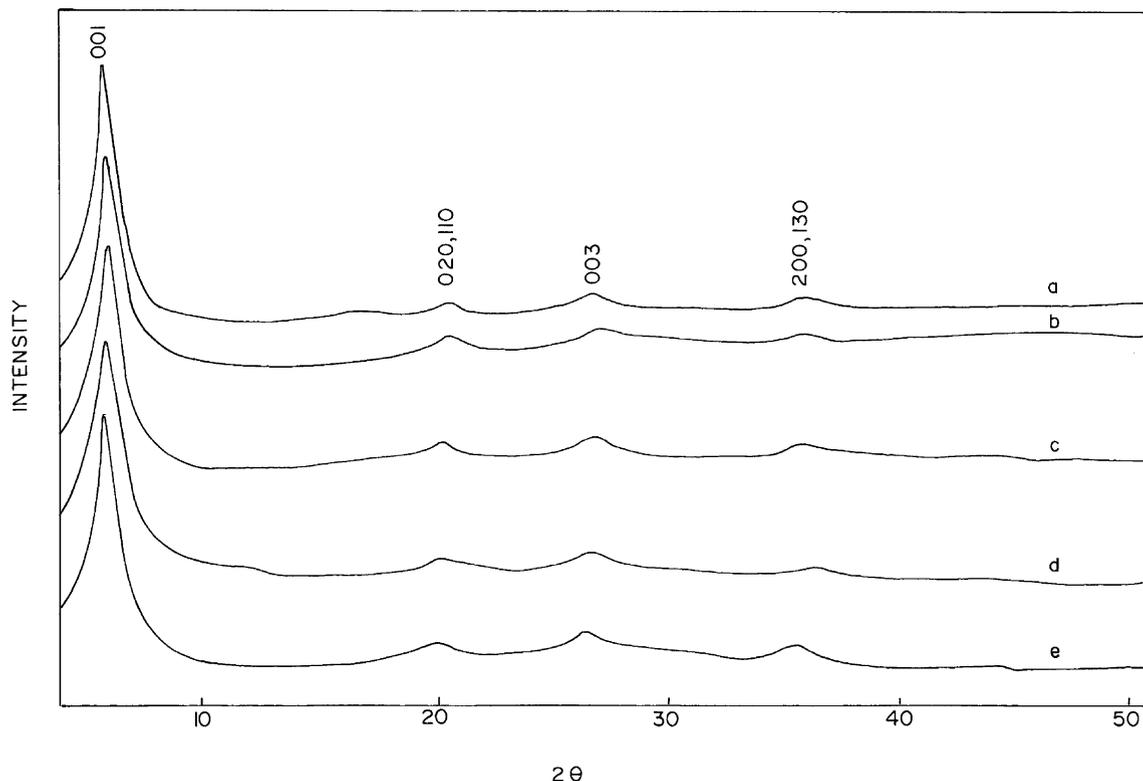
Fig. 3. Powder XRD pattern of catalysts: (a) Al-PILC; (b) Cu-Al-PILC-25(US); (c) Cu-Al-PILC-50(US); (d) Cu-Al-PILC-75(US); (e) Cu-Al-PILC-25(S) (prepared under normal stirring).

the symmetry of the complex on immobilization of the complex. The presence of this band also indicates that the introduction of the complex into the pore structure of the pillared clay is easier and faster under ultrasonic agitation (Fig. 4, curves c and d) than under conditions of normal stirring (Fig. 4, curve e). From this we may conclude that the Cu-Cl$_{14}$Pc has lost its symmetry to enable itself to intercalate between the layers of the clay. In an earlier report on the encapsulation of metal phthalocyanine complex in Y zeolite, a considerable shift of the peaks at 1477 and 1370 cm^{-1} has been attributed to the change in the molecular symmetry of the Cu-complex in the encapsulated state [13]. The absence of any additional bands in the FT-IR spectra indicates that only a physisorption or 'physical entrapment' of Cu-Cl$_{14}$Pc in Al-PILC occurs and no chemical interaction is expected to have taken place between the matrix and Cu-Cl$_{14}$Pc molecules.

The UV–VIS diffuse reflectance spectra of the samples (Fig. 5) show that there is a clear red shift in the electronic spectra, due to ligand-based electronic (π–π^*) transitions of Cl$_{14}$Pc on immobilization. This can be attributed to the dispersion of Cu-Cl$_{14}$Pc in the Al-PILC matrix. The absorption maxima of Cu-Cl$_{14}$Pc have shifted from about 665 and 375 nm to about 675 and 385 nm when immobilized by ultra-sonication. However, the shift is not that pronounced in the sample where immobilization was attempted by simple stirring. Thus, without the step involving ultrasonication, the dispersion of the Cu-Cl$_{14}$Pc seems to be poor. This observation is further supported by independent EPR investigations of the samples. The spectrum for neat Cu-Cl$_{14}$Pc shows dipolar broadened EPR signals at $g_{||} = 2.122$ and $g_{\perp} = 2.054$, which do not change in the sample Cu-Al-PILC-25(S) prepared under normal agitation. These g values change
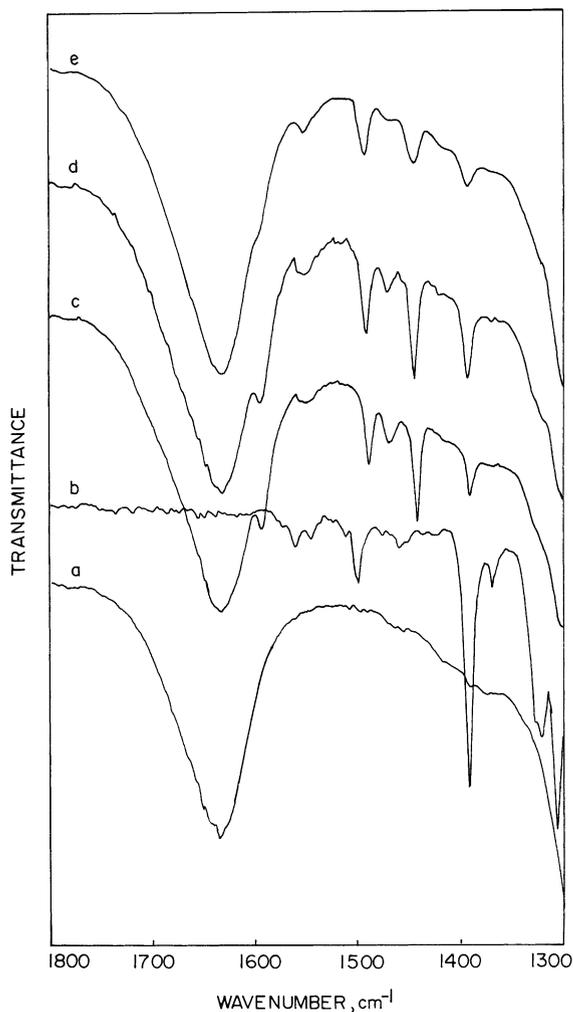
Fig. 4. FT-IR spectra of catalysts: (a) Cu-Cl$_{14}$Pc; (b) Al-PILC; (c) Cu-Al-PILC-25(US); (d) Cu-Al-PILC-75(US); (e) Cu-Al-PILC-25(S) (prepared under normal agitation) recorded in fluorolube medium.

to 2.136 and 2.057, respectively, for the other three samples, Cu-Al-PILC-25(US) to Cu-Al-PILC-75(US) prepared under ultrasonic agitation. These observations point to the presence of smaller clusters of the complex in Al-PILC compared to the neat complex. Earlier, UV–VIS and EPR spectral studies have provided unequivocal evidence for the encapsulation of Cu-Pc in the supercages of zeolite Y, in which due to restricted dimension of the supercage, individual Cu-Pc molecules could be immobilized [2,13].

However, the absence of additional hyperfine and superhyperfine signals in the present set of samples reveals that the molecules are present as agglomerates. The size of the agglomerates differs with the method of preparation and that is reflected in the *g* parameters. In our samples, the complex probably exists as isolated, small clusters inside the pores of Al-PILC without any distortion of the Cu-Cl$_{14}$Pc moiety.

3.4. Catalytic activity

The results on the hydroxylation of phenol using these Cu samples as catalysts are summarized in Table 3. It may be noted that Al-PILC itself has negligible activity in this reaction (<1 wt.% conversion of phenol in 3 h) and that Fe present in the parent clay has no role in the hydroxylation of phenol. The seat of catalytic activity is the central Cu atom of the Cu-Cl$_{14}$Pc complex, as has been reported earlier [2]. The 'neat' Cu-Cl$_{14}$Pc complex showed only marginal activity. This is attributed to the poor dispersion of the metal centers in the neat complex. In other words, Cu-Cl$_{14}$Pc remains as chunk in its 'neat' state, and hence only a few Cu centers are available for the catalytic activity. The sample, Cu-Al-PILC-25(S) synthesized by employing magnetic stirring, displayed better activity than the neat complex. However, the samples prepared under ultrasonication, show much higher activity and more important, a higher H$_2$O$_2$ efficiency. In all the Cu immobilized samples, the turnover number is above 1, increasing up to about 13 for Cu-Al-PILC-75(US). The observed turnovers are somewhat similar to those reported for the encapsulated Cu-Cl$_{14}$Pc in large pore X and Y zeolites [2]. The data show that ultrasonication disperses the Cu-Cl$_{14}$Pc well, and more Cu centers are available for the reaction. With higher catalyst concentration in the reaction medium, the H$_2$O$_2$ efficiency increases up to about 36%. The ratio of catechol to hydroquinone (plus benzoquinone) in the product varies from 1.5 to 3 showing negligible product shape selectivity.

The kinetic date given in Fig. 6 show that the reaction proceeds only after 1 h of addition of H$_2$O$_2$. There appears to be some induction period for the reaction and this limits H$_2$O$_2$ efficiency in the overall reaction. The kinetic data also show that the first formed product is *para*-benzoquinone and not catechol (though in small quantity), but with time we see that catechol and
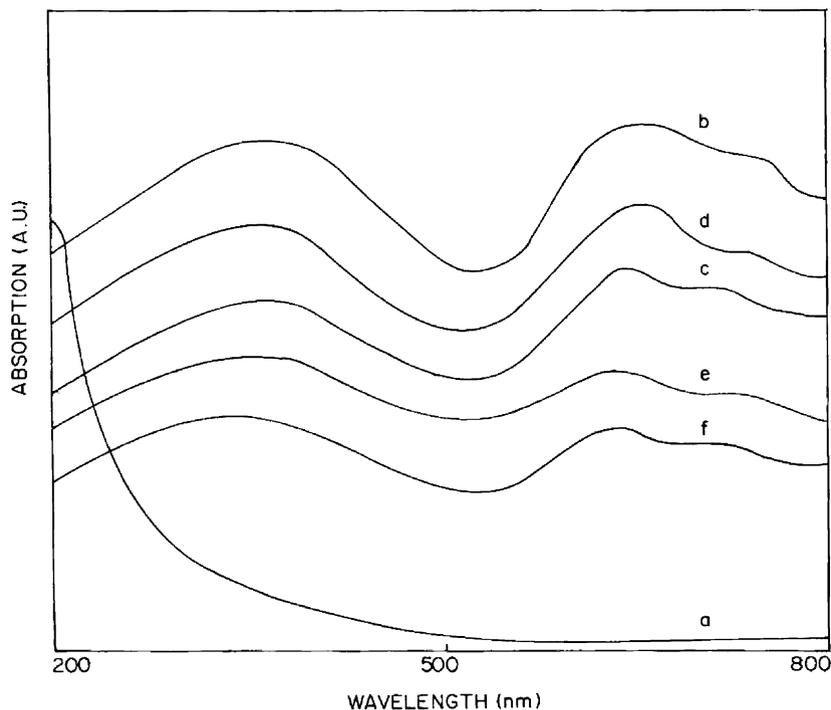
Fig. 5. Diffuse reflectance UV spectra of catalysts: (a) Al-PILC; (b) Cu-Cl$_{14}$Pc; (c) Cu-Al-PILC-25(US); (d) Cu-Al-PILC-50(US); (e) Cu-Al-PILC-75(US); (f) Cu-Al-PILC-25(S) (prepared under normal agitation).

Table 3
Hydroxylation of phenol over Cu-Cl$_{14}$Pc immobilized on Al-PILC[a]

Catalyst	Catalyst concentration (mg/g phenol)	TON	H$_2$O$_2$ selectivity[b] (mol%)	Product distribution (%)			
				BQ	CAT	HQ	Others[c]
Cu-Cl$_{14}$Pc	10	<1.0	3.3	1.8	92	5.4	0.8
Cu-Al-PILC-25(US)	10	4.3	6.4	16.0	66	14	4.0
Cu-Al-PILC-50(US)	10	10.4	19.6	12.0	74	12	2.0
Cu-Al-PILC-75(US)	10	12.9	27.6	3.1	58	38	0.9
Cu-Al-PILC-25(US)	50	4.3	31.2	3.6	56	36	4.4
Cu-Al-PILC-50(US)	50	3.2	29.1	3.0	55	40	2.0
Cu-Al-PILC-75(US)	50	2.8	29.8	8.0	59	32	1.0
Cu-Al-PILC-25(US)	100	2.2	31.8	7.4	70	22	0.6
Cu-Al-PILC-50(US)	100	2.0	35.9	7.0	63	30	–
Cu-Al-PILC-75(US)	100	1.6	35.0	2.6	54	43	0.4
Cu-Al-PILC-25(S)	10	4.4	3.9	24.0	50	26	–

[a] Conditions: temperature: 353 K; phenol to H$_2$O$_2$: 3 mol; solvent: water; duration: 3 h; batch reactor.

[b] H$_2$O$_2$ consumed in the formation of benzoquinone (BQ), catechol (CAT) and hydroquinone (HQ).

[c] Higher boiling fractions.
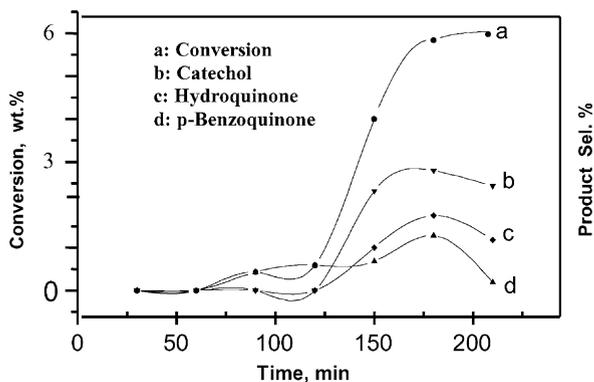
Fig. 6. Kinetic plots for hydroxylation of phenol over Cu-Al-PILC-25(US). Reaction conditions: temperature: 353 K; phenol to H_2O_2: 3 mol; solvent: water.

hydroquinone turn up to be the major products. Further work is in progress to understand the mechanism and the formation of metal-oxo intermediates in this reaction.

4. Conclusions

Cu-Cl$_{14}$Pc is successfully immobilized on Al-PILC using a novel ultrasonication method. The metal complex probably exists as small clusters inside the pores of Al-PILC and is active in the hydroxylation reaction of phenol to catechol and hydroquinone using H_2O_2 as oxidant under moderate conditions. The solid catalyst can be easily separated from the products of the reaction. The immobilized Cu-Cl$_{14}$Pc shows better activity than the neat complex due probably to the isolation of Cu active sites within the pores.

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