MONTMORILLONITE TREATED WITH RHODAMINE-6G MECHANOCHEMICALLY AND IN AQUEOUS SUSPENSIONS
Simultaneous DTA-TG study

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Abstract

The mechanochemical solid-state adsorption of the cationic dye rhodamine-6G (R6G) by montmorillonite was investigated by XRD and simultaneous DTA-TG. Five different mixtures of R6G and montmorillonite were investigated. They contained 10, 20, 35, 50 and 100 mmol R6G per 100 g clay. The solid R6G was ground with the clay for five minutes. Mixtures were ground both in the absence of water (dry grinding) and with the adding of drops of water periodically, (wet grinding). There were no differences between samples obtained by wet or dry grinding. X-ray and DTA data were compared with those of R6G-montmorillonite obtained from aqueous suspensions. The mechanochemical products were different from those obtained from aqueous suspensions. The X-ray and DTA studies suggest that the mechanochemical adsorption of organic cations takes place on the external surfaces of the clay whereas in suspensions the adsorption takes place into the interlayer space. In the latter case the final stages of oxidation occur in temperatures higher than those of the neat dye whereas in the former they occur at lower temperatures.

Keywords: DTA, mechanochemical adsorption, montmorillonite, organo-smectites, rhodamine-6G

Introduction

Rhodamine-6G (R6G, Scheme 1), is an important fluorescent red dye which is widely used in the dying of paper, wool and silk directly and cotton mordanted with tannin and many other products. This basic dye is cationic and is adsorbed by smectite minerals from aqueous solutions by the mechanism of cation exchange [1–6], described by the following equation:

$$M\text{-}Smec(s)+[R6G]Cl(aq)\rightarrow R6G\text{-}Smec(s)+MCl(aq)$$
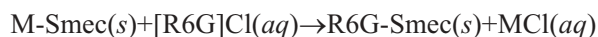
where *Smec* is the smectite mineral, *M* is the exchangeable cation initially present in the exchange position of the mineral. The adsorbed cations are located in the

interlayer space, on the broken bonds surface and when the clay flocculates also in the interparticle space [7].

Many cationic dyes do not obey Beer's law in aqueous solutions and the characteristic spectral features of their aqueous solutions change with concentration. For example, visible absorption spectra of a metachromic dye in solutions of different concentrations show either one, two, or more bands, the intensities of which depend on dye concentration. The longer wavelength feature is characteristic for a very dilute solution and is called 'α-band'. Increasing dye concentration results in the gradual replacement of the α-band by a new, shorter wavelength 'β-band'. Further increase in the dye concentration may cause a gradual substitution of the β-band by another diffuse band closer to blue wavelengths, called the 'γ-band' [7, 8].

The deviation from Beer's law, and the shifts of the absorption bands to shorter wave-lengths as the dye concentration increases, are due to the formation of dimers and higher aggregates in solution. The α-band is attributed to the monomeric form of the dye, whereas the β- and γ-bands are attributed to dimers and higher aggregates of the dye, respectively. Band α arises from a $\pi \rightarrow \pi*$ transition. Bands β and γ are, in fact, due to blue shifts of band α. A blue shift of the $\pi \rightarrow \pi*$ transition is an indication that interactions between π electrons of the aromatic rings occur during dye aggregation. Such a change to the spectrum is termed 'metachromasy', and dyes which exhibit this effect are 'metachromic dyes' [9, 10].

The cationic dye R6G consists of a xanthene moiety which is responsible for its characteristic $\pi \rightarrow \pi*$ absorption at visible wavelengths. In addition, this cation possesses a phenyl ring, the plane of which is perpendicular to that of the three xanthene rings, and consequently has only a small effect on the $\pi \rightarrow \pi*$ transition. This dye is metachromic, forming dimeric species in aqueous solutions but due to steric hindrance, R6G dimerizes only to a small extent [11, 12].

The adsorption of most metachromic dyes by montmorillonite is accompanied with metachromasy. There appear to be three reasons for metachromasy. (1) Metachromasy results from the π interactions which occur between the oxygen plane of tetrahedral substituted clay and the aromatic rings of the adsorbed dye cations which are located inside the interlayer space. In this interaction, atoms of the oxygen plane of the smectite skeleton donate lone electron pairs to the π anti-bonding orbitals of the dye cations [13–15]. (2) In the case of flocculated clay, metachromasy occurs due to the dimerization of the cations inside the interparticle space [15–18]. (3) Metachromasy results due to dye aggregation on the external surface of the clay [19]. These aggregations are also associated with π interactions.

In previous thermal analysis studies of montmorillonite- and Laponite-dye complexes it was shown that thermal curves of complexes with π interactions differ from those of complexes with no π interactions. Mass spectrometry of thermal evolved gases of the former complexes showed that oxidation reactions occur with several DTA exothermic peaks along the temperature range 250–900°C whereas in the latter the dye oxidation was completed below 700°C [20–24]. It appears that thermal analysis can serve as a tool for the study of the interactions between aromatic cationic dyes and clay minerals.

Due to steric hindrance π interactions are not expected to occur between R6G and the oxygen planes of the clay. In this dye the planar xanthene group is constrained to be roughly perpendicular to the phenyl ring and consequently cannot be at such a sufficiently short distance from the oxygen plane to permit π interactions between the two components [1]. The adsorption of R6G by smectites from aqueous solutions was studied by several investigators who showed by visible spectroscopy that metachromasy in R6G-smectites occurs to a small extent and only under special conditions which lead to flocculation of the clay in the aqueous suspensions [1-6].

A mechanochemical technique is sometimes used for the adsorption of organic matter by clay minerals. In many studies it has been shown that this technique increases the adsorption and shortens the time necessary for the reaction [25]. In a previous study we described a mechanochemical adsorption of the cationic dye crystal violet by montmorillonite [26]. A simultaneous DTA-TG study together with an X-ray study showed that by grinding the dye-clay mixture the adsorbed cations were located on the external surfaces of the clay. Washing with water was essential for the penetration of the organic cations into the interlayer space. In the present paper we describe a mechanochemical adsorption study of R6G by montmorillonite and we compare the mechanochemical adsorption products with those obtained from aqueous suspensions.

Experimental

Materials

Wyoming bentonite (Na-montmorillonite) was supplied by Wards' Natural Science Establishment, Inc. It was ground and sieved to 80 mesh and the non-clay fraction was separated by sedimentation. The original sample contained 74 mmol Na$^+$ and 18 mmol Mg^{2+} plus Ca^{2+} per 100 g clay. R6G was purchased from Merck and was used as supplied. C, N and Cl analyses showed that the sample contained 75%. After ignition the sample left a residue of 1.1%.

Methods

Dye-clay complexes obtained by mechanochemical treatment

Five mixtures containing 1.0 g of clay and different amounts of R6G were manually ground with a mortar and pestle for 5 min in air atmosphere. The total loadings were 10, 20, 35, 50 and 100 mmol R6G per 100 g clay (dry grinding). Similar mixtures were ground and during the grinding drops of distilled water were added periodically (wet grinding).

Dye-clay complexes obtained from aqueous suspensions

Increasing amounts of aqueous solutions of R6G were added drop by drop to bottles containing well dispersed 0.6 and 1.9% clay suspension. The total loadings were 10,

20, 35, 50 and 100 mmol R6G per 100 g clay. After 24 h the organo-clay complexes were separated by centrifugation.

X-ray diffraction patterns of oriented clay samples on glass slides were obtained on a Philips Automatic Powder Diffractometer, (PW 1710) with a Cu tube anode. Simultaneous DTA-TG curves of 10 mg samples were recorded in air using a Shimadzu 'DTG-50' Instrument. Heating rate was 10°C min^{-1}.

Results and discussion

X-ray diffraction data

Grinding up to five minutes did not show any significant effect on the diffractogram of R6G powder. Basal spacings of 1.53, 1.57, 1.71, 1.76 and 1.67 nm were recorded for air-dried montmorillonites loaded with 10, 20, 35, 50 and 100 mmol R6G per 100 g clay, respectively prepared from 1.9% aqueous suspensions. Slightly higher spacings were obtained with samples from 0.6% clay suspension. After heating the samples as films on glass slides at 360°C for five hours the basal spacings of these samples decreased to 1.43–1.49 nm. These basal spacings indicate that the dye cations are located inside the interlayer space [1].

Diffractograms of air-dried montmorillonite ground with different amounts of R6G with loadings between 10 and 100 mmol per 100 g clay, under dry or wet conditions, showed that each of the samples contained free non-adsorbed dye. The intensities of the peaks which characterize R6G increased with increasing amounts of dye in the mixture. There were almost no differences between wet and dry ground mixtures. The peaks were not observed in the diffractograms of samples obtained from aqueous suspensions. The basal spacings of the ground products were between 1.23 and 1.26 nm. The wet ground samples almost always gave larger spacings and sharper peaks. After heating the samples at 360°C for five hours their basal spacings decreased to 0.97 nm and the excess R6G was not observed any more. This basal spacing after heating indicates that the dye cations did not penetrate into the interlayer space during dry or wet grinding [7].

DTA-TG curves of R6G

DTA, TG and DTG curves of R6G are depicted in Fig. 1 and the characteristic features are summarized in Table 1. The DTG curve shows six stages in the mass loss. Three distinct DTG maxima appear at 258, 344 and 635°C. The latter peak has a shoulder at 580°C. Two very weak and broad peaks appear at about 60–120 and 700°C. The first mass loss stage below 120 $^{\circ}$C is mainly due to the evolution of humidity water. In the second mass loss stage the DTA curve shows a weak endothermic reaction beginning at 229 and reaching a minimum at 249°C. The discord between the endothermic DTA peak and the DTG peak and the fact that the endothermic reaction begins before the mass loss is attributed to a melting reaction accompanied by water evolution. The third mass loss stage is associated with two
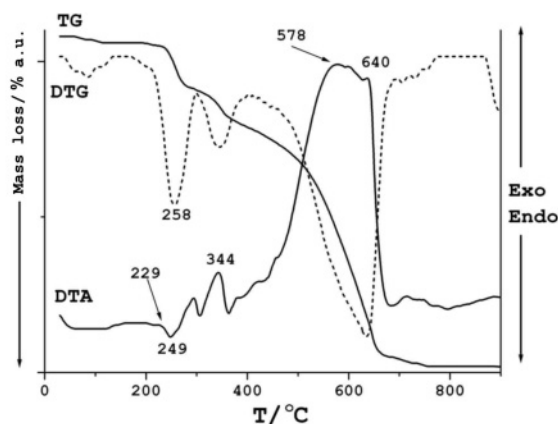
Fig. 1 DTA, TG and DTG curves of R6G

small exothermic peaks at 295 and 344°C indicating that in this stage water is obtained by the combination of the H atoms of the organic dye with oxygen (oxidation). The fourth and fifth stages are accompanied by two attached exothermic peaks at 578 and 640°C. Thermal evolved gas analysis (by mass spectrometry) of several cationic dyes showed previously [21–23] that H_2O is evolved in the temperature range 20-715°C whereas CO_2 and NO_2 are evolved in the temperature range 500–715°C. Based on these data we assume that the attached intense exothermic peaks at 578 and 640°C represent the oxidation of the organic cation which results in the formation of H_2O, CO_2 and NO_2.

Table 1 Assignment of thermal reactions, temperature range and DTA peak temperature and the corresponding mass loss of air-dried neat R6G

Reaction	Temperature range/°C	DTA peak temperature/°C	Mass loss/mass%
Humidity water loss	r.t.–120	60–120 b, w[EN]	3.1
Melting and dehydration	240–270	249[EN]	12.0
H oxidation	270–350	344[EX]	9.3
H, C and N oxidation	350–600	578[EX]	43.0
C and N oxidation	600–670	640[EX]	28.4
	670–800	720 b, vw[EN]	3.1

EN – endothermic peak; EX – exothermic peak; b – broad; v – very; w – weak;
r.t. – room temperature

DTA-TG curves of samples obtained from aqueous suspensions

Our previous simultaneous DTA-TG-EGA studies showed that these curves can be divided into three regions [20]. The application of the EGA makes it possible to explain their DTA-TG peaks. In the first region, up to 250°C, the endothermic dehydra-

tion of the clay with a DTA peak at about 100°C was the major thermal reaction. In the second region between 250–580°C with three DTA peaks the exothermic oxidation of the adsorbed R6G was the major thermal reaction. The first exothermic peak in this region at 390°C is the consequence of the combination of hydrogen atoms of R6G with oxygen atoms from air. The second peak at 420°C is due to the combination of H, C and N simultaneously with oxygen and consequently is the most intense. The third exothermic peak at 505–525°C is associated with the combination of C and N with oxygen.

The third region occurred at temperatures above 580°C. The major thermal reactions of this region were the dehydroxylation and recrystallization of montmorillonite and the last stages of the oxidation of the organic matter. The exothermic oxidation of R6G overlapped the endothermic dehydroxylation reaction. The DTA curve of untreated montmorillonite showed an endothermic peak at 695°C. In the presence of organic matter this peak shifted to lower temperatures. The CO_2 and NO_2 evolution curves showed two peaks at 610–650 and 665–680°C. A distinct endothermic peak is observed in DTA curves of montmorillonite treated with up to 20 mmol R6G per 100 g clay. With higher loadings small exothermic peaks were detected and their intensity increased with the loading [20].

In thermal EGA study of the adsorption of crystal-violet and acridine-orange by two smectites [21–24] we showed that in montmorillonite in which the adsorption of these dyes is accompanied by interactions between the oxygen plane and the dye, the thermal oxidation of the dye cations by air continued up to 800–900°C. In Laponite, where there are no π interactions of this type the oxidation was completed at 640–700°C. In the case of R6G-montmorillonite π interactions occur to a small extent only [1], and consequently the oxidation of R6G in the third thermal region occurs to a small extent. In thermal EGA-MS study of the adsorption of R6G by these two smectites it was shown that the evolution of CO_2 and NO_2 due to the oxidation of adsorbed R6G by air lasted up to 800 and 640°C in montmorillonite and Laponite, respectively [20].

Table 2 Mass loss (in mass% of air-dried samples) at temperature 25–220°C (column A, first region) and above 580°C column B, (third region in the TG curves) of R6G–montmorillonite complexes obtained in 1.9% (concentrated) and 0.6% (dilute) aqueous clay suspensions

Mmol R6G/100 g clay	1.9% clay suspension		0.6% clay suspension	
	A	B	A	B
0	8.1[a]	2.9	8.1[a]	2.9
10	8.3[b]	4.8	10.0[b]	4.4
20	7.7	4.4	5.0	8.2
35	7.0	11.1	4.8	10.5
50	6.3	9.4	9.4	1.4
100	n.d	n.d	2.9	6.9

n.d. – not determined; a – basal spacing of this sample is 1.25 nm, indicating the presence of a water monolayer in the interlayer space; b – basal spacing of this sample is 1.53 nm, indicating the presence of a water bilayer in the interlayer space

In the present study the complexes were prepared from 0.6 and 1.9% suspensions. Very similar DTA curves were obtained in spite of the different clay concentrations in the preparations of the samples. The mass loss in the dehydration stage and in the final stage of the different complexes, were determined from the TG curves and are presented in Table 2. The table shows that in the dehydration stage, mass loss decreased with increasing amount of dye. This is proof to the fact that the dye was adsorbed into the interlayer space replacing water molecules. In the third stage mass loss increased with loading up to 35 mmol per 100 g clay and then decreased. This suggests that the extent of interactions between the dye and the clay first increases with loading, but decreases with excess dye. The shape of the different dye-clay associations were recently described by Yariv [7]. When the amount of dye is below 35 mmol R6G per 100 g clay in one of the principal associations the dye is located in the interlayer space and is able to form π bonds with the oxygen plane of the clay. With higher amounts of dye the clay flocculates and the added dye is located in the interparticle space with no π interactions with the oxygen plane.

Table 3 Assignment of thermal reactions, DTA peak temperature (PT) and corresponding mass loss (ML) in mass% of air-dried samples, in thermal analysis of R6G-montmorillonite complexes obtained by mechanochemical treatment, dry grinding

Reaction	Temperature range/°C	Loading of montmorillonite/ mmol R6G/100 g clay				
		10	20	35	50	100
Clay dehydration PT^{EN}/°C	r.t.–220	80	90	85	90	85
ML/%		7.0	7.8	7.8	7.6	7.1
R6G melting PT^{EN}/°C	240–260	236	240	245	248	247
ML/%		0.5	2.0	3.2	3.8	5.9
H oxidation PT^{EX}/°C	280–350	302	302	310	310	314
ML/%		0.2	1.5	1.6	2.1	3.1
H, C and N oxidation PT^{EX}/°C	350–420	395	400	408	408	413
ML/%		1.5	2.3	3.5	4.3	5.6
C and N oxidation PT^{EX}/°C	420–550	457	480	490	495	505
ML/%		3.0	7.8	14.1	18.7	31.9
Clay dehydroxylation PT^{EX}/°C	550–700	670	670	675	680	680
ML/%		3.1	4.6	3.6	3.2	2.4
Untreated montmorillonite						
Clay dehydration PT^{EN}/°C	r.t.–120	90				
ML/%		8.1				
Clay dehydroxylation PT^{EN}/°C	580–700	670				
ML/%		2.9				

r.t. – room temperature; EN – endothermic peak; EX – exothermic peak

DTA-TG curves of samples obtained by mechanochemical treatments

Representative DTA and TG curves of samples obtained by grinding of mixtures containing 10 and 100 mmol R6G per 100 g clay, are depicted in Fig. 3. There are no significant differences between wet and dry grinding. Shapes of DTA and TG curves of samples ground with 20, 35 and 50 mmol dye per 100 g clay are similar to those of 10 and 100 mmol R6G per 100 g clay.

TG curves of these samples show the following stages of mass loss: Up to 220°C the dehydration of montmorillonite, 240–260 melting of excess dye accompanied by its dehydration, 280–350°C first stage of hydrogen oxidation and formation of charcoal, 350–420°C completion of combination of hydrogen (oxidation) and first stage of carbon and nitrogen combination with oxygen (oxidation), 420–550°C oxidation of charcoal, completion of carbon and nitrogen combination with oxygen (oxidation) and above 550°C, the dehydroxylation of montmorillonite.

Table 4 Assignment of thermal reactions, DTA peak temperature (*PT*) and corresponding mass loss (*ML*) in mass% of air-dried samples, in thermal analysis of R6G–montmorillonite complexes obtained by mechanochemical treatment, wet grinding

Reaction	Temperature range/°C	Loading of montmorillonite/ mmol R6G/100 g clay				
		10	20	35	50	100
Clay dehydration PT^{EN}/°C	r.t.–220	90	90	90	90	85
ML/%		7.2	6.7	7.5	7.2	6.6
R6G melting PT^{EN}/°C	240–260	240	245	245	245	245
ML/%		0.7	1.3	2.0	3.0	5.0
H oxidation PT^{EX}/°C	280–350	302	303	308	310	314
ML/%		0.6	0.8	1.2	1.6	1.7
H, C and N oxidation PT^{EX}/°C	350–420	390	395	410	408	410
ML/%		1.5	2.2	3.7	4.3	6.7
C and N oxidation PT^{EX}/°C	420–550	457	470	485	490	505
ML/%		3.4	6.1	11.0	15.6	24.0
Clay dehydroxylation PT^{EN}/°C	550–700	670	675	675	680	685
ML/%		3.7	2.4	3.5	2.5	3.0
Untreated montmorillonite						
Clay dehydration PT^{EN}/°C	r.t.–120	90				
ML/%		8.1				
Clay dehydroxylation PT^{EN}/°C	580–700	670				
ML/%		2.9				

r.t. – room temperature; EN – endothermic peak; EX – exothermic peak

In Tables 3 and 4 the DTA peak temperatures and the corresponding mass loss (in mass% of air-dried samples) are depicted together with the descriptions of the thermal reactions occurring during the thermal analysis of R6G-montmorillonite

complexes obtained by dry and wet grinding, respectively. The tables show that the DTA endothermic peaks do not depend on the loading of the clay whereas the exothermic peaks shift to higher temperatures with increasing loading probably due to higher amounts of charcoal. The tables also show that mass loss associated with the dehydration of the clay does not depend on the loading indicating that water is not evolved from the interlayer space during grinding. This peak is accompanied by mass loss due to water evolution. The appearance of an endothermic peak at 245°C in all the samples shows that some dye is present in a non-adsorbed state. However, the fact that the thermal oxidation of the dye in the ground dye-clay complexes is completed at 550°C before the completion of the oxidation of the neat dye at 670°C (Fig. 1 and Table 1) indicates that the dye is almost completely adsorbed by the clay. It is therefore concluded that some of the dye, which was not adsorbed by the clay during the mechanochemical treatment, was adsorbed during the thermal analysis, probably at about 250°C.
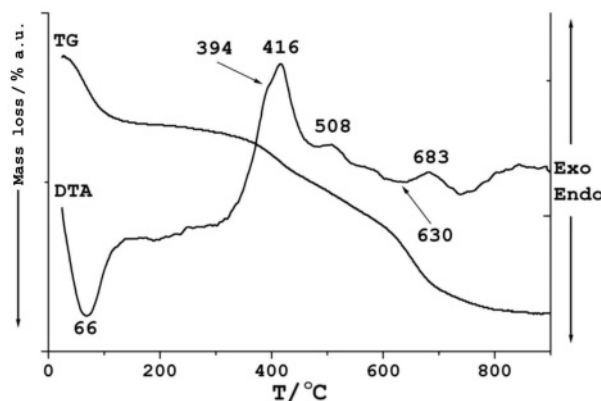

Fig. 2 DTA-TG curves of a sample containing 35 mmol R6G per 100 g montmorillonite obtained from an aqueous suspension
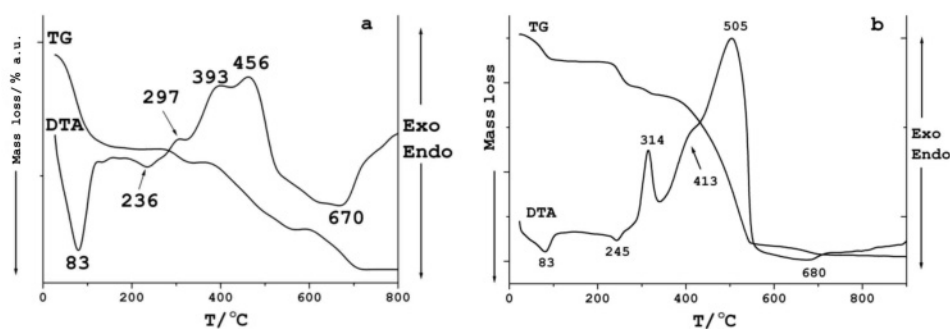

Fig. 3 DTA-TG curves of samples obtained by mechanochemical treatments.
a – 10 mmol R6G per 100 g clay; b – 100 mmol R6G per 100 g clay; dry grinding

By comparing Figs 2 and 3 it is obvious that the complexes which were obtained in aqueous suspensions differ from those obtained by the mechanochemical treatment. The X-ray study of the complexes obtained from aqueous suspensions revealed that the adsorbed dye cations were located in the interlayer space. Some of these adsorbed cations formed π bonds with the clay and their oxidation continued up to 800°C. The present X-ray and DTA studies suggest that the mechanochemical adsorption of R6G took place on the external surface of the clay and no bonds were formed between the dye and the clay. The oxidation of the organic matter was completed already below 550°C.

Conclusions

Dye–clay complexes obtained by mechanochemical treatments differ from those obtained from aqueous suspensions. In the former the dye is located on the external surface of the clay, whereas the dye is in the interlayer space when it is prepared in aqueous suspensions.

The adsorption of the dye into the interlayer space increases its thermal stability and the final stages of its oxidation occur in temperatures higher than the final stages of the oxidation of the neat dye. On the contrary, the adsorption of the dye onto the external surfaces of the clay decreases its thermal stability and the final stages of its oxidation occur at temperatures lower than the final stages of oxidation of the neat dye. The thermal stabilization is attributed to π interactions of the dye with the clay which also lead to metachromasy.

The shape of the DTA curves of the samples obtained from the aqueous suspensions differed from that obtained by the mechanochemical treatment. In the former, there were only minor shifts of the exothermic peak temperatures with increasing loading of the clay. In the latter the exothermic peak temperatures shift considerably with the loading of the clay.

In the samples from the aqueous suspensions, the mass loss associated with the dehydration of the clay decreased with the loading, indicating that water was replaced by the dye cations which penetrated into the interlayer. In the mechanochemical products the clay dehydration mass loss did not show any dependency on the loading because the dye did not penetrate into the interlayer space.

In samples from the aqueous suspensions the peak of the dehydroxylation of the clay shifted to lower temperatures with increasing loading [20]. In the mechanochemical products this shift was not observed. It is suggested that the shift of this peak is due to a thermal reaction between the OH groups of the clay and the thermal product of the adsorbed dye cations. This reaction occurs only when the dye is located inside the interlayer space.

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