ENCAPSULATION OF Co PHTHALOCYANINE IN ALUMINA-PILLARED CLAYS AND THEIR CHARACTERIZATION

NEELAM JAGTAP AND VEDA RAMASWAMY*

Catalysis Division, National Chemical Laboratory, Pune 411 008, India

Abstract—Alumina-pillared montmorillonite clays (Al-PILC), prepared under ultrasonic (US) agitation and normal stirring (S) methods, have been used as a host material to encapsulate Co phthalocyanine (CoPc) complex. The amount of Co varies from 0.27 to 1.48 wt.% in the samples, depending on the input concentration of Co. Powder X-ray diffraction and other characterization techniques reveal that the structure of Al-PILC remains intact after the incorporation of the complex into the pores through a pyridine solution of the complex by ultrasonic agitation. A substantial decrease in the BET surface area and total pore volume of Al-PILC points to the occupation of the CoPc moieties within the porous structure of the pillared clay. This is further supported by the observation of a band at 1489 cm^{-1} in the Fourier transform infrared (FTIR) spectra of the encapsulated samples. The FTIR and diffuse reflectance ultraviolet-visible (DRUV-Vis) spectral results indicate that the encapsulated CoPc complex in the clay matrix undergoes distortion in order to accommodate itself within the pores of the Al-PILC. The encapsulated samples prepared by ultrasonification show better dispersion of the complex than the samples prepared under normal stirring conditions. Compared to the 'neat' complex, the encapsulated samples (CoPc in Al-PILC) exhibit greater turnover in the test reaction of the oxidation of benzyl alcohol to benzaldehyde with tert-butyl hydroperoxide as the oxidant at 373 K. The method of preparation and consequent site isolation of CoPc in Al-PILC influence the catalytic activity.

Key Words—Al-PILC, Co Phthalocyanine, Encapsulated Co-complex, Ultrasonification.

INTRODUCTION

Inorganic mimics of enzymes, metal complexes containing porphyrin, and salen and phthalocyanine ligands (Herron, 1986; Raja and Ratnasamy, 1996; Jacob *et al.*, 1998; Armengol *et al.*, 1999) are some of the alternative catalysts which have been tested for oxidation and hydroxylation reactions. The porous inorganic mantle is supposed to provide the right steric configuration to the metal complexes and orient them in a way that the access to the metal center is regulated. Encapsulation of transition metal complexes within the cages and void spaces of many porous materials such as zeolites and mesoporous materials have been reported (Balkus and Gabrielov, 1995; Parton *et al.*, 1992; De Vos *et al.*, 1994). Their results have shown that the bulkier metal complexes such as phthalocyanines, having molecular dimensions of >1.2 nm, do not fit easily within the zeolite cages and are distorted after encapsulation. Pillaring of clays by alumina, for example, transforms the unstable clay structures into highly porous and stable structures. The robust oxide particles, which form the pillars between the clay layers, prevent the collapse of the expanded layers and lead to the formation of large pores with dimensions >2 nm, depending on the extent of pillaring (Pinnavaia *et al.*,

1984; Figueras, 1988). These pores facilitate the introduction and stabilization of the metal complexes. Ramaswamy *et al.* (2002) first used pillared clays as a host for the encapsulation of Cu phthalocyanine using an ultrasonic technique.

In this report, alumina-pillared montmorillonite (Al-PILC), prepared using ultrasonic agitation, was used as the host to encapsulate a Co phthalocyanine (CoPc) complex in the porous structure. The results of physicochemical characterization carried out by powder X-ray diffraction (XRD), X-ray fluorescence (XRF), FTIR, ultraviolet-visible spectroscopy (UV-Vis) and low-temperature N$_2$-sorption techniques are examined in an attempt to understand the presence of the complex within the pores of the pillared clay. The resulting solids have been tested for the oxidation of benzyl alcohol using tertiary butyl hydrogen peroxide (TBHP) as the oxidant.

EXPERIMENTAL

Materials and preparation

The Na$^+$ in the Na-form of montmorillonite, Kunipia F, (Kunimine industries, Japan) was exchanged for Ca^{2+} ions and then used for pillaring with aluminum chlorohydrol [Al$_{13}$] by means of an ultrasonic technique as well as a conventional stirring method. The Ca exchange was carried out by stirring the clay with 0.1 M Ca (NO$_3$)$_2$ for 6 h at 353 K. Then the clay was filtered, washed with deionized water and air dried. An aqueous solution of chlorohydrol was mixed with clay suspension

* E-mail address of corresponding author:
v.ramaswamy@ncl.res.in

54

in water (5%) to provide 20 meq of Al^{3+} g^{-1} of clay. The mixture was agitated in an ultrasonic bath (Shesin, Japan, operating frequency of 38 kHz, 360 watts) at ambient temperature (300 K) for 20 min (Katdare *et al.*, 1994, 1997). The product was filtered, washed with deionized water until free of chloride ions ($AgNO_3$ test) and air dried. The sample was calcined at 673 K in a programmable furnace at a heating rate of 10 K min^{-1} for 6 h. This sample was used further for the encapsulation of CoPc (Figure 1). In a typical preparation, a solution of 50 mg of CoPc ($CoC_{32}H_{16}N_8$, Lona Industries, Mumbai) dissolved in 20 mL of pyridine was added to 1 g of Al-PILC suspended in 20 mL of pyridine. This suspension was ultrasonificated for 20 min at 300 K. The suspension was washed with pyridine and then with acetonitrile. The sample was then subjected to soxhlet extraction using pyridine as the first solvent (12 h), followed by acetonitrile (6 h), thereby removing all the CoPc loosely bound to the surface (Ramaswamy *et al.*, 2002). The sample was dried at 473 K for 2 h and labeled as CoPc-50 (US). Samples containing 100 and 200 mg of CoPc were also prepared in the same manner and referred to as CoPc-100 (US) and CoPc-200 (US), respectively. For comparison, samples containing 50, 100 and 200 mg of CoPc/g of Al-PILC were prepared by a conventional stirring method, *i.e.* stirred magnetically rather than ultrasonically, for 20 min at 300 K in pyridine, treated as above and labeled as CoPc-50 (S), CoPc-100 (S) and CoPc-200 (S), respectively. The catalytic oxidation of benzyl alcohol over the encapsulated clay catalysts was carried out in a batch reactor (50 mL capacity, fitted with a condenser and a magnetic stirrer) using toluene as solvent. The catalyst (10 wt.%) was dispersed in the solvent (5 mL) containing the substrate (5 mmol) and stirred at 373 K. The oxidizing agent (TBHP 70 wt.% in water, Aldrich), corresponding to a substrate:oxidant mole ratio of 1, was added in one lot. Product aliquots were collected periodically, centrifuged to remove the solid particles and analyzed by a gas chromatographic technique using a HP-5, 5% phenyl methyl siloxane (30 m × 320 μm × 0.25 μm) capillary column and FID.

Catalyst characterization

The XRD profiles of the pillared and complex encapsulated clay samples were recorded on a Rigaku Miniflex powder X-ray diffractometer using Ni-filtered CuKα radiation (λ = 0.15406 nm). The FTIR spectra of the samples were recorded in a flurolube medium using a Shimadzu model 8300 FTIR instrument. The DRUV-Vis spectra of the solid samples were recorded in the region 200 to 800 nm (Shimadzu UV2101 model) with $BaSO_4$ as the reference material. In order to identify the components of the spectra, they were fitted with Gaussian curves using Origin 6.1 software. The amount of Co incorporated was estimated by the XRF technique using an X-ray wavelength dispersive spectrometer (Rigaku model 3070). The Brunauer Emmett Teller (BET) surface area of the samples was determined by N_2 adsorption at 77 K using an Omnisorb 100 CX (Coulter Corporation, USA) instrument. Prior to N_2 adsorption, the samples were evacuated at 423 K. The specific surface area, S_{BET}, was determined from the linear part of the BET equation. The relative pressure p/p_0 was in the range 0.001−0.1. The pore-size distribution was calculated using the Barrett-Joyner-Halenda (BJH) method. The pore volume was estimated using the *t*-plot (Sing, 1970).

RESULTS AND DISCUSSION

Chemical analysis

The amount of Co phthalocyanine in the encapsulated samples, determined by XRF, is in the range 2.6−14.3 wt.%, which is 2−3 times greater than the $CuCl_{16}Pc$ in Al-PILC reported by Ramaswamy *et al.* (2002). This is due to the structural differences between the two complexes and consequent steric hindrance during encapsulation. Nearly 60−70% of the input CoPc has been incorporated successfully in the pillared clay by the ultrasonic method (Table 1). Comparison of the encapsulated samples prepared by the two methods [CoPc-(US) and CoPc-(S)] indicate better dispersion and encapsulation of the complex when ultrasonic agitation is employed.

Structural and textural properties

The powder XRD profiles of the pillared and the encapsulated samples are shown in Figure 2. The encapsulated pillared clay samples did not show any major change in *d* value (1.81 nm) compared to the host
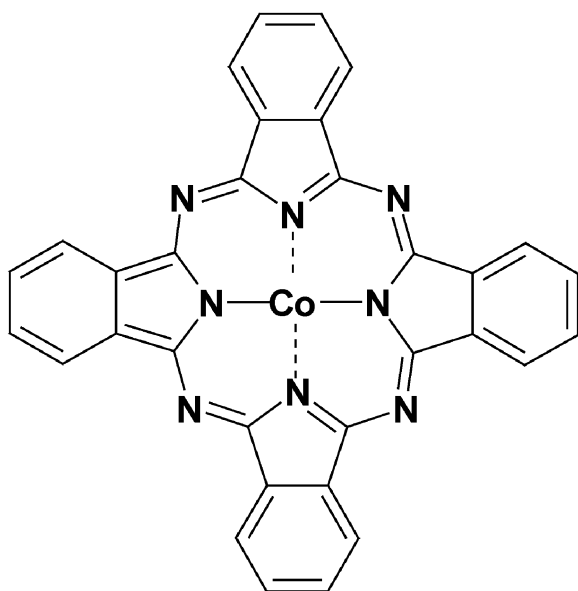

Figure 1. Structure of the 'neat' Co (II) phthalocyanine complex.

Table 1. Chemical analysis and textural data on encapsulated pillared clay samples.

Samples	Concentration of CoPc in Al-PILC[a] (mg/g of clay)		PXRD[b]		Density[c] of CoPc $(g\ cm^{-3})$	BET surface area[d] $(m^2\ g^{-1})$	Total pore volume[e] $(cc\ g^{-1})$
	Input	Experimental	Intensity	FWHM			
Al-PILC	–	–	5600	0.45		226	0.11
CoPc-50 (S)	50	26	2000	0.78	0.52	112	0.06
CoPc-100 (S)	100	68	n.d.	n.d.	1.36	82	0.06
CoPc-200 (S)	200	143	n.d.	n.d.	2.38	60	0.05
CoPc-50 (US)	50	30	3400	0.71	0.75	120	0.07
CoPc-100 (US)	100	60	3900	0.73	1.20	95	0.06
CoPc-200 (US)	200	136	5000	0.82	2.26	77	0.05

[a] Determined from XRF
[b] From the 001 peak of the Al-PILC and the encapsulated samples
[c] Calculated from the surface area data and the amount of CoPc in the encapsulated clay
[d] Calculated from the nitrogen adsorption isotherm using the BET equation
[e] Determined from the nitrogen adsorption isotherm
n.d.: not determined

Al-pillared clay sample. This indicates that ultrasonification or stirring of the Al-PILC does not damage the pillared structure and the structure is retained upon encapsulation. The sharp and intense 001 peaks observed in CoPc-50 (US), CoPc-100 (US) and CoPc-200 (US) indicate that the number of pillars is greater and that they are more uniformly distributed than those of CoPc-50 (S). The broad nature of the 001 reflection in the samples prepared by stirring shows that the sample is less crystalline compared to the ultrasonically prepared samples (shown for a typical CoPc-50 (S) sample, Figure 2). Also, upon encapsulation, the 001 reflection becomes broader, suggesting some loss in crystallinity. On increasing the concentration of the complex, significant changes in the powder XRD patterns of the

encapsulated samples are noted. Additional peaks due to the complex are observed, the peaks being more prominent in the sample CoPc-200 (US). This result indicates that at greater loading, part of the complex remains on the surface of the clay matrix as an independent phase.

Table 1 lists the surface area measurements for all samples. The BET surface area of the samples calculated from N_2 adsorption isotherms decrease gradually from 226 to 60 m^2g^{-1} as the concentration of CoPc increases. The steady decrease in surface area and pore volume is due to the entrapment of the complex in the pore structure of the pillared clay and has been observed in other reports on encapsulation of different metal complexes in other porous materials (Raja and
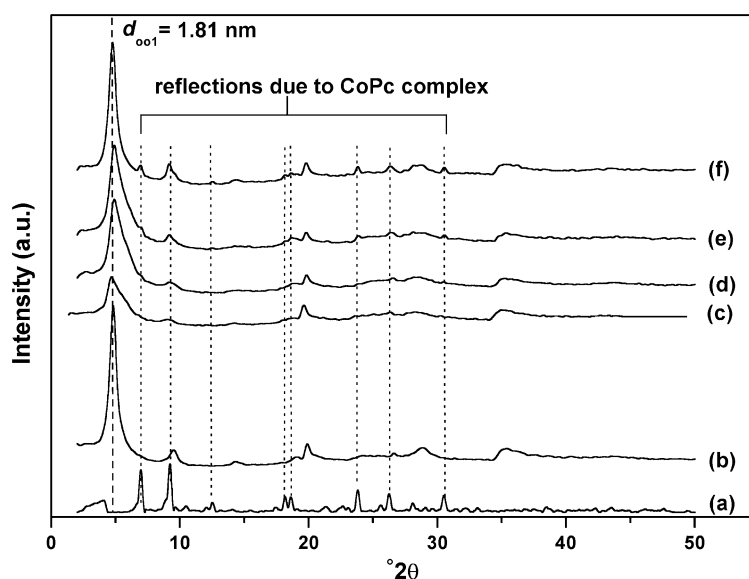

Figure 2. Powder XRD patterns of samples: (a) the 'neat' CoPc complex; (b) Al-PILC; (c) CoPc-50 (S); (d) CoPc-50 (US); (e) CoPc-100 (US); and (f) CoPc-200 (US).

Ratnasamy, 1996; Ferreira *et al.*, 2000, 2002; Ramaswamy *et al.*, 2002). Analysis of the textural data of the encapsulated samples shows that when compared with Al-PILC, there is a decrease in the total pore volume, indicating that the complex is entrapped in the pores. The pore diameter is of the order of 1.9 to 2 nm for the pillared clay and the complex encapsulated samples. The density of CoPc complex in the encapsulated clay samples is calculated from the total pore volume and wt.% of CoPc in the sample (Table 1). The density increased with increase in the complex loading indicating that on greater loading of the complex, aggregation of CoPc occurs.

FTIR spectra of the samples

Vibrational spectroscopy can provide information on both encapsulated metal complexes and on the crystallinity of the host material. The spectra of all encapsulated samples are dominated by very intense bands of the clay in the range $3700-3300$ cm^{-1} due to surface OH groups, and in the range $1300-450$ cm^{-1} due to lattice vibrations of the clay framework (data not shown) (Coudurier and Lefebvre, 1994). Bands due to the complex have very low intensity due to their low concentration and are only detected in the region where typically the PILC does not absorb, specifically in the range of 1600 to 1300 cm^{-1} (Figure 3). In this region, the bands at 1332 and 1426 cm^{-1} are due to C$-$C bond stretching in the isoindoline ring. The bands at 1524 and 1595 cm^{-1} are attributed to stretching of the C$-$C bond in the pyrrole ring, while the bands at 1610 cm^{-1} are attributed to the C=N stretching frequency (Janczak and Kubiak, 2003; Zhan *et al.*, 2002). These bands are shifted towards the higher frequency compared to the 'neat' complex (Table 2). An additional band at 1469 cm^{-1} is due to metal-free phthalocyanine present as an impurity in the 'neat' complex (Kobayashi *et al.*, 1970). The shifting of these bands in the encapsulated state provides evidence for the distortion of the complex either due to the porous structure or strong interactions with the surface OH groups of the alumina pillars. The bands due to the bending vibrations and metal ligand vibrations are not seen as being due to their overlap with the clay vibrations. The encapsulation of CoPc in Al-PILC is confirmed by the absence of these bands in the pillared clay. The interpretation above is further supported by the DRUV-Vis spectroscopic studies. Despite the limited information on the vibrational modes of the complex, the present IR spectral data provide sufficient evidence for the encapsulation of the complex within the clay matrix. An additional band at 1489 cm^{-1} observed in the spectra of encapsulated samples may be due to the Co pyridine complex formed during the encapsulation process (Stymne *et al.*, 1980).

DRUV-Vis analysis

The DRUV-Vis spectra of the solid 'neat' complex and CoPc-encapsulated clay samples are shown in Figure 4. The 'neat' CoPc complex shows absorption maxima at 273 and 327 nm (Soret or B band) and 616 and 673 nm (Q band). A shoulder at 720 nm observed in the 'neat' complex is not seen in the encapsulated samples due to the low concentration of the complex. The bands observed for the 'neat' and encapsulated samples are listed in Table 3. The Q band consists of a $\pi-\pi^*$ transition from the HOMO of a_{1u} symmetry to the LUMO of e_g symmetry, while the B band is due to the transition from the molecular orbital of a_{2u} symmetry to the LUMO (Bernstein and Lever, 1992; Rollmann and Iwamoto. 1968). The splitting value of Q band is equal to ~60 nm and is probably due to the vibronic coupling in the excited state (Janczak and Kubiak, 2003). The sample, prepared by the stirring method, showed bands almost in the same region of the 'neat' complex, whereas in the ultrasonificated samples, there is a clear red shift in both the Soret and Q bands. This shows that the complex is well encapsulated inside the pores of the Al-PILC clay in the ultrasonification method. Hence, the complex exhibits a distortion resulting in the red shift of the bands. It should be noted here that the spectra of the CoPc and CoPc(py)$_2$ complex are similar, as they have the same ground-state configuration of Co(II) (Janczak and Kubiak, 2003). There is a clear red shift in both the Soret and the Q bands except for the CoPc-200 (US) sample. This is due to agglomeration of CoPc complex at greater loading and suggests that 100 mg of loading per g of clay may be the optimum level of complex loading. Also, upon encapsulation, the bands are broadened significantly compared to the 'neat' complex (Table 3). This could be attributed to the interaction of the complex with the host clay matrix. The overall intensity of the patterns increased with increase in the complex con-

Table 2. FTIR spectral data of 'neat' and encapsulated CoPc samples.

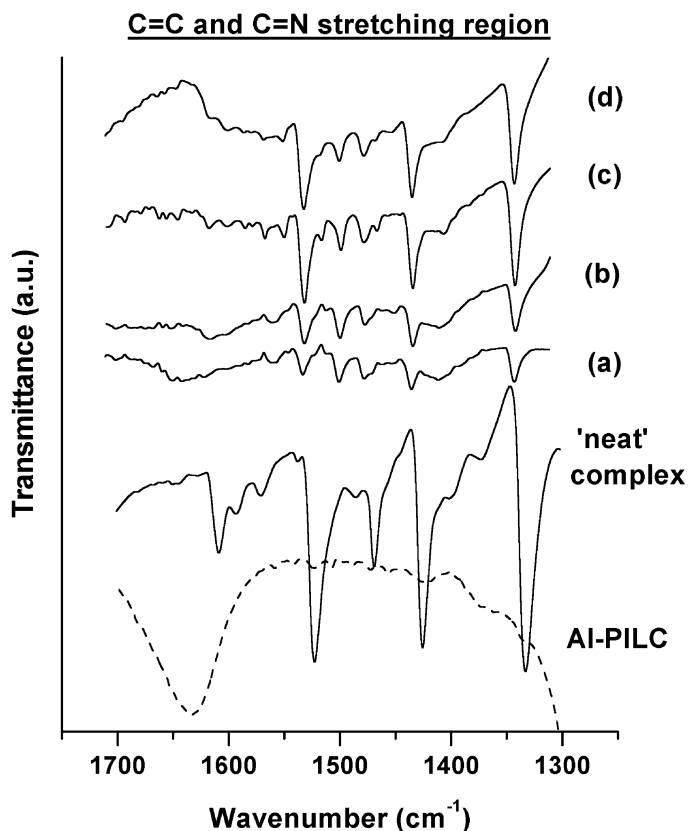| Samples	ν_{C-C} of isoindoline (cm^{-1})	ν_{C-C} of pyrrole (cm^{-1})	$\nu_{metal-free\ phthalocyanine}$ (cm^{-1})	$\nu_{CoPc(py)_2}$
'Neat' CoPc	1332, 1426	1524	1469	−
CoPc-50 (S)	1339, 1430	1529	1475	1489
CoPc-50 (US)	1342, 1435	1535	1478	1489
CoPc-100 (US)	1340, 1433	1535	1478	1489
CoPc-200 (US)	1336, 1432	1530	1476	1489

C=C and C=N stretching region

Figure 3. FTIR spectra of the 'neat' complex, Al-PILC and CoPc-encapsulated samples: (a) CoPc-50 (S); (b) CoPc-50 (US); (c) CoPc-100 (US); and (d) CoPc-200 (US). The band due to clay at 1633 cm^{-1} is subtracted from the encapsulated samples for the purpose of clarity.

centration indicating a larger amount of complex encapsulation. A shoulder at ~245 nm is ascribed to the absorption due to clay. Thus, DRUV-vis spectral results also point to the encapsulation of complex within the clay structure and that the ultrasonification method is an efficient means of encapsulation.

Catalytic activity

The results of the oxidation of benzyl alcohol using the encapsulated Co samples as catalysts are summarized in Table 4. The 'neat' CoPc complex showed a low turnover number (TON) in this reaction, while in the encapsulated state, the CoPc complex is more active, the TON being greater by an order of magnitude than its encapsulated counterpart. This is due to the better dispersion of the metal centers in the encapsulated samples. The samples, synthesized by employing magnetic stirring, exhibited better catalytic activity than the 'neat' complex. As the concentration of CoPc increased from 2.6 to 14.3 wt.% in CoPc (S) samples, the conversion increased from 15 to 43 mole %, respectively. On the other hand, ultrasonically prepared samples show a greater degree of conversion of benzyl alcohol. As the concentration of CoPc increases from 3 to 13.6 wt.%, the conversion increases from 19 to 57 mole %. The TON decreases in both sets of samples as the concentration of CoPc increases which is due to the agglomeration of particles. It is seen that agglomeration

Table 3. DRUV-Vis spectral bands (nm).

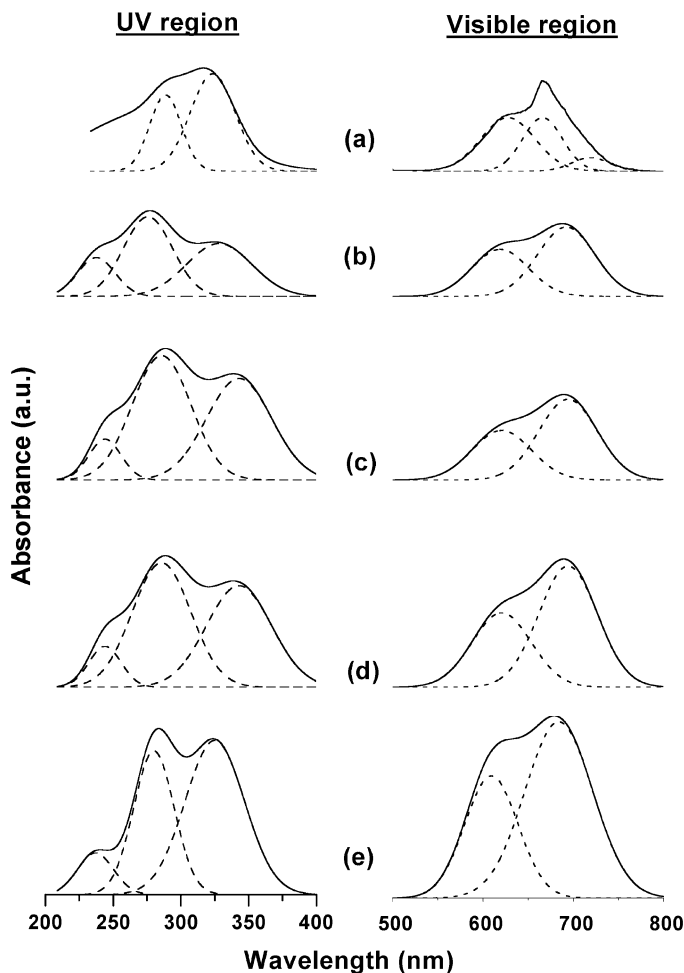| Samples	Soret/B band	Q band	FWHM	
			$\lambda_{610-630}$ nm	$\lambda_{670-700}$ nm
'Neat' CoPc	273, 327	616, 673	70	69
CoPc-50 (S)	274, 328	616, 682	78	75
CoPc-50 (US)	288, 343	623, 696	78	78
CoPc-100 (US)	288, 344	623, 696	78	77
CoPc-200 (US)	283, 324	609, 684	78	90

Figure 4. DRUV spectra of samples: (a) the 'neat' CoPc complex; (b) CoPc-50 (S); (c) CoPc-50 (US); (d) CoPc-100 (US); and (e) CoPc-200 (US).

is more pronounced in the CoPc (S) samples (TON = 307−158) than in the CoPc (US) samples (TON = 354−218). Comparison of the CoPc (S) and CoPc (US) samples with similar input concentration show that the agglomeration is greater in the CoPc (S) set of samples. It can be concluded that the catalytic efficiency of the samples (in terms of activity per Co atom) prepared by the ultrasonification method is greater than those prepared by the stirring method. These results show that ultrasonic agitation leads to better dispersion of CoPc, thus enhancing site isolation and preventing particle-to-particle aggregation, thereby increasing the number of Co centers available for the reaction. The results from the linear regression analysis of the conversion values in mole % for the CoPc complex-unencapsulated clay samples prepared by the two methods (S and US) are given in Table 5.

When benzyl alcohol was oxidized in the absence of a catalyst, the reaction was found to be highly unselective (68 wt.%) towards benzaldehyde. In order to prove the heterogeneity of the reaction, a typical experiment was

carried out for 1 h and the solid catalyst was filtered hot. A GC analysis of the filtrate gave 13 wt.% conversion. The reaction was continued with the filtrate alone under the same conditions for 5 h. The conversion did not

Table 4. Catalytic activity for oxidation of benzyl alcohol over encapsulated pillared clay samples[a].

Catalyst	Conversion (mole %)	TON[b]
'Neat' CoPc	47	24
CoPc-50 (S)	15	307
CoPc-100 (S)	30	234
CoPc-200 (S)	43	158
CoPc-50 (US)	19	354
CoPc-100 (US)	38	340
CoPc-200 (US)	57	218

[a] Conditions: temperature − 373 K; substrate-oxidant ratio (mol) − 1; solvent− toluene; duration − 5 h; batch reactor
[b] moles of substrate converted per mole of Co in the catalyst

Table 5. Linear regression analysis of conversion (mole %) for CoPc encapsulated pillared clay samples.

Samples prepared by	A	Error	B	Error	R	SD
Stirring	8.5	5.5646	0.17857	0.0421	0.97336	4.5434
Ultrasonification	9.5	6.2192	0.2443	0.047	0.98198	5.0779

According to the equation $Y = A + BX$, R is the correlation coefficient, SD is the standard deviation.

increase from 13 wt.%. This experiment proves that the oxidation reaction over all the encapsulated samples was heterogeneous and that the phthalocyanine complex did not leach out into the solution. It was also confirmed (using GC) that TBHP is converted to *tert* butanol during the catalytic process.

CONCLUSIONS

Successful encapsulation of Co phthalocyanine within alumina-pillared clay (Al-PILC) using an ultrasonic technique was achieved. Characterization of the samples by XRD, BET surface area, FTIR, XRF and UV-Vis spectroscopic techniques reveal that the Co complex is present within the porous structure of the Al-PILC. The method is effective at incorporating ~70% of the input complex concentration. Formation of a Co-pyridine complex during the synthesis is noted from the additional FTIR band at 1489 cm^{-1}. An increase in the density of CoPc in the encapsulated samples from 0.52 to 2.38 g cm^{-3} and a steady decrease in surface area with increase in CoPc concentration are due to the encapsulation of the complex in the porous structure of the clay. The presence of CoPc within the pores of Al-PILC is further supported by FTIR and DRUV-Vis spectral data. The red shift in the absorption bands is due to the distortion of the complex upon encapsulation. The broadening of the Q band is indicative of the interactions of the complex within the clay matrix. The encapsulated samples display better catalytic activity for the oxidation of benzyl alcohol than the 'neat' complex due to dispersion and isolation of Co active sites in the pillared clay. At greater concentration, agglomeration of the complex takes place, aggregation being more pronounced in the samples prepared by the conventional stirring method. The ultrasonically prepared samples have greater TON values than the samples prepared by the stirring method, indicating that ultrasonification leads to better dispersion of the complex in the clay matrix.

ACKNOWLEDGMENTS

REFERENCES

Armengol, E., Corma, A., Fornés, V., García, H. and Prince, J. (1999) Cu^{2+}-phthalocyanine and Co^{2+}-perfluorophthalocyanine incorporated inside Y faujasite and mesoporous MCM-41 as heterogeneous catalysts for the oxidation of cyclohexane. *Applied Catalysis A: General*, **181**, 305−312.

Balkus Jr., K.J. and Gabrielov, A.G. (1995) Zeolite encapsulated metal complexes. *Journal of Inclusion Phenomena and Molecular Recognition in Chemistry*, **21**, 159−184.

Bernstein, P.A. and Lever, A.B.P. (1992) Protonation of cobalt tetrapentoxyphthalocyanine as a function of oxidation state. *Inorganica Chimica Acta*, **198−200**, 543−555.

Coudurier, G. and Lefebvre, F. (1994) *Catalyst Characterization. Physical Techniques for Solid Materials*. Plenum Press, New York, pp. 11−44.

De Vos, D.E., Thibault-Starzyk, F., Knops-Gerrits, P.P., Parton, R.F. and Jacobs, P.A. (1994) A critical overview of the catalytic potential of zeolite supported metal complexes. *Macromolecular Symposia*, **80**, 157−184.

Ferreira, R., Silva, M., Freire, C., Castro, B. and Figueiredo, J.L. (2000) Encapsulation of copper (II) complexes with pentadentate N$_3$O$_2$ Schiff base ligands derived from acetylacetone in NaX zeolite. *Microporous Mesoporous Material*, **38**, 391−401.

Ferreira, R., Freire, C., Castro, B., Carvalho, A., Pires, J. and Carvalho, M.B. (2002) Encapsulation of copper (II) complexes with pentadentate N$_3$O$_2$ Schiff base ligands in a pillared layered clay. *European Journal of Inorganic Chemistry*, **11**, 3032−3038.

Figueras, F. (1988) Pillared clays as catalysts. *Catalysis Review Science and Engineering* **30**, 457−499.

Herron, N. (1986) A cobalt oxygen carrier in zeolite Y. A molecular 'ship in a bottle'. *Inorganic Chemistry*, **25**, 4714−4717.

Jacob, C.R., Varkey, S.P. and Ratnasamy, P. (1998) Zeolite-encapsulated copper (X$_2$-salen) complexes. *Applied Catalysis A: General*, **168**, 353−364.

Janczak, J. and Kubiak, R. (2003) Stereochemistry and properties of the M (II)-N(py) coordination bond in the low-spin dipyridinated iron (II) and cobalt (II) phthalocyanines. *Inorganica Chimica Acta*, **342**, 64−76.

Katdare, S.P., Ramaswamy, Veda and Ramaswamy, A.V. (1997) Intercalation of Al oligomers into Ca^{2+}-montmorillonite using ultrasonics. *Journal of Material Chemistry*, **7**, 2197−2199.

Katdare, S.P., Ramaswamy, Veda and Ramaswamy, A.V. (1999) Ultrasonication: a competitive method of intercalation for the preparation of alumina pillared montmorillonite catalyst. *Catalysis Today*, **49**, 313−320.

Kobayashi, T., Kurokawa, F., Uyeda, N. and Suito, E. (1970) The metal-ligand vibrations in the infrared spectra of various metal phthalocyanines. *Spectrochimica Acta*, **20**, 1305−1311.

Parton, R., De Vos, D. and Jacobs, P.A. (1992) Pp. 555−578

in: *Microporous Solids: Synthesis, Structure and Reactivity.* Proceedings of the NATO Advanced Study Institute on Zeolite (E.G. Derouane, F. Lemos, C. Naccache and F.R. Riberio, editors). Kluwer, Dordrecht, The Netherlands.

Pinnavaia, T.J., Tzou, M.S., Landau, S.D. and Raythatha, R.H. (1984) On the pillaring and delamination of smectite clay catalysts by polyoxy cations of aluminium. *Journal of Molecular Catalysis*, **27**, 195−212.

Raja, R. and Ratnasamy, P. (1996) Selective oxidation with copper complexes incorporated in molecular sieves. *Studies in Surface Science and Catalysis*, **101**, 181−190.

Ramaswamy, Veda, Sivarama Krishnan, M. and Ramaswamy, A.V. (2002) Immobilization and characterization of copper chlorophthalocyanine on alumina-pillared montmorillonite. *Journal of Molecular Catalysis A: Chemical*, **181**, 81−89.

Rollmann, L.D. and Iwamoto, R.T. (1968) Electrochemistry, electron paramagnetic resonance and visible spectra of cobalt, nickel, copper and metal-free phthalocyanines in dimethyl sulfoxide. *Journal of the American Chemical Society*, **90**, 1455−1463.

Sing, K.S.W. (1970) *Surface Area Determination* (D.H. Everett and B.H. Ottewill, editors). Butterworths, London, p. 25.

Stymne, B., Sauvage, F.X. and Wettermark, G. (1980) A spectroscopic study of complexation of phthalocyanines with pyridine. *Spectrochimica Acta*, **36A**, 397−402.

Zhan, H., Wang, M. and Chen, W. (2002) In situ synthesis of metallophthalocyanines in inorganic matrix. *Materials Letters*, **55**, 97−103.