FIRING-ACTIVATED INTERACTION OF MONTMORILLONITE WITH TIN(IV) AND COPPER(II) PHTHALOCYANINE DYES

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The adsorption of phthalocyanines Pcs complexes onto montmorillonite MMT clay differs from that of the other complexes like porphyrins, in that the adsorption process can be completed only after firing treatment of the solid mixture. The MMT particles act as a complex-hosting matrix, and the actual adsorption process of the complexes onto the MMT occurs only after firing. This firing treatment generates different colors on firing the solid mixtures to different temperatures. When tin(IV) phthalocyanine dichloride Sn(IV)PcCl$_2$ complex is adsorbed onto the MMT, the chloride ligands are replaced by oxygen, and the complex is more protected from decomposition due to firing and solution effects. Both complexes, diamagnetic Sn(IV)PcCl$_2$ and the paramagnetic Cu(II)Pc are found in a free radical state on the MMT surface or intercalated in the interlayer after firing, produced by electron transfer from the complexes to the MMT. It was found by X-ray powder diffraction investigation that firing treatment of the air-dried metal Pc-MMT samples induces intercalation of the complexes in the MMT interlayer.

Keywords: phthalocyanine, montmorillonite, firing, adsorption, free radical

1. Introduction

Pcs and metal-Pcs are intensely colored compounds that have high thermal stability and semiconducting properties. They have been used for various technical applications such as gas sensors, electronic, and optical devices, including dye sensitized solar cell and photodynamic therapy [1-4]. Few attempts to adsorb the Pcs onto clays and other adsorbents have been made, possibly due to the low solubility of these compounds in most known solvents [5], which makes the process of adsorption complicated. In the bulk polymerization of methyl methacrylate, the catalytic behavior of cobalt(II) Pc immobilized on bentonite clay, with different complex loadings ranging from 0.2 to 2.2 wt%, in the presence of n-butyl amine solvent, was investigated without using an activator or cocatalyst [6]. Novel cationic Ga(III) Pc (hydroxo[tetrakis(N,N,N-trimethy]anilinium) phthalocyaninato gallium(III), has been synthesized and its

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adsorption and photochemical activity on clay has been examined. The complex has been adsorbed without aggregation on the clay surface under high density conditions [7]. Through ion exchange and in situ crystallization of the synthetic clay layers, Pc and metal Pcs have been introduced into the galleries of anionic and cationic clays. The Pcs were found to be oriented parallel to cationic hectorite clay layers (gallery heights 4.5-6.5 Å) and perpendicular to anionic layered double hydroxide clay layers (gallery height 18.2 Å) in correlation with the respective layer charge densities of their hosts [8]. As a host material for encapsulating the Co(II) Pc complex, alumina-pillared MMT clays (Al-PILC) prepared under ultrasonic agitation and normal stirring methods have been used. The occupation of the Co(II) Pc moieties within the porous structure of the pillared clay is indicated by a significant decrease in the BET surface area and total pore volume of Al-PILC [9]. In the presence of typical natural interferents such as ascorbic acid and uric acid, nanostructured film composites of sodium MMT clay and nickel PC were self-assembled by layer-by-layer technique and applied as electrochemical sensors for dopamine [10]. Nickel(II) Pc (1.8 wt%)/bentonite/HSO^{3-} and copper(II) Pc (1.8 wt%)/bentonite/ HSO^{3-} have been shown to have different catalytic performances, initiating systems in the early phase of aqueous methyl methacrylate polymerization in the temperature range of 40-60 °C [11]. Via acid thermal treatment and through pillaring with titania and vanadia, pure bentonite clay has been modified. The Iron(II) Pc complex on the modified bentonite supports was immobilized at 0.5 wt% loading [12]. The formation and characterization of zeolite-encapsulated and metal-PC complexes intercalated with clay has been investigated [13]. Anion exchange reactions were synthesized and characterized by ancillary techniques in a series of hybrid metal (Zn, Cu, and Co) layered simple hydroxides functionalized by the surfactants dodecylsulfonate or dodecylsulfate and tetrasulfonate metal (Cu, Co)-Pcs [14]. Complexes of anionic copper(II) Pc monosulphonate and copper(II) Pc tetrasulphonate were successfully intercalated by direct synthesis method into the intergallery of Mg-Al layered double hydroxides. Results of XRD suggested an inclined anion orientation in the interlamellar space [15].

The aim of the current study is to investigate the interaction between copper and tin Pc and MMT upon firing, and to study the production of different ceramic colored phases that could have industrial applications.

2. Materials and methods

The tin(IV) Pc complex (Sn(IV)PcCI_2) was prepared according to the method described previously [16]. copper(II) Pc (Cu(II)Pc) and all other chemicals were obtained from Sigma-Aldrich. The MMT clay sample was obtained from Podmore and Sons. A Beckman DU-7 and Perkin-Elmer Lambda 5

Uv/Vis spectrophotometers were used for electronic absorption analysis. The diffuse reflectance spectra of the powder samples in the 30000-14000 cm^{-1} rang were measured on a Unicam SP. 700 spectrophotometer. Mossbauer spectra were measured on a Canberra Multichannel Analyzer using ^{57}Co as a source. The ESR spectra were measured on a Varian El04A X-band spectrometer. X-ray diffraction patterns were measured on a Philips diffractometer using CuKα radiation.

1 g of the MMT clay sample was added to a 75 ml solution of the Pc complex in chloroform or dimethyl formamide (DMF). The complexes were mixed with the MMT in different concentrations. The mixtures were stirred at room temperature for different periods of time, then filtered and air dried.

3. Results and discussions

The powdered mixtures obtained from the reaction of MMT and the Sn(IV)$PcCI_2$ or Cu(II)Pc complexes in chloroform or DMF in different concentrations, after drying, showed different colors. The fi1trate of the mixture was almost colorless, due to the low solubility of the complexes. The MMT retained all the undissolved crystals on the surface producing a solid mixture containing two phases. The samples undergo a color transformation upon firing in air for a few minutes. The color of the air dried powdered samples is green when low concentrations of the Sn(IV)$PcCl_2$ complex (0.5%, 5%) are used, while the use of high concentrations (10%, 20%) gives the powdered samples a grey color. The solution containing low complex concentrations has the potential to dissolve most of the crystals, giving the sample a green color, while the use of high concentrations gives the sample a grey color due to the retention between the MMT particles of large quantities of the undissolved crystals. Firing the samples causes the crystals of Sn(IV)$PcCI_2$ to migrate on the surfaces of MMT, resulting in intense green colors at 400-500 ^oC, when 10% and 20% concentrations are used. Table 1 and 2 show the color of the powdered Sn(IV)$PcCl_2$-MMT and Cu(II)Pc-MMT samples produced from the 2 hour reaction of the mixtures in chloroform and the dried samples were heated for 5 minutes.

3.1 Visible absorption and diffuse reflectance spectra

The visible absorption spectra in the adsorbed state of both the Sn(IV)$PcCl_2$ and Cu(II)Pc complexes do not vary from those of the original spectra in solution, but as the sample is fired to a higher temperatures, the intensity of the absorption bands becomes stronger using the same concentrations of the mixtures. The complex reaches a maximum concentration spread over the MMT at this temperature. The MMT particles therefore act as a complex-hosting matrix, and the actual adsorption process of the PCs onto the MMT occurs only after firing.

Table 1

The colors of the Sn(IV)PcCl$_2$-MMT samples reacted in chloroform for 2 hours and the dried samples heated for 5 minutes at different temperatures

MMT-Sn(IV)PcCl$_2$ concentration	R.T.	100 ^{o}C	200 ^{o}C	300 ^{o}C	400 ^{o}C	500 ^{o}C	600 ^{o}C
0.5%	green	green	green	green	Green-grey	grey	grey
5%	green-grey	green-grey	green-grey	green-grey	grey	grey	grey
10%	grey	grey	grey	grey	grey	green	grey
20%	grey	grey	grey	grey	grey	green	grey

Table 2

The colors of the Cu(II)Pc-MMT samples reacted in chloroform for 2 hours and the dried samples heated for 5 minutes at different temperatures

MMT-Cu(II)Pc concentration	R.T.	100 ^{o}C	200 ^{o}C	300 ^{o}C	400 ^{o}C	500 ^{o}C	600 ^{o}C
0.2%	very light Blue	very light blue	very light blue	blue-purple	blue-purple	green	light green
1%	light blue	light blue	light blue	blue-purple	blue-purple	green	light green
5%	blue	blue	blue	green-blue	green-blue	green	light green
10%	dark blue	dark blue	dark blue	dark-blue	dark blue	dark blue	light blue
20%	dark blue	dark blue	dark blue	dark-blue	dark blue	dark blue	light blue

The diffuse reflectance spectrum of the Sn(IV)PcCl$_2$ complex is characterized by two weak bands at 16000 and 14700 cm^{-1}. These bands appeared slightly modified on MMT. The spectrum of the green sample heated at 400 ^{o}C shows that the intensity of these bands has increased, and the band that appeared at 14700 cm^{-1} was shifted to 14000 cm^{-1} (Fig. 1). The diffuse reflectance spectrum of the Cu(II)Pc complex is also characterized by two weak bands at 16000 and 14500 cm^{-1}. When the complex was in the adsorbed state, the spectra appeared unchanged. On heating, the intensity of the two bands increased as the temperature was raised. The band at 16000 cm^{-1} appeared in the same position and the other band at 14500 cm^{-1} nm was shifted to 14300 cm^{-1} (Fig. 2). The increase in the intensity of the bands with heating is due to the start of melting of the complexes. The Sn(IV)PcC1$_2$ changes to Sn(IV)Pc at 500-530 ^{o}C, and at 550 ^{o}C the structure breaks down completely [17]. No evidence was found in these experiments for the demetallation of the complexes by heating on the MMT

surface up to 600 ^{o}C, however, the two complexes have different thermal stabilities.

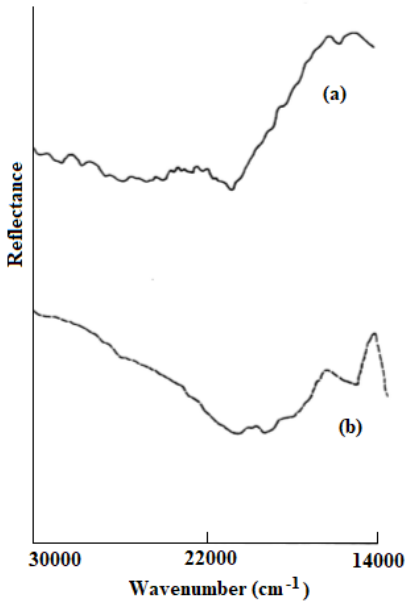

Fig. 1. Diffuse reflectance spectra of (a) Sn(IV)PcC1$_2$, (b) 20% Sn(IV)PcC1$_2$-MMT sample heated at 400 °C for 5 minutes

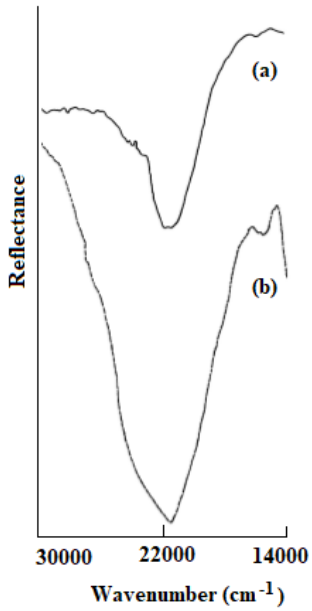

Fig. 2. Diffuse reflectance spectra of (a) Cu(II)Pc, (b) 1% Cu(II)Pc-MMT sample heated at 400 °C for 5 minutes

3.2. Mossbauer spectroscopy

The Sn(IV)PcCl$_2$ complex Mossbauer spectrum is shown in Fig. 3. The spectrum is in the form of a doublet with an isomer shift of 0.28(1) mms^{-1} and a quadrupole splitting of 1.00(1) mms^{-1}. The Mossbauer parameters of the complex in the adsorbed state show a decrease in the isomer shift, which may be due to the replacement of the chloride ligands coordinated to the tin atom by a stronger ligand such as oxygen, which is more electron negative and pulls more electron density from the tin (probably s-electron density). This leaves the tin atom with less s-electron density at the nucleus, which in turn leads to a decrease in the isomer shift (Table 3 and 4). Fig. 4 shows the Mossbauer spectra of the 20% Sn(IV)PcCl$_2$-MMT sample fired for 5 minutes at different temperatures.

The effect of firing on the Sn(IV)PcCl$_2$ complex in the absence of the MMT was also investigated. Heating the complex at 500 ^{o}C under air caused the doublet to be o broader indicating a different Sn(IV) environment. At 600 ^{o}C, a new site in the spectrum appeared, caused by the destruction of the complex. The parameters of the heated Sn(IV)PcCl$_2$ in the absence of the MMT are given in Table 5. It is clear that the MMT surface preserves the fired complex. This is evident from the high values of the linewidth of the sample fired in the absence of the MMT.

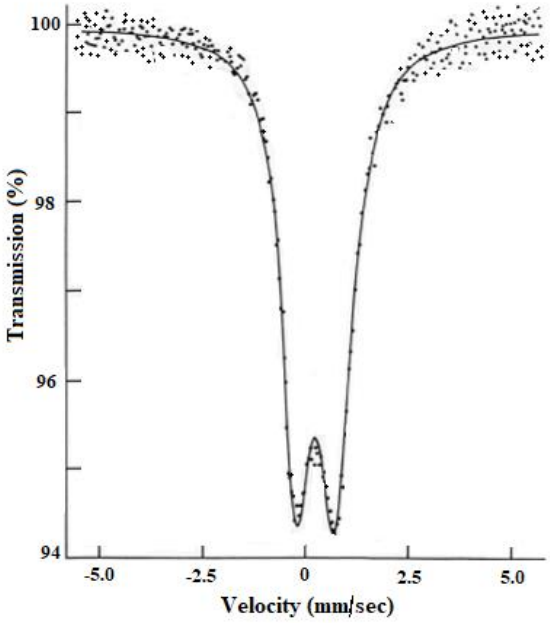

Fig. 3. ^{119}Sn Mossbauer spectrum at 77 ^{o}K of Sn(IV)PcC1$_2$

Table 3

The ^{119}Sn Mossbauer parameters at 77 ºK of the MMT sample reacted with Sn(IV)PcCl$_2$ for 2 hours in chloroform and heated at different temperatures for 5 minutes.

Sample	Temp. of firing	δ mms^{-1}	Δ mms^{-1}	Γ mms^{-1}
20% Sn(IV)PcCl$_2$-MMT	R.T.	0.21(3)	0.82(3)	0.49(3) 0.49(5)
=	200 ºC	0.24(2)	0.86(2)	0.50(2) 0.43(3)
=	500 ºC	0.12(4)	0.78(4)	0.45(4) 0.52(6)
=	600 ºC	0.009(1)	-	0.67(1)
10% Sn(IV)PcCl$_2$-MMT	R.T.	0.23(2)	0.91(2)	0.60(2) 0.57(4)
=	200 ºC	0.24(4)	0.84(4)	0.42(4) 0.52(8)
=	500 ºC	0.14(2)	0.87(2)	0.43(3) 0.52(4)
5% Sn(IV)PcCl$_2$-MMT	R.T.	0.20(3)	0.84(3)	0.50(3) 0.52(6)
=	200 ºC	0.28(3)	0.92(3)	0.58(3) 0.48(6)
=	500 ºC	0.17(3)	0.75(3)	0.50(3) 0.52(6)

Table 4

The ^{119}Sn Mossbauer parameters at 77 ºK of the MMT sample reacted with Sn(IV)PcCl$_2$ for 24 hours in chloroform and heated at different temperatures for 5 minutes.

Sample	Temp. of firing	δ mms-1	Δ mms-1	Γ mms-1
10% Sn(IV)PcCl2-MMT	R.T.	0.25(2)	0.88(2)	0.48(2) 0.42(4)
=	200 ºC	0.20(2)	0.87(2)	0.47(3) 0.44(4)
=	400 ºC	0.20(2)	0.82(2)	0.48(4) 0.52(2)
=	600 ºC	0.03(1)	-	0.74(1)

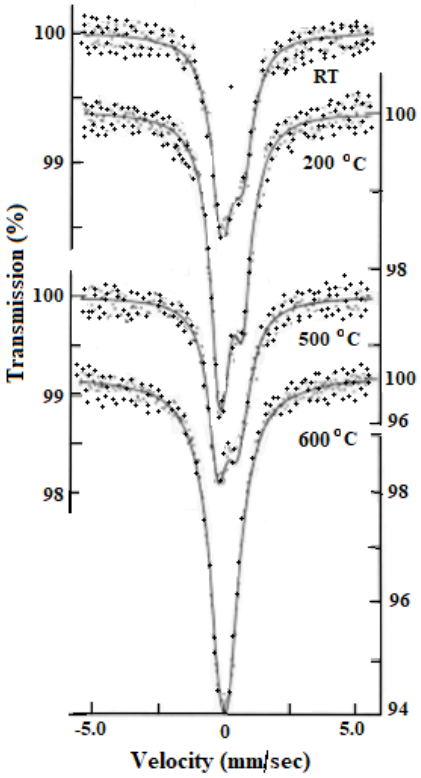

Fig. 4. ^{119}Sn Mossbauer spectra at 77 ^{o}K of 2% Sn(IV)PcC1$_2$-MMT sample heated at various temperatures for 5 minutes

Table 5

The ^{119}Sn Mossbauer parameters at 77 ^{o}K of the fired Sn(IV)PcCl$_2$ complex at different temperatures for 5 minutes

Temp. of firing	δ mms^{-1}	Δ mms^{-1}	Γ mms^{-1}
300 ^{o}C	0.26(1)	1.02(1)	0.46(1) 0.50(1)
500 ^{o}C	0.20(2)	0.94(2)	0.65(2) 0.70(2)
600 ^{o}C	0.05(1) 0.11(1)	- 4.71(4)	0.98(1) 0.80(6)

3.3. Electron spin resonance spectra (ESR)

ESR investigations on both the Sn(IV)PcCl$_2$ and Cu(II)Pc complexes have shown free radical signals. Metal free Pc and several other diamagnetic metal Pcs have been reported to display an ESR signal [18-20]. This resonance line at about the g-value of the free electron was attributed to a broken π-bond in the Pc matrix [21]. Researchers have suggested that the centers responsible for the free radical resonance are oxygen impurities absorbed by the compounds. They were unable

to distinguish between the electrons being on the surface or in the bulk of the complex [22]. The Sn(IV)$PcCl_2$ complex showed a signal at g-value of 2.016. When the complex was reacted with MMT, the intensity of the signal was reduced and overlapped with that of the structural Fe(III). Firing the Sn(IV)$PcCl_2$-MMT powder sample caused a decrease in the intensity of the signal with increasing firing temperature.

The Cu(II)Pc shows a signal at g = 2.068. When the complex is in the adsorbed state, this signal increases in intensity. The g = 2.068 signal decreases in strength on firing the sample at 200 ^oC and a new signal at g = 2.022 appears. This new signal also remained at 400 ^oC in the fired sample. At 500 ^oC the sample showed a very broad signal, however, remnants of the new signal were still clear. Fig. 5 shows the ESR spectrum of the Cu(II)Pc-MMT sample fired at 200 ^oC.

It appears from the behavior of the diamagnetic Sn(IV)$PcCl_2$ and the paramagnetic Cu(II)Pc complexes that these complexes, when present on the MMT surface, retain a radical species. The diamagnetic tin complex showed no change in its signal on the MMT surface, apart from the decrease in the intensity of the signal on firing. The paramagnetic copper complex showed a new signal, which may be due to a radical formation induced by firing the complex on the MMT surface. This signal is responsible for the increase in intensity of the original copper signal in the air dried Cu(II)Pc-MMT sample. When the new signal appeared, it overlapped the original one, and this original signal began to decrease in intensity, behavior that is similar to that found with the tin complex. The behavior of both the tin and copper complexes does not agree with the idea of the oxygen center being responsible for the free radical resonance reported by other researchers [22], in which they found, that firing up to 300 ^oC in oxygen increases the spin concentration in the metal free Pc. The results obtained from the current experiment are in agreement with those obtained on carbon blacks and charred hydrocarbons [23]. It was found in these compounds that the oxygen broadens the resonance line and decreases the spin concentration. The unpaired electron in these compounds was attributed to a broken π-bond in the molecular matrix. This suggestion applies to our experience, and the idea of a broken π-bond in the Pc matrix is supported by the behavior of the Sn(IV)$PcC1_2$ complex and also by the appearance of a new signal in the Cu(II)Pc-MMT sample fired at 200 ^oC. This degree of firing temperature seems to be enough to produce an unpaired electron when the compound is in the adsorbed state. It is understood that Pcs serve as electron donors or acceptors [2]. The former types of reaction may take place on the MMT, leaving a π radical Pc cation on the surface or in the interlayer.

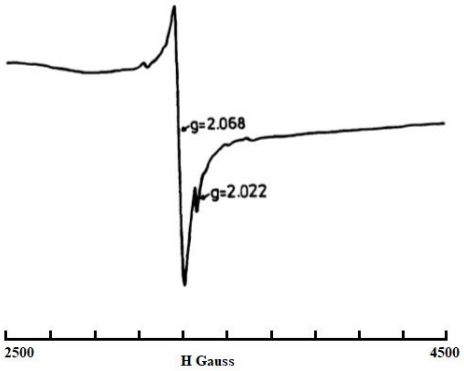

Fig. 5. ESR spectrum at room temperature of Cu(II)Pc-MMT sample fired at 200 °C

3.4. X-ray powder diffraction

Montmorillonite gives a basal spacing of 9.6 Å, when no molecules are between the unit layers. The X-ray powder diffraction studies showed that firing treatment of the air-dried metal Pc-MMT samples induces intercalation. A basal spacing of 13.6 Å was found for the dried metal Pc-MMT samples. This basal spacing increased to 14 Å when the sample was fired at 200 °C. The basal spacing of 14 Å indicates an interlayer separation of 4.4 Å which may represent a Pc molecule planar to the MMT layers (Fig. 6).

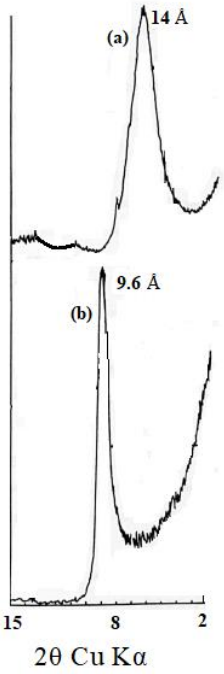

Fig. 6. X-ray powder diffraction patterns of (a) original montmorillonite (b) metal Pc-MMT sample fired at 200 °C

Firing the sample at 400 ^{o}C, reduces the basal spacing to 13.4 Å. It appears that when the Pc complexes are adsorbed onto the MMT, they are protected from solution attack and firing treatment. The mechanism of adsorption is initiated by firing, which causes the intercalation of the complexes into the MMT interlayer and the migration over the surface. These intercalated colored species may all be radicals produced by electron transfer from the complexes to the MMT.

4. Conclusions

The adsorption process of Pcs onto MMT can be completed only after firing treatment of the solid mixture. This firing treatment generates different colors at different temperatures. When the Sn(IV)PcCl$_2$ complex is adsorbed on MMT, the chloride ligands are replaced by oxygen, and the complex is more protected from decomposition due to firing process. The diamagnetic Sn(IV)PcCl$_2$ and the paramagnetic Cu(II)Pc, when present on the MMT surface, retained radical species. The firing treatment of the air-dried metal Pc-MMT samples induces intercalation of the complexes in the MMT interlayer.

R E F E R E N C E S

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