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PHENANTHROLINE Cu(II)-BENTONITE COMPOSITE CHARACTERIZATION

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The penetration of the phenanthroline ligand into the interlayer space of the Cu-bentonite results in the formation of $Cu(Phen)_3$–bentonite composite. The expansion of the d_{001} basal spacing of the Cu-Bent from 14.24 to 17.7 Å on intercalation and the colour change indicate the cation immobilized dimeric ligand species' presence, which are thermally stable up to 315°C. The shift to higher frequency of the ring vibrations resulted from the π interactions is associated with the linkage of the tilted monomers to the smectite layers at elevated temperatures. The OH stretches and the bending peaks decrease in the intensity in parallel with an easy exchange between the water groups and the aromatic backboned ligands at room temperature.

Keywords: *adsorption, bentonite, copper, 1,10-phenanthroline*

Introduction

The acid strength of the bentonite minerals is dependent on the interlamellar cation characteristics which balance the positive charge deficiency within the octahedral layers [1, 2]. Inorgano-clay composites of definite gallery heights prepared by partial exchange between the cations and organic intercalants such as alkylammonium ions, bicylic amine cations and metal chelate complexes seem specially important for developing microporous layered materials [3–5]. However, little is understood about the thermal stability which is further enhanced upon intercalation and the structure of organo-bentonite smectite group clay composites [6]. Reported in this work are the probable consequences of the Cu^{2+}-induced adsorption of 1,10-phenanthroline on bentonite surface examined by FTIR, thermal analysis (DTA, TG-DTG), XRD, UV-VIS and surface area measurement techniques.

Experimental

Material and methods

The Wyoming bentonite sample (Sigma; CEC: 92 meq/100 g clay) was converted into Cu-Bentonite (Cu-Bent) form by saturating the clay aqueous solution with $CuCl_2 \cdot 2H_2O$ (Merck, 99.0%). The metal concentration retained by the bentonite was determined by the data from Unicam UV2 UV-VIS spectrophotometer as 0.22 mmol g^{-1} clay. The Cu-Bent was reacted with 1,10-phenanthroline (Merck, 99.5%) in alcohol at 75°C for 3 h; the ligand to cation molar ratio: 3/1 [7]. The solid phase was filtered off and then purified by washing out with alcohol repeatedly until the supernatant did not show any excessive ligand.

Vibrational spectra were scanned in the region 4000–200 cm^{-1} using a Mattson-1000 FTIR spectrometer at a resolution of 4 cm^{-1}. XRD patterns were recorded by a Rigaku 2000 automated diffractometer using Ni-filtered CuK_α radiation. Thermal data were collected on a Rigaku TG 8110 analyzer equipped with TAS 100 (range: 20–1000°C) under dynamic nitrogen atmosphere (80 cm^3 min^{-1}) at a heating rate of 10°C min^{-1}. Calcinated α-alumina was taken as the reference. Surface areas were measured by nitrogen adsorption at 77 K using Quantachrome Monosorb Analyzer.

Results and discussion

The OH stretches, the Si–O vibrations and the bending peaks of untreated bentonite (Bent) are shown within the ranges 3700–3100, 1200–900 and 750–450 cm^{-1}, respectively (Fig. 1a). The inner hydration shell which is directly linked to the cation gives rise to a maximum absorption at 3631 cm^{-1}. The outer coordination sphere of the cation gives a broad H-bonded OH stretch centred at 3432 cm^{-1} and weaker HOH bending peak at 1640 cm^{-1} [8]. The alteration of the outer coordination shell of Cu-Bent causes the shift of the OH band at 3432 cm^{-1} to 3523 and 3429 cm^{-1} while the location of the band at 3631 cm^{-1} remained constant (Fig. 1b). The colour change from gray to bright green during the

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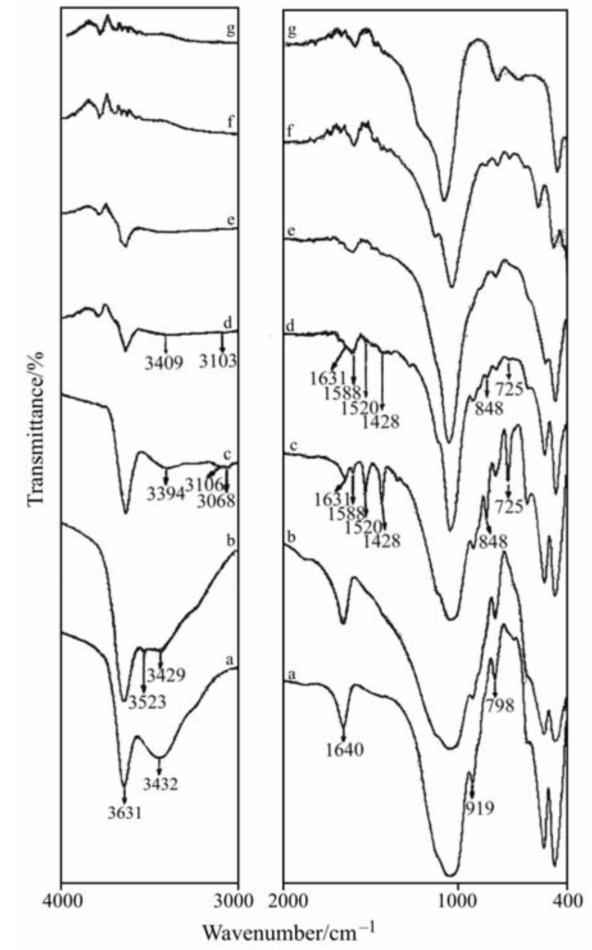

Fig. 1 FTIR spectra of a – untreated bentonite, b – Cu-bentonite, c – Cu(Phen)$_3$-bentonite and d–g – the composite heated at different temperatures for 1 h in air: d – 150°C, e – 350°C, f – 550°C and g – 750°C

organo-clay reaction may be interpreted in terms of the replacement of outer sphere water entities by phenanthroline species [9]. The intensity decrease of the bending band is accompanied by further shift of the OH stretch to 3394 cm^{-1} when the phenanthroline ligand penetrates into the cation modified bentonite as a neutral entity (Fig. 1c) [7, 10]. Also seen in the same spectrum is the shift to lower frequency (1428 cm^{-1}) of the C–N aromatic stretch as an indication of binding through the N atoms of the ligand to exchangeable cation and/or water molecule [11]. Consequently, the changes in the position of the C–H stretching and C=C skeletal peaks which appear at higher frequencies (1588 and 1520 cm^{-1}) than the analogous metal chelate complexes demonstrate the contribution from the π interactions occurring between the O-plane of Cu-Bent and the phenanthroline monomers with the aromatic rings lying parallel to the aluminosilicate layers [12]. At this stage, the dimeric moieties in the galleries renders organophilic interactions, giving positive charge to the originally hydrophilic silicate layers [13].

In order to confirm that organic composites decomposed over a wide temperature range, the sample was heated from room temperature to 750°C stepwise. The thermal treatment of Cu–Bentonite–Phenanthroline (Cu-Bent-Phen) composite at 350°C resulted in a dehydration process as indicated by the shift of the band at 3394 cm^{-1} to higher frequency and the weakening of the peak at 3631 cm^{-1}, and in particular, there were large changes in the intensities of all the vibrational modes associated with the phenyl ring. It is clearly shown in Fig. 1d that the ring vibrations (1520 and 1428 cm^{-1}) almost disappeared as the decomposition proceeded. It can be concluded, therefore, that the main mass losses over the temperature range 200–500°C were due to the decomposition of organic composite [14]. The stability of the Cu-Bent-Phen complex up to 315°C, as seen by thermal analysis curves and detailed in Table 1, may be ascribed to the shielding effect of alumino-silicate layers [15]. This is characteristic for monomeric ligand species located in an acidic environment, such as the interlayer space. Cu-Bent-Phen required temperatures higher than 550°C for the clay matrix dehydroxylation, proving that the organic matter which is covalently incorporated into the crystal lattice [13, 16] desorbed/decomposed in the temperature range 350–750°C (Fig. 1e–g). The C–N stretch at 1588 cm^{-1} that persisted in all comparative spectra denotes the oxidation-initialized disintegration of organo-clay species and the much weaker peaks detected in the range 1300–1500 cm^{-1} (Fig. 1f) may be related to the organic residues [9].

The endothermic DTA peaks of the untreated bentonite (Bent) in the temperature ranges 20–193 and 566–739°C (the mass losses: 5.15 and 3.25%, respectively) correspond to loss of the bulk of the interlayer water and dehydroxylation of lattice water, respectively (Fig. 2a and Table 1) [9, 17]. The DTA curve of Cu(Phen)$_3$-Bent composite shows a very broad endotherm from 20 to 150°C whereas the TG curve exhibits a mass loss of 4.68% up to 150°C (Fig. 2b) and this has been attributed to removal of free water from the clay matrix [2, 18]. A mass loss of 5.92% in the temperature range 317–437°C, the exothermic DTA peak at 495°C accompanied by a mass loss of 8.98% in the temperature interval 438–540°C and three sequential DTG peaks in the region 350–700°C (Fig. 2b and Table 1) signify the stepwise release of the organic moiety and thus, conversion of the Cu(Phen)$_3$-Bent composite to lower Cu(Phen)$_{3-x}$-Bent species [14] and to other residual organic products. The absence of an endothermic peak at the melting point of the ligand (117–120°C) suggests that a bilayer of ligand and/or water was aggregated rapidly on the external surface of bentonite prior to the decomposition to the phenanthroline monomers inside the interlamellar particles [15, 19]. This required that the

Table 1 Thermal analysis data of Bent and the Cu-Bent-Phen

Sample	Temperature range/°C	Mass loss/%
Bent	20–193 566–739	5.15 3.25
Cu-Bent-Phen	15–116 317–437 438–540 541–695	4.68 5.92 10.22

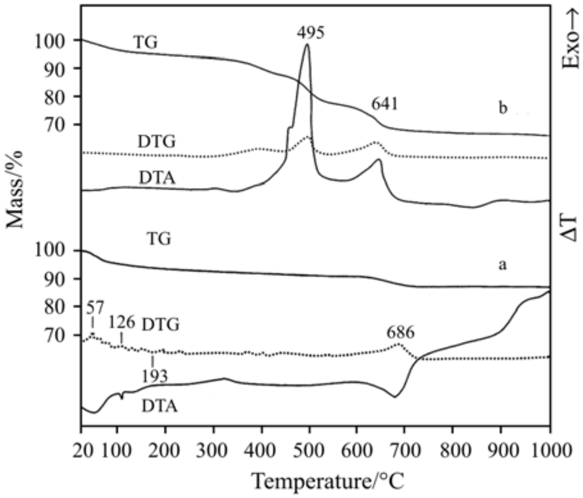

Fig. 2 TG, DTG and DTA curves of a – untreated bentonite and b – Cu(Phen)$_3$-bentonite

partial removal of the bilayer phenanthroline species from Cu-Bent in some yet unknown way was predominated slightly above 350°C. The exothermic DTA peak at 641°C with a significant mass loss (10.22%) in the temperature range 600–700°C may be related to oxidation and conversion of the monoligated constituent into metal oxide, i.e., CuO.

The presence of monomeric phenanthroline species in the interlayer space of the organoclay composite was unequivocally proven from the X-ray measurements of the sample. A strong reflection at 6.20(2θ) (d_{001} value 14.24 Å) and medium reflections at 19.80 and 34.96(2θ) (d_{020} and d_{006} values of 4.48 and 2.56 Å) of the major montmorillonite constituent and a very sharp reflection at 26.64(2θ) (*d* value 3.34 Å) of the quartz external component [20] were detected in the XRD spectrum of untreated bentonite (Fig. 3a). The expansion by 1.2(2θ) of the d_{001} spacing of Bent on the formation of the complex (Fig. 3b) may be related to the intercalation extent of the ligand. By subtracting the thickness of the SiO_2–Al_2O_3–SiO_2 sheet (9.0 Å) from the d_{001} value of Cu(Phen)$_{2.9}$-bentonite complex (17.7 Å), the height of the complex was estimated as 8.7 Å. The 3-D picture of the complex for which the height determined from the bond lengths as 8.9 Å is in conformity with the values of similar complexes [21] was illustrated in Fig. 4. The surface area decrease of the Cu-Bent-Phen complex (21.7 $m^2\ g^{-1}$) with respect to that of the Bent (33.0 $m^2\ g^{-1}$) may be interpreted as an outcome of the formation of dimeric ligand species in the interparticle spaces of the mineral. The amount of the ligand removed from the Cu-Bent-Phen structure (0.64 mol) is consistent with the ligand/metal ratio (2.9) which was confirmed by the mass loss of the corresponding exothermic peak and there appears a decomposition pathway proceeding via a strongly chemisorbed intermediate over the clay.

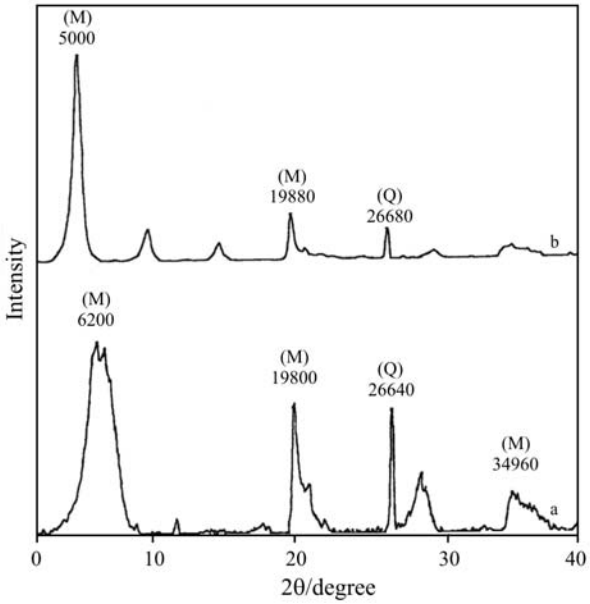

Fig. 3 XRD patterns of a – untreated bentonite and b – Cu(Phen)$_3$-bentonite

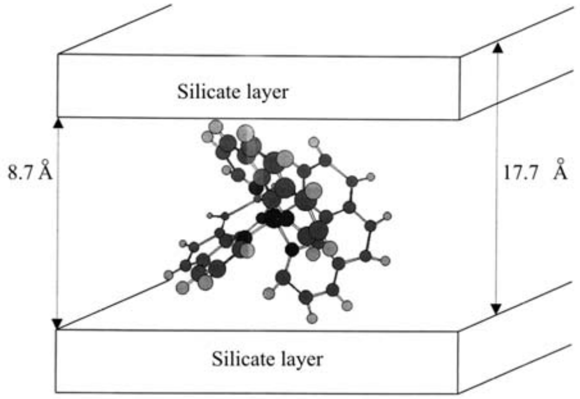

Fig. 4 3-D representation of Cu-(Phen)$_3$ complex in the interlayer space of bentonite

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