

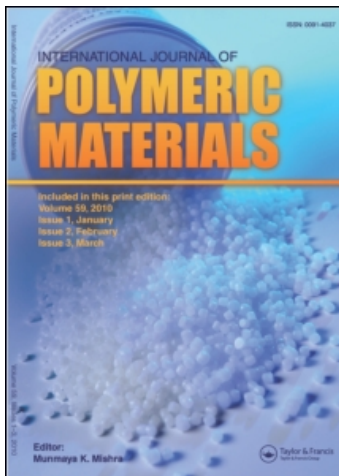
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Catalytic Behavior of Cobalt (II) Phthalocyanine Immobilized on Bentonite Clay in Bulk Polymerization of Methyl Methacrylate

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The catalytic behavior of cobalt (II) phthalocyanine (CoPc) immobilized on bentonite clay, with different complex loadings ranging between 0.2 and 2.2 wt%, in the presence of n-butyl amine solvent, was investigated in bulk polymerization of methyl methacrylate without using an activator or cocatalyst. The interaction of CoPc molecules with a bentonite surface, encouraged by the amine, involved the inclined stacking model, i.e., interaction between N-atoms of the macro-ring system and OH's of the support. Two different mechanistic pathway regions could be suggested, depending on complex loadings. The first was in the range, 0.2–1.0 wt% CoPc, behaving in ionic fashion as the bare bentonite. Isolated oriented molecules probably activated bentonite through the exposure of new internal acid sites during intercalation. The second, in the range of 1.4–2.2 wt% CoPc, proceeded via combined mechanisms, ionic functioned by bentonite support and free radical functioned by complex packed oriented stacks, staggered in clay galleries to cover a fraction of internal active acid sites. The number of polymer chains formed per one CoPc center (reaction turnovers) was >2–~10 with diluted catalyst samples. With higher loadings, one chain was formed per active site. Such behaviors, without a detectable effect on polymer characteristics or enchainment sequence, were studied in light of intercalation, orientation and accessibility models.

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Keywords bulk polymerization, cobalt (II) phthalocyanine, immobilized, orientation, poly methyl methacrylate

INTRODUCTION

The development of catalysis has been devoted for a long time to the wide application of metal complexes and organometallic compounds as catalysts [1–4].

Among the studied complexes, metal phthalocyanines (resembling the natural porphyrins structurally) have become known to catalyze many reactions both in liquid and gas phases [e.g., 5–10]. Immobilization of such complexes on a suitable solid matrix was considered as one of the promising approaches for their stabilization against dimerization and other destructive processes [1,10–12].

Cobalt phthalocyanine (CoPc), immobilized on different supports, has attracted attention as an efficient initiator in a variety of polymerization reactions [3,13,14]. Usually, metal complexes are applied in polymerization processes through using an activator, e.g., methylaluminoxane (MAO), to form the active combination required for the reaction. Cocatalyst (e.g., NaHSO₃) may be used in some redox-initiated reactions to prepare the redox-pair active species [14].

In the present work, the catalytic behavior of cobalt phthalocyanine immobilized on bentonite clay, as a member of the montmorillonite-dominated group, was studied in bulk polymerization of methyl methacrylate without using an activator or cocatalyst. We attempted to correlate the obtained mechanistic results of the reaction under these conditions with various parameters governing the immobilization process of the supported CoPc on such silicate structures as bentonite clay.

EXPERIMENTAL

Catalyst Preparation

Cobalt phthalocyanine (CoPc) was prepared according to a method described elsewhere [15]. Immobilized CoPc on bentonite clay (Indian type) catalyst samples, of loading range between 0.2 and 2.2 wt%, were prepared via a modified impregnation technique [5]. This was effected by refluxing appropriate amounts of the complex in *n*-butylamine (nBA) for 1 h after which the dried bentonite was added. Reflux was continued for another 2 h and the excess solvent was finally distilled off. The catalyst was then dried at 200°C for 9 h under a flow of purified nitrogen gas.

Catalyst Characterization

XRD patterns were recorded in the range 4–80° on a Philips X'pert MPP diffractometer, with a goniometer of type PW 3050/10 using nickel-filtered CuK α radiation ($\lambda = 1.5406 \text{ \AA}$).

FTIR measurements were performed by using a Thermoscientific Nicolet 6700 at a resolution of 5.3 cm^{-1} over the wave number $4000\text{--}200\text{ cm}^{-1}$.

The texture of various samples was investigated via BET surface area determination and pore size analysis, based on adsorption–desorption isotherms of N_2 at -196°C [16].

Scanning electron microscopy (SEM) was carried out on a JEOL JSM-5400 instrument working at 30 kV. The surface of the catalyst sample was sputter-coated with gold for 3 min.

The previously described method assigned for determining the total acidity of various clays [17] was applied in the present study for bentonite support and different bentonite-supported catalyst samples. The results were expressed in terms of mequiv./100 g sample.

The dissolution technique, applied previously in our laboratories for several metal phthalocyanines [e.g., 5], was adopted in the present work to estimate the degree of interaction of the complex with the support surface. The dissolution was performed at 25°C in a mixture of 1:1 DMF- CHCl_3 . The extracted free-noninteracted fraction of CoPc was determined spectrophotometrically at $\lambda = 662\text{ nm}$.

Bulk Polymerization of Methyl Methacrylate (MMA)

The catalytic activity of various samples was measured in the bulk polymerization of methyl methacrylate [18]. For this purpose, the freshly distilled stabilizer-free monomer (2.8 g) was introduced into the polymerization tube (20 ml capacity) together with a weighed sample of the catalyst (0.06 g) of different complex loadings (concentration of which varied between 7.5×10^{-6} and $82.5 \times 10^{-6}\text{ mol}\%$ CoPc with respect to the monomer). The reaction mixture was deaerated by passing pure dry nitrogen and the reaction tube was then sealed and placed in a water thermostat adjusted at 80°C for 5 h. Reaction for more than 5 h could result in a polymeric product difficult to dissolve and thus separate in the medium. After cooling to room temperature, the tube was carefully opened and the content was dissolved in acetone with occasional shaking. The solution was filtered to separate the catalyst and the filtrate was run in methanol to precipitate the polymer (10 ml of alcohol for each 1 ml of the polymer solution). In some experiments, pure O_2 was used instead of N_2 atmosphere for the polymerization reaction. The produced polymer was filtered and dried under vacuum at 40°C until it reached constant weight. The polymer yield (or % conversion) was then calculated as:

$$\begin{aligned} &\text{Polymer yield (Y\%)} \\ &= (\text{weight of the produced polymer/weight of monomer}) \times 100. \end{aligned}$$

Characterization of Poly(methyl methacrylate) (PMMA)

Molecular weight distribution analysis of the produced polymer was carried out through gel permeation chromatography (GPC). The measurements were performed in toluene of HPLC grade as the mobile phase with a rate of elution, 0.7 ml/min at 40°C. Molecular weights were determined relative to monodisperse polystyrene standards. Calculations were performed using the Millennium 32 Chromatography Manager with gel-permeation application software.

The tacticity analysis of the polymeric products was performed via ^1H NMR spectra obtained on a Bruker-300 MHz spectrometer with a superconducting magnet and 5 mm dual probe head. CDCl_3 was used as the solvent and tetramethylsilane as an internal reference.

RESULTS AND DISCUSSION

Performance of the Immobilized Complex Samples in Bulk Polymerization of MMA

Bulk polymerization of methyl methacrylate (MMA) was carried out at 80°C for 5 h in N_2 atmosphere in the presence of parent bentonite (B), pure polycrystalline cobalt phthalocynine (CoPc) and various immobilized cobalt phthalocyanine/bentonite (CoPc/B) samples.

As shown in Table 1, the conversion of MMA without using a catalyst or initiator is very low. The pure complex or its ligand shows almost an inhibiting effect to the polymerization process. The same observation has been reported for pure Ni (II) and Cu (II) phthalocynine [18]. The dimerization of CoPc molecules seems to be responsible for the lack of activity as reported for some

Table 1: Bulk polymerization data (% yield) of MMA for 5 h at 80°C in the presence of various solid catalysts.

Runs	Polymer yield (%)
MMA only	0.1
Pure nonactivated bentonite (B)	0.2
Phthalocyanine ligand (Pc)	n.d.
Cobalt phthalocyanine (CoPc)	n.d.
Bentonite in the presence of O_2	37.4
CoPc (1.8 wt%)/B in the presence of O_2	n.d.
CoPc (wt%)/B	
0.2	31.0
0.6	31.8
1.0	33.0
1.4	36.5
1.8	43.0
2.2	41.0

other reactions [6,7]. The bentonite support without any pretreatment produces the same low polymer yield as the MMA monomer itself. It has become accepted that polymerization of MMA in the presence of treated and untreated bentonite proceeds mainly ionically [19,20]. The results show also that, in the presence of O₂ instead of N₂ atmosphere, bentonite clay produces a much higher yield of PMMA (viz., 37.4%), which may be linked with possible activation of surface acid sites, mainly OH groups [20].

In the presence of bentonite-supported CoPc, it is clear that the polymer yield increases with the increase in % complex loading. In view of the inactivity of the polycrystalline unsupported CoPc complex and the low activity of the parent bentonite support, one should refer the observed activity of the supported CoPc/B system to some favorable interaction between the complex and the clay surface. The immobilization process of the complex on bentonite surface seems to prepare the proper active combination, encouraging the polymerization process to proceed without activator or cocatalyst. It prevents the deactivation of CoPc molecules by site isolation, producing a stable and active catalyst system.

In contrast to the parent bentonite support, pure CoPc complex and various immobilized CoPc/B catalyst samples were completely inactive in the presence of O₂ atmosphere. This can be attributed to the formation of some O₂⁻ adduct, mainly μ -oxo species, which were reported for some metal phthalocyanines to be inactive in several reactions [e.g., 5–7]. The results may also suggest that the interaction of CoPc molecules with a bentonite surface involves most likely the same clay acid sites that could be activated by O₂ (i.e., OH groups). This can be understood in view of the inclined stacking model of CoPc molecules on the clay surface, where the interaction may take place between nitrogen atoms of the macro-ring system and the OH's of the support, i.e., via asymmetric Brønsted interactions [8,19–21].

Catalytic Activity in the Polymerization Process as a Function of Complex Loading

The polymerization was carried out at selected optimized conditions, namely, using CoPc of a 0.06 g sample weight, i.e., 67.5×10^{-6} mol% CoPc with respect to MMA monomer, for 5 h at 80°C in N₂ atmosphere, without an activator or cocatalyst. The choice of this catalyst weight was based on the reasonable polymer yield and better polydispersity and tactospecificity of the produced polymer.

Table 2 includes % conversion, weight-average molecular weight (\overline{M}_w), polydispersity index ($\overline{M}_w/\overline{M}_n$) linked with the nature of growing chains and their distribution on the surface active sites, and tactospecificity (in %) of the formed polymers (from ¹H-NMR spectra). As shown from this table, the

Table 2: Bulk polymerization of MMA data at 80°C for 5 h on CoPc/bentonite catalyst samples of different complex loadings.

CoPc loading (wt%)	Catalyst weight (g)	% conversion	\bar{M}_w ($\times 10^{-5}$)	Tactospecificity ^a					
				\bar{M}_w/\bar{M}_n	I(mm)	H(mr)	S(rr)	β	α
0.2	0.06	31.0	4.84	3.6	17.9	34.4	47.7	2.90	2.80
0.6	0.06	31.8	5.85	2.58	6.8	38.2	55.0	1.03	2.90
1.0	0.06	33.0	8.40	2.18	6.4	38.8	54.8	0.93	2.82
1.4	0.06	36.5	1.99	3.63	11.4	37.3	51.3	1.70	2.80
1.8	0.02	26.5	3.92	3.58	3.1	40.7	56.2	0.42	2.70
1.8	0.04	33.7	7.51	1.94	5.0	39.2	55.8	0.72	2.80
1.8	0.06	43.0	5.94	2.27	5.5	39.4	55.1	0.78	2.80
2.2	0.06	41.0	4.84	2.14	17.5	34.6	47.9	2.80	2.80

^aI: isotacticity, H: heterotacticity and S: syndiotacticity (ratios in %).

increase in complex loading could lead to a gradual increase in the polymer yield up to 1.8 wt% CoPc, after which some decrease occurs. The observed decrease at a complex loading of 2.2 wt% may be referred to some clustering due to the complex-complex interaction in the solid state or to some change in the mode of complex orientation on the support surface [5,8].

Plotting the number average molecular weights \bar{M}_n against the % conversion, within the narrow range mentioned, results in two different linear relationships that appear shown in Figure 1(a). These plots may suggest two different mechanistic pathway regions; the first one being in the range, 0.2–1.0 wt% CoPc and the other one being in the range, 1.4–2.2 wt% CoPc. Wide molecular weight distributions (MWD) were observed for all polymers produced ($\bar{M}_w/\bar{M}_n \geq 2$), where syndiotactic structures were predominant.

In another approach, the calculated number of polymer chains produced per one CoPc center, (mol PMMA/mol CoPc), i.e., the reaction turnover, is illustrated in Figure 1(b), as a function of % complex loading. With diluted catalysts (viz., 0.2 and 0.6 wt% CoPc), >2–~10 chain units are produced per active site, whereas with higher loadings, only one chain seems to be formed per one active site. This may imply that the polymerization behavior in the presence of low loadings of CoPc/B approaches that one occurring with bare bentonite support; proceeding mainly in ionic fashion [19]. The complex in this case may be considered as an activator to the bentonite clay in the polymerization process. With higher loadings (≥ 1.4 wt% CoPc), combined mechanisms may be operating, namely, the ionic one functioned by bentonite clay and the free radical one functioned by the complex itself. The contribution of the latter mechanism should increase with the increase of the complex concentration in the catalyst system.

The catalyst activity can also be expressed in terms of specific activity parameter [a], where, $[a] = Y$ (in %)/ α , noting that α represents the fractional degree of coverage of clay surface with CoPc molecules [5,8]. The plot of $\ln [a]$ vs $\ln \alpha$,

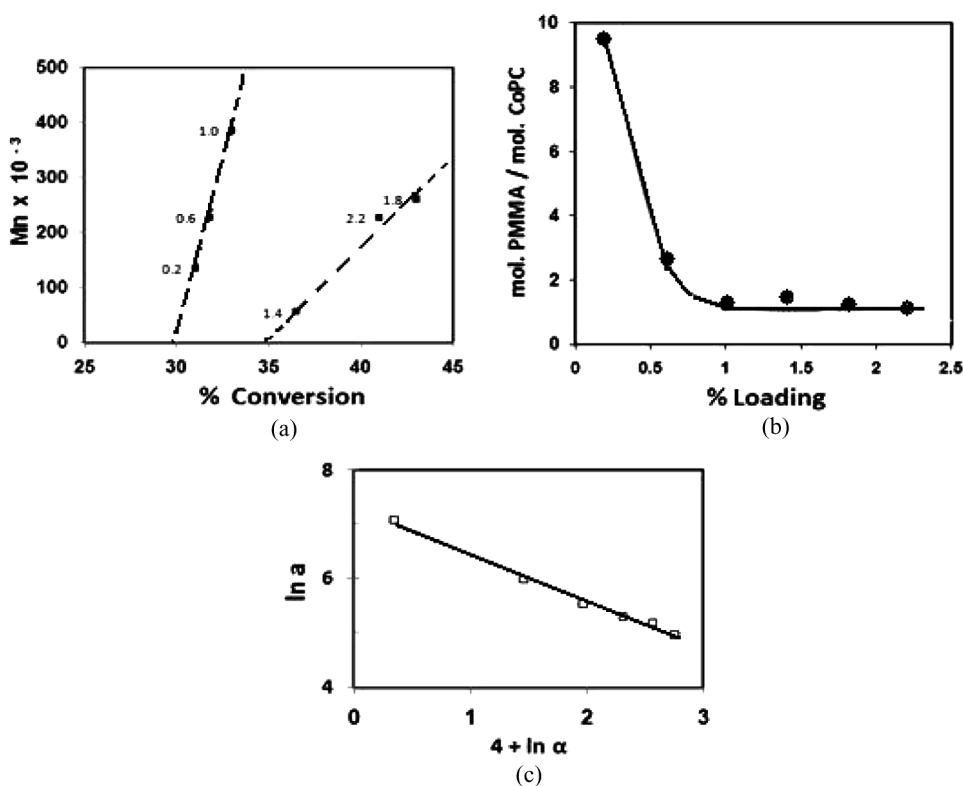


Figure 1: Relation between: (a) \bar{M}_n of PMMA and % of monomer conversion, (b) Number of polymer chains per CoPc center and complex loadings, (c) Specific activity ($(a) = Y/\alpha$) and fractional degree of coverage (α).

illustrated in Figure 1(c), fits an empirical relationship of the type: $\ln [a] = A - B \ln \alpha$, where the constants A and B are 3.77 and ~ -1 (a.u.), respectively. This indicates that the specific activity decreases with the packing of oriented complex molecules on the clay surface, confirming probably that the operating active sites involve isolated separate complex species [5,9]. It is to be mentioned here that the extent of immobilized CoPc on the bentonite surface in the present study did not reach the monolayer coverage of the support (for $\alpha = 1.0$, the CoPc loading should be 7.7 wt%). According to the obtained linear relationship, it can be expected that for monolayer coverage with CoPc, assuming A constant = 3.77, the calculated maximum conversion should be 43.3%. This may lead us to conclude that the highest conversion observed in this work (viz., 43.0%), with the complex loading of 1.8 wt%, seems to be the maximum activity that could possibly be achieved within monolayer coverage conditions. Generally, the results obtained suggest that the catalytic behavior of CoPc immobilized on bentonite clay surface in the polymerization process depends on the mode of distribution on and interaction of CoPc species with bentonite.

Stereoregularity and Tacticity Statistics of the Produced Polymers

Referring to Table 2, it is clear that the polymers produced in the presence of CoPc/B catalyst samples of different loadings show dominant syndiotactic structures; that increase at the expense of % isotacticity. The β values (viz., $4[\text{mm}][\text{rr}]/[\text{mr}^2]$) of the syndiotactic polymers produced are close to 1, except for the diluted sample of 0.2 wt% and the most concentrated one of 2.2 wt%, indicating most probably the chain-end control mechanism [22].

However, the α values (viz., $2[\text{rr}]/[\text{mr}]$) of the produced polymers are markedly far from 1 with all studied catalyst samples, indicating no enantio-morphic–site control approach [22]. These findings run in agreement with those observed using NiPc and CuPc/bentonite systems [18]. For the samples of 0.2 wt% and 2.2 wt% loadings, the discrepancy mentioned in β values is shown to be linked with the presence of higher % of isotacticity; the samples behaving almost as the bare bentonite clay [19]. This can be accepted in view of the higher degree of surface dispersion of the complex molecules in diluted samples and their close packing in the concentrated sample, oriented to expose larger fraction of clay surface.

The $^1\text{HNMR}$ results showed average ratios for the produced polymers as $(\text{rr}/\text{rm}/\text{mm}) = 55:39:6$ (where, rr = syndio, rm = hetero and mm = isotacticity). Close data were obtained previously in the presence of AIBN [23], $\text{CCl}_4/\text{Ru}(\text{II})$ [24] as well as with NiPc and CuPc systems [18], which were accepted to produce polymers via higher contribution of free radical initiation.

Further trials were made to elucidate the polymerization mechanism on the transition state of the growing carbocation through tacticity statistics [24,25], based on $^1\text{HNMR}$ analysis of $-\text{CH}_2$ groups (of triad distribution). If chain-end-model is assumed, [24], the distributions are considered in terms of σ , i.e., the probability that a monomer adds at a polymer chain to give the same configuration as that of the preceding units. The calculated probabilities of different configurations (P_i , P_s , P_h) of the polymers produced on the immobilized CoPc samples under study, shown in Figure 2(a), fit reasonably to the theoretical probability curves of Bovey et al. [26] in terms of σ particularly those of isotacticity. Regardless of the catalyst loadings used, sets of linear relationships verifying empirical equations: $P_i = 0.46 \sigma$, $P_s = 0.59 - 0.28 \sigma$ and $P_h = 0.43 - 0.22 \sigma$, were obtained as in Figure 2(b); the σ values being chosen for different samples which best correspond to the set of the experimental probability ratios. These findings reveal that, although the studied catalyst samples have a regulating role in the polymerization process, the chain-end control mechanism seems to be prevailing, where the enchainment is most likely catalyst-independent [24]. More contribution of free radical mechanism may be suggested with concentrated catalyst samples.

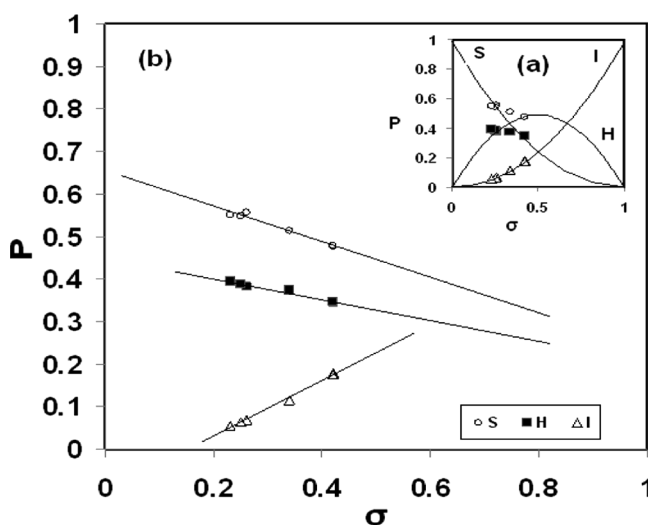


Figure 2: Calculated probabilities of different configurations of the PMMA produced: isotactic (I), heterotactic (H) and syndiotactic (S). (a) The data obtained fitting theoretical curve of Bovey et al. (26). (b) Linear relationships of probabilities (p_i , p_h and p_s) vs. σ .

Structural Characteristics of the Investigated Catalyst Systems

The XRD patterns of parent bentonite support, nBA-treated bentonite (t-B) and the immobilized CoPc sample of 1.8 wt% loading are illustrated in Figure 3. The pattern of the parent bentonite support shows characteristic lines for the sodium form, with d-spacings: 12.45, 4.48, 3.12, 3.02, 2.57, 1.71, and 1.50 Å, characterizing montmorillonite with low substitution of iron and magnesium for aluminum (*ASTM Card Index No 03-0015*). This sample may be that one known as Indian Bihar bentonite [27] of characteristic d spacings of 11.50 (100%), 4.45 (80%), 3.03 (40%) and 2.57 (70%) Å, as based on chemical analysis, silica/alumina ratio of 3.5 and marked weight loss of ca. 14% on heating [8]. For bentonite treated with n-butyl amine solvent (t-B), in the same manner as in the complex supporting process, almost the same pattern of the original sample was retained with some structural modifications. Such modifications can be summarized in disappearance of the weak bands at 4.23 Å ($2\Theta = 21$), 3.02 Å ($2\Theta = 29.5$), and 2.46 Å ($2\Theta = 36.5$), and the appearance of a new band with d spacing of 1.33 Å ($2\Theta = 70.2$). This may reflect the role of nBA as intercalant and/or as an organic modifier to bentonite clay [28].

The XRD pattern of the immobilized CoPc complex on the bentonite surface showed mainly the modified clay bands with additional small peaks at d of 7.16 Å ($2\Theta = 12.3$) and 3.40 Å ($2\Theta = 25$), of free uncombined complex. In general, these observations together with a detectable increase in the

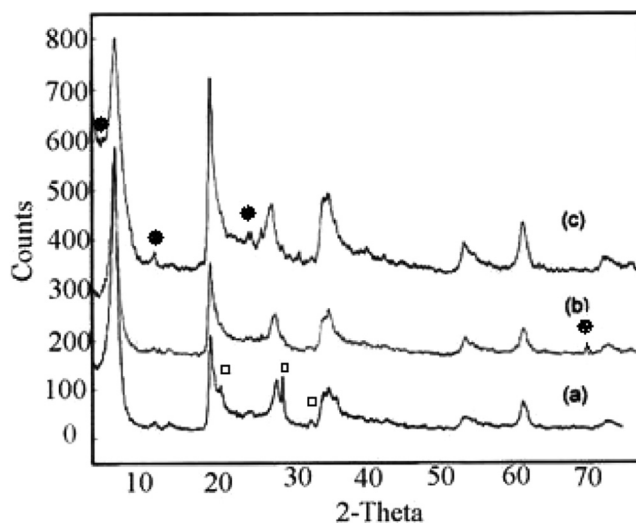


Figure 3: XRD patterns of: (a) parent bentonite (B), (b) nBA-treated bentonite (t-B), and (c) 1.8 wt% CoPc/B. (□) bands disappeared after nBA-treatment of bentonite. (●) bands appeared in the treated bentonite and the immobilized CoPc (1.8 wt%)/B catalyst.

intensities may point to the interaction of CoPc with the bentonite surface, probably via intercalation, assisted by the presence of nBA solvent medium.

The FTIR spectra of parent and nBA-treated bentonite, and various immobilized CoPc/bentonite samples are shown in Figure 4. The spectrum of the parent bentonite (Figure 4a) shows the typical bands as recorded

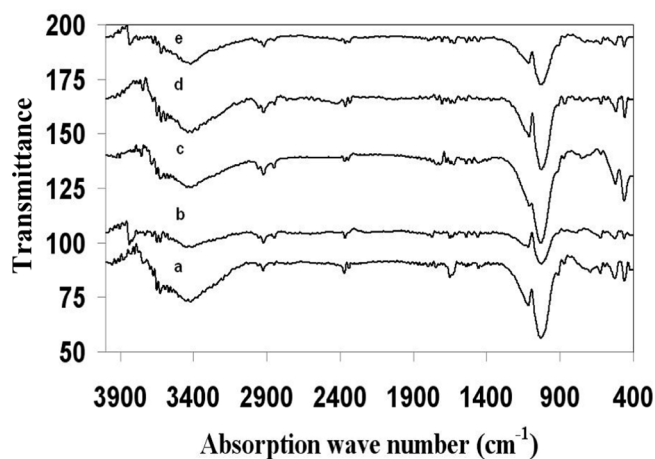


Figure 4: FTIR spectra of (a) parent bentonite (B), (b) nBA-treated bentonite (t-B), (c) 1.4 wt% CoPc/B, (d) 1.8 wt% CoPc/B, and (e) 2.2 wt% CoPc/B.

recently for montmorillonite minerals [29,30]. However, the spectrum obtained for nBA-treated bentonite (Figure 4b) showed an additional sharp band at 3819 cm^{-1} , which corresponds probably to $\text{CH}_2\text{-NH}_2$ stretching, resulting from the nBA solvent. The same effect was assumed from the appearance of a band at 433 cm^{-1} , the disappearance of the two bands at 350 and 388 cm^{-1} and the displacement of the band at 914 cm^{-1} to 928 cm^{-1} characterizing Al–OH stretching and that one at 871 cm^{-1} to 885 cm^{-1} of –OH deformation linked to Fe^{+3} and Al^{+3} octahedral sheet. These observations may point to the interaction of n-BA with a bentonite surface, modifying its active sites. Probable intercalating action cannot be excluded, as reported elsewhere for several aliphatic primary amines [28,31].

In the FTIR spectra of the different immobilized CoPc samples (Figures 4c, d, and e), a similar shift appeared in the absorption band at 871 cm^{-1} to 885 cm^{-1} , due mainly to n-BA effect. A new band appeared at 744 cm^{-1} , particularly in the sample of 1.8 wt% CoPc, may be referred to the pure polycrystalline CoPc complex; Co–N stretching is exhibited in the region around 730 cm^{-1} . This shift may be a result of the interaction of the complex with the clay surface. Confirming these interaction models, new weak bands were also detected at 422 and 285 cm^{-1} characterizing the CoPc phase [32]. These findings reveal the existence of a fraction of CoPc as an interacted phase with some active sites in the clay gallery, while the other fraction remains probably freely mobile on the clay surface.

Textural and Morphological Characteristics of the Investigated Catalysts

Nitrogen adsorption-desorption isotherms at 77 K for all samples shown in Figure 5(a) are of type II of Brunauer's classification [16]. All isotherms exhibit narrow hysteresis loops, except that one for the sample of the highest complex loading (2.2 wt%), which shows a completely reversible isotherm approaching to that on pure complex [8]. The isotherm on parent bentonite has a hysteresis loop of the type H4, according to the IUPAC classification [16], characterizing the slit-shaped pores. However, the isotherms on nBA-treated bentonite and on different immobilized catalyst samples show the hysteresis loops of the type H3, characterizing aggregates of plate-like particles.

The obtained data of specific surface area (S_{BET}), BET-C constant, total pore volume (V_p) taken at 0.95 P/P₀ and average pore diameter ($r^{-\text{PP}}$) assuming parallel plate model for which the superscript (pp) is used, are summarized in Table 3. Obviously, a sharp decrease in the specific surface area of the parent bentonite is observed upon treatment with nBA, accompanied with an expansion of 0.88 nm in the pore radius. This may run in harmony with the previous findings [28,31], where intercalated alkylamines into kaolinite were

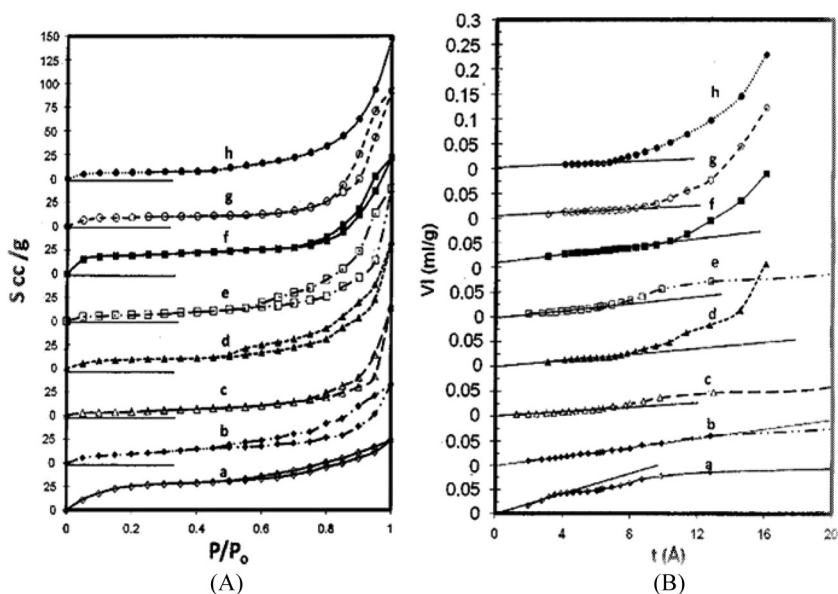


Figure 5: (A) N_2 adsorption-desorption isotherms, (B) V_t - t plots, on: parent bentonite clay (a), treated-bentonite (b) and immobilized CoPc/B of different complex loadings: (c) 0.2 wt%, (d) 0.6 wt%, (e) 1.0 wt%, (f) 1.4 wt%, (g) 1.8 wt%, and (h) 2.2 wt%.

shown to increase the basal spacing linearly with the length of alkyl chains by 0.255 nm per carbon atom, assuming a bilayer arrangement with alkyl chains being perpendicular to the clay layers. Accordingly, for nBA treatment, an expansion of 1.02 nm can be expected, being satisfactorily coincident with our pore analysis results. The immobilization process of CoPc in different loadings in the presence of nBA solvent is shown to be associated with a decrease in BET surface areas and a general increase in the pore dimensions (V_p and r^{-PP}). This may confirm the cooperative effect of the solvent and the intercalation of the complex expanding the clay interlayer distances, as was expected

Table 3: Surface parameters of bentonite, treated bentonite and CoPc/B of different complex loadings.

Sample	C_{BET}	S_{BET} (m ² /g)	S_t (m ² /g)	V_p (ml/g)	r^{-PP} (nm)
Bentonite (B)	37.0	98.60	91.0	0.115	1.17
Treated Bentonite* (t-B)	32.5	38.82	41.6	0.079	2.05
0.2 CoPc/B	13.5	18.16	21.0	0.181	9.97
0.6 CoPc/B	229.0	31.45	28.0	0.208	6.61
1.0 CoPc/B	38.0	24.75	30.0	0.217	8.77
1.4 CoPc/B	367.0	58.88	56.0	0.19	3.23
1.8 CoPc/B	732.5	29.52	27.0	0.221	7.49
2.2 CoPc/B	1000.0	21.63	22.0	0.229	10.59

*Parent bentonite clay treated with n-butylamine (nBA).

elsewhere [33]. The expansion values, shown for the immobilized samples to exceed the molecular dimensions of the CoPc complex (around 1.30 nm [5]) as well as that extent expected by the nBA-solvent effect, may suggest that a great deal of the complex is inserted (intercalated) as aggregates of packed inclined edge-on stacks of CoPc, enhancing the accessibility of central cobalt ions. The interaction, here, should involve N's of the macrocycle system of the complex and OH's of the clay support, located probably as edge sites in its gallery [11].

For pore structure analysis, V_1 - t plots were constructed, where V_1 is the amount adsorbed in ml/g and t is the statistical thickness in Å. In the present study, the reference t -curves of [34,35] based on nonporous solids were adopted. The agreement between the values of S_{BET} and S_t (Table 3) ensures the correct choice of the reference t -curves. From the V_1 - t plots shown in Figure 5(b), the downward deviation observed for the parent bentonite indicates predominance of the micropores, whereas the upward deviation in the plot of nBA-treated bentonite reflects the creation of some mesopores of limited size in addition to the existing narrow pores. The supported samples show an increase in the upward deviations linked with more evolution of mesopores, confirming the penetration mechanism of CoPc molecules, i.e., eliminating most of the bentonite micropores, as assisted probably by the nBA solvent.

The SEM micrographs of bentonite support and some selected catalyst samples are shown in Figure 6. The micrograph (a) of parent bentonite

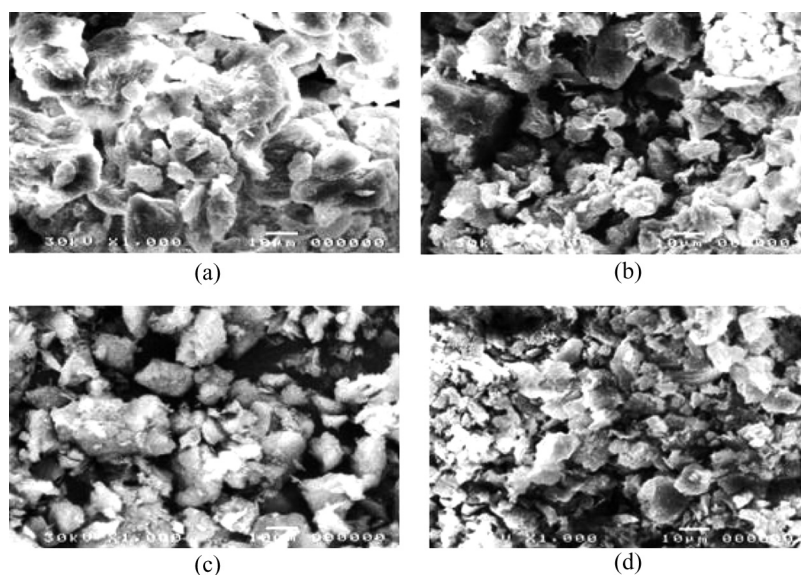


Figure 6: SEM micrographs of: (a) parent bentonite, (b) 0.2 wt% CoPc/B, (c) 1.0 wt% CoPc/B, and (d) 1.8 wt% CoPc/B.

support reveals homogeneous distribution of large particles with several interspaces. Micrograph (b) of the 0.2 wt% CoPc/B sample shows the typical bentonite crystal features with larger interlayer spaces (ranging between 1 and 3 nm) together with some spreaded noncrystalline CoPc. Collections of the complex crystals appear to protrude from the bentonite surface and interspaces, with a fraction clearly entrapped. Increasing CoPc loading to 1.0 wt% (micrograph c), a larger amounts of the complex seems to be entrapped forming larger particles. More interspaces are observed, with some smaller guest species, starting to collect on the top surface. By increasing the complex loading to 1.8 wt% (micrograph d), large amounts of the smaller complex particles appear on the surface and in the voids. Part of these probably escaped from the bulk to the external surface as dispersed disintegrated particles, decorating the bentonite surface.

Interaction Characteristics of the Investigated Catalyst System

The dissolution technique was applied previously in our laboratories to elucidate the nature of metal-support interaction in several supported cobalt phthalocyanine complex systems [5]. In the present study, the fraction of free CoPc (in wt%) extracted in 1:1 CHCl_3 -DMF solution was determined spectrophotometrically, from which the interacted fraction was plotted in Figure 7 as a function of CoPc loading. This figure includes also the total acidity estimated according to [17], as expressed in terms of mequiv./100 g sample. It is evident

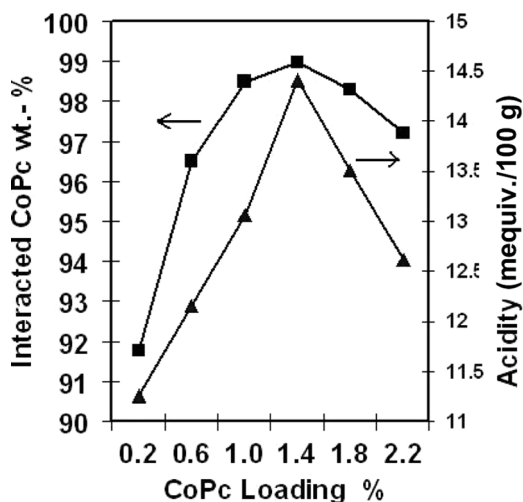


Figure 7: Interacted fraction of CoPc, wt% and total acidity (mequiv./100 g sample) as a function of CoPc complex loadings.

that, a major fraction of the complex exhibits interaction with bentonite surface and/or penetration in the clay interlayers. The interacted fraction increases with the CoPc loading up to 1.4 wt%, above which a little decrease is observed. Such increase in the interacted fraction is accompanied with a parallel increase in the total acidity of the catalyst system. This may suggest that the fraction of the complex intercalated into the clay galleries increases with the increase of the % loading. The intercalation leads probably to exposure of increased number of internal acid sites, confirming the inclined edge-on orientation of the complex on bentonite surface. This may ensure that the CoPc complex activates bentonite clay through exposure of new active acids sites. One can thus conclude that, in the diluted region of the immobilized CoPc, (<1.0 wt% loading), the polymerization reaction proceeds ionically via the active acid sites of bentonite support. With CoPc loadings ≥ 1.4 wt%, the packed aggregates of oriented stacks, being staggered in the clay galleries, seem to cover a fraction of the clay active acid sites with more contribution of free radical mode of the polymerization. A part of the complex probably escapes to the external surface with less interaction degree and more accessibility to monomer molecules.

CONCLUSIONS

In the present work, the catalytic behavior of cobalt (II) phthalocyanine immobilized on bentonite clay, in different loadings (between 0.2 and 2.2 wt%), was studied in bulk polymerization of methyl methacrylate, without using an activator or cocatalyst. The immobilization process of the complex in presence of n-butyl amine could lead to preparation of an active combination, encouraging the polymerization reaction to proceed without activator or co-catalyst. The interaction of CoPc molecules with bentonite surface was assumed to involve the same clay acid sites (OH groups), that could be activated by O₂, favoring the inclined stacking model of CoPc, i.e., between N-atoms of the macro-ring system and OH's of the support (asymmetric Brønsted interactions). In the diluted region of the immobilized CoPc, (<1.0 wt% loading), the intercalated CoPc complex molecules activated bentonite support through exposure of new active acid sites, where the polymerization reaction seemed to proceed ionically. With higher loadings (≥ 1.4 wt% CoPc), combined mechanisms took place; ionic one functioned by bentonite clay and free radical one functioned by the complex, the contribution of which increases with increasing the complex loading in the catalyst system. The packed aggregates of oriented stacks, being staggered in the clay galleries, seemed to cover a fraction of the internal clay active acid sites, leading to more contribution of free radical mode of the polymerization reaction. All the produced polymers were characterized by broad molecular weight distributions

($\overline{M}_w/\overline{M}_n \geq 2$) and predominating syndiotactic structures. The chain-end control mechanism seemed to be prevailing, where the enchainment could most likely be catalyst-independent.

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