

FORMATION OF POLYMERIC SPECIES IN THE INTERLAYER OF BENTONITE

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Abstract—Infrared spectroscopic, X-ray powder diffraction, diffuse reflectance, and electron-spin resonance examination of homoionic bentonite from Sardinia treated with diazomethane indicates that polymethylene was formed in the interlayer position. Polymerization can be attributed to the acidic properties of the residual water in the interlamellar space, depending on the nature of the exchanged ion. The presence of an interlayer polymer causes the clay to assume strong hydrophobic properties.

Key Words—Bentonite, Hydrophobic, Infrared spectroscopy, Interlayer, Polymerization.

INTRODUCTION

The reaction of montmorillonite with organic compounds allowed some investigators to draw conclusions as to the structure of the mineral. Berger (1941, 1947) interpreted the reaction of H-montmorillonite with diazomethane as a methylation of hydroxyl groups of the clay. The hydrophobic properties shown by the clay after the reaction were considered to be the main evidence of this hypothesis (Aragón de la Cruz, 1965; Martin-Vivaldi and Del Pino Vazquez, 1956; Deuel, 1957). Edelman (1947) pointed out that Berger's results could be explained by the presence of some inverted silica tetrahedra, according to the Edelman-Favejee structure. However, surface hydroxyls have been excluded by diffraction data. Therefore, other investigators (Brown *et al.*, 1952; Vivaldi and Hendricks, 1952; Greenland and Russell, 1955) concluded that esterification did not take place and suggested that only polymeric species or alteration products were present in the clay after the reaction. Exhaustive methylation with diazomethane on the NH_4^+ -exchanged form of bentonite gives rise to the formation of $[\text{N}(\text{CH}_3)_4]^+$ ions (Franco *et al.*, 1978). Very different results were obtained when H-, Mg-, and Ca-bentonites were treated with diazomethane (Gessa *et al.*, 1978) suggesting the formation of organic hydrophobic species in the clay. The aim of the present work was to identify such organic structures further and to clarify the nature of the interactions between the clay surfaces and the organic matter.

MATERIALS AND METHODS

Homoionic forms of the $<2\text{-}\mu\text{m}$ fraction of bentonite from Uri, Sardinia, were prepared by treating the mineral several times with an aqueous solution of the appropriate metal chloride. Care was taken to remove

excess salt by washing with distilled water and by dialysis. H-bentonite was obtained by treating a suspension of the mineral with 1 N HCl, followed by water washing and centrifugation. The H-bentonite contained a small amount of exchangeable Al (~12% of the cation-exchange capacity) (Gessa *et al.*, 1978). The reaction with CH_2N_2 was carried out at 0°C by adding dropwise different volumes of a 0.6 N CH_2N_2 solution in ether to an ether suspension of the clay (45, 90, 180, or 340 ml of solution per gram of clay). The reaction was accompanied by a vigorous effervescence due to the release of nitrogen. Future reference to the samples will be made by indicating the exchanged ion (M) and extent of the CH_2N_2 treatment, e.g., Cu-bent(45).

The structural and chemical modifications of the mineral were studied by infrared spectroscopy (IR) and X-ray powder diffraction (XRD) as well as by diffuse reflectance (M = Cu, Ni) and electron-spin resonance spectroscopy (ESR) (M = Cu). Spectral measurements were carried out on samples dehydrated for one week at room temperature and ~40% relative humidity. X-ray diffraction basal spacings, $d(001)$, were determined with a Philips PW 1049/50 diffractometer using Ni-filtered $\text{CuK}\alpha$ radiation. The depth of the interlayer was determined by the difference of the observed $d(001)$ value and the c dimension (9.6 Å) of the montmorillonite silicate sheet (Brown, 1961; Clementz *et al.*, 1973; McBride *et al.*, 1975). X-ray powder diffraction (XRD) data were registered for treated M-clays, for treated M-clays washed with a 1 N KCl solution, and for treated M-clays after drying at 110°C. X-band ESR spectra were obtained on a Varian E-9 spectrometer, using diphenylpicrylhydrazyl (DPPH) as a standard marker. Diffuse reflectance spectra were measured on a Beckman DK 2A instrument equipped with a reflectance unit. IR spectra were recorded on a Beckman 4250 spectrophotometer using the KBr-pellet technique. Analyses of C, H, and N were obtained using a Perkin-Elmer 240 microanalyzer. Thermal analyses were carried out on a Dupont 900 apparatus equipped with a thermogravimetric analyzer at a heating rate of 10°C/min under a stream of nitrogen at 40 ml/min.

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Table 1. Analytical data.

Sample ¹	C (% wt)	H (% wt)	N (% wt)	H/C ²	C (% wt) ³	H ₂ O (% wt)
H-bent	0.37	1.74	—	—	—	8.91
H-bent(45)	5.63	2.38	—	2.02	5.59	6.85
H-bent(90)	10.14	2.72	0.77	1.87	10.10	4.42
H-bent(180)	16.88	3.65	0.70	2.04	16.81	1.51
H-bent(340)	33.56	6.25	0.89	2.01	33.47	<1
Mg-bent	0.33	2.61	—	—	—	12.43
Mg-bent(180)	6.32	2.47	0.85	2.18	6.24	7.02
K-bent	0.42	1.39	—	—	—	6.26
K-bent(180)	1.46	1.28	0.49	—	1.37	5.25
Mn-bent	0.35	2.16	—	—	—	13.47
Mn-bent(340)	6.67	2.59	0.90	2.08	6.55	7.45
Cu-bent	0.44	1.52	0.36	—	—	7.25
Cu-bent(340)	24.56	4.71	1.35	1.88	24.38	3.21

¹ Value in parentheses refer to volume in ml of CH₂N₂ solution used per g of clay.

² The atomic ratio H/C has been calculated after correction for the C and H content of the untreated clays and of the water.

³ After washing with 1 N NaCl and 1 N HCl solutions.

RESULTS

Analytical data

The analytical data of the diazomethane treated samples, listed in Table 1, show the following relationships: (1) The M-clays showed an atomic ratio of H/C = 2, quite independently of the carbon content. (2) The analytical data and H/C ratio did not change after washing the clays with 1 N NaCl, 1 N HCl, or 1 N NaCl at pH = 10 by adding NaOH solutions. (3) A decrease in water content exists with increasing carbon content. Indeed, treatment with CH₂N₂ did not change the water content of the K-exchanged samples. (4) All the treated samples contain less than 1% nitrogen independent of the carbon content. No nitrogen was detected in the bentonites after washing with acidic or alkaline solutions.

Infrared spectra

With the exception of the K-bent, the IR spectra of the treated samples [e.g., see the spectrum of H-bent(45) in Figure 1] were different from those of the untreated clays by: (1) new absorption bands at 2920 and 2850 cm⁻¹, attributable to the asymmetric and symmetric stretching vibrations of a methylene group; (2) a double band at 1470 cm⁻¹ compatible with the CH₂ scissor vibration; (3) two bands at 730 cm⁻¹ and 720 cm⁻¹ characteristic of a polymethylene chain (Nakanishi, 1962; Thompson and Torkington, 1945a, 1945b).

The intensity of the new bands increased as the carbon content increased and as the water-bending vibration bands decreased. Xylene extraction removed the previously mentioned 2920, 2850, 1470, 730, and 720 cm⁻¹ absorption bands [e.g., see the spectrum of

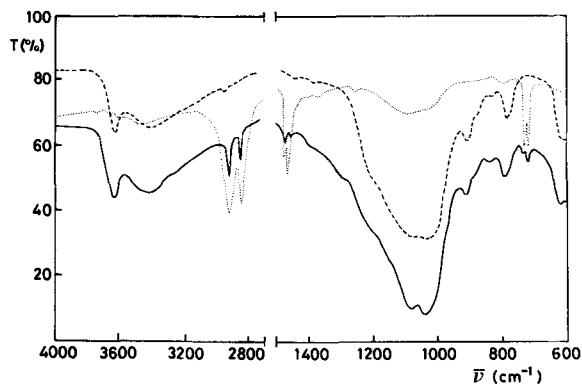


Figure 1. Infrared spectra of Uri bentonites (KBr phase) — H-bent(45); - - - H-bent(45) after extraction with xylene; extracted residue.

H-bent(45) in Figure 1]. However, these bands are in the spectrum of the yellowish-white solid obtained after evaporation of the xylene solution and are identical to those reported for a polymethylene chain formed by diazomethane on catalytic surfaces (Buckley *et al.*, 1950). The extraction of the organic species from the clays was difficult, and three days were necessary for extracting the polymer from H-bent(45). It was necessary to leave those samples characterized by a larger carbon content for longer periods of time.

X-ray powder diffraction data

XRD data of the M-bentonites, plotted in Figure 2 vs. the amounts of diazomethane used in the reaction show, with the exception of K-bentonite, a variation of all the d(001) values towards a limiting value of about 14 Å, independently of the exchanged ion. The d(001) of the other treated samples decreased if the starting value was higher than 14 Å and increased if it was lower (e.g., Cu-bent). It is meaningful to note the increase of the basal spacing in Cu-bentonites, in spite of the partial dehydration of the samples. This effect is also found for Mg-bent, which maintains the same spacing in spite of the water lost during the reaction. The d(001) values are not modified on washing the treated clays with 1 N KCl solutions, but achieve a common value of 13.4 Å on heating at 110°C and recover the ~14 Å value after a second washing with KCl solutions.

Diffuse reflectance and ESR spectra

Diffuse reflectance and ESR spectra of Cu-bentonite samples with and without diazomethane treatment show interesting differences which are related to variations of the interlayer distance. The electronic spectrum of Cu-bent (see Figure 3) shows a medium intensity band and a weak shoulder at lower frequencies in agreement with an axially elongated octahedral geometry (Hathaway and Billing, 1970). The principal band

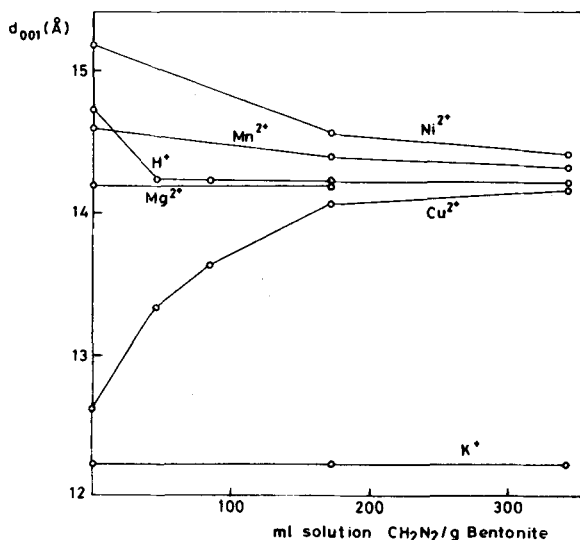


Figure 2. Variation in the $d(001)$ spacing of M-bentonites as a function of methylation with a 0.6 N CH_2N_2 solution in ether.

at 750 nm is consistent with the ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$ transition. This band shifts towards higher frequencies in the spectrum of the sample treated with CH_2N_2 . This behavior suggests an increased tetragonal distortion of the cuprate (II) ion after the reaction. Also the ESR spectrum confirms this interpretation; in fact the g -values of Cu-bent ($g_{\parallel} = 2.34$ and $g_{\perp} = 2.10$), indicating an elongated octahedral environment for the ion, are modified by the diazomethane treatment ($g_{\parallel} = 2.38$ and $g_{\perp} = 2.06$). In particular, the decrease of g_{\perp} , as it is known (Hathaway and Billing, 1970) is related with a more pronounced distortion in Cu (II) geometry in agreement with the observed diffraction data.

DISCUSSION

The stability of the $d(001)$ values of the treated M-bentonites, washed with KCl and heated at 110°C suggests that the organic species formed in the reaction are present in the interlayer space of the montmorillonite. This interpretation is substantiated by the increased $d(001)$ value of the Cu-bent after the reaction in spite of the expected collapse owing to the dehydration. The interlayered organic species also prevent the collapse of Mg-bent. The increased $d(001)$ value in Cu-bentonites agrees with the distortion in the coordination sphere of the ion shown by ESR and electronic spectra. The common limiting value in all the clays treated with diazomethane suggests that one species, identical for all the samples, determines the interlayer distance, independently of the exchanged ion. The mean value of interlayer depth ($\sim 4.7 \text{ \AA}$) is compatible with the requirements of a planar polymeric species (either branched or unbranched). IR and analytical data show

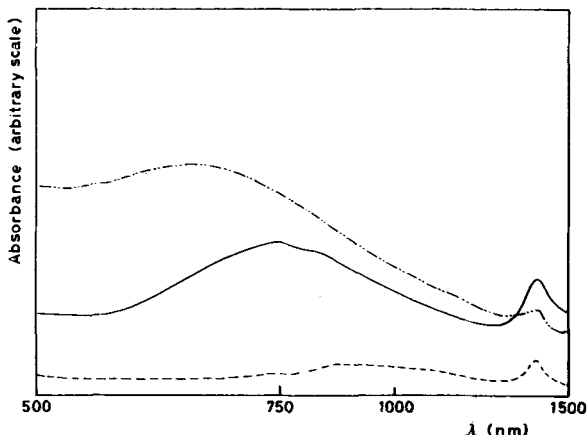


Figure 3. Diffuse reflectance spectra of Cu-bent(340) (—), H-bent (---) and Cu-bent(340) (- · - ·).

the organic species to be interlayered polymethylene chains, which cannot be easily removed from the clay. The K-bent treated with diazomethane behaves like an untreated clay. It is possible that the small C-amount ($< 2\%$ wt) is due to polymeric species deposited outside the interlayers; however, no CH_2 absorption was detected in the IR spectrum of K-bent(340).

On the basis of these results the formation of nitrogenous compounds and the complexation of the exchanged ion by diazomethane or its derivatives can be excluded. In fact, the ion is present as an aquo-ion after the reaction (as indicated for Cu-bent by spectroscopic techniques) and is exchangeable, partially with neutral solutions and almost completely with acid solution, without changes in the C-content and in the IR spectra (Gessa *et al.*, 1978). The thermogravimetric data show that only K-bent(180) is not dehydrated. It is suggested that the observed dehydration of the other samples is related to the phase separation which takes place during the reaction between the growing polymeric chains and the water, giving the bentonites a strongly hydrophobic behavior (Gessa *et al.*, 1978). It is noteworthy that protic or Lewis acids convert diazomethane to polymethylene by an ionic chain reaction (Davies *et al.*, 1963; Hammond and Williams, 1962). The strong acidity of the water of the montmorillonites, in relation to the polarizing effect of the exchanged ion, has also been reported (Mortland, 1968). Other findings in this laboratory on comparable treatments with diazomethane reveal an increase of the C-content with increased acidity of the aquo-ions, according to the scale of acidity reported by Mortland (1968). On this basis it can be concluded that the catalytic role on the polymerization reaction is due to the acidity of the exchanged aquo-ions. In this way the catalytic ineffectiveness of the K^+ ion is also explainable in terms of its low acidic properties.

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Резюме—Гомоинный бентонит из Сардинии, обработанный диазометаном, изучался с помощью инфракрасной спектроскопии, порошкового метода рентгеноструктурного анализа, рассеянного отражения и электронноспинного резонанса. Было установлено, что полиметилген формируется в межслойных промежутках. Полимеризация связана с кислотными свойствами остаточной воды в межслойном пространстве, зависящими от природы обменного иона. Присутствие межслойного полимера обуславливает сильные гидрофобные свойства глины.

Resümee—Untersuchungen mit Infrarotspektroskopie, Röntgenpulverdiffraktometrie, diffusen Reflexionsvermögen, und Elektronenspinresonanz an Bentonit von Sardinien, der nur eine Art von Kation hat und der mit Diazomethan behandelt wurde, zeigen die Bildung von Polymethylen in der Zwischenschichtposition. Die Polymerisation kann auf die sauren Eigenschaften des Restwassers im interlamellaren Zwischenraum zurückgeführt werden, die von der Art des ausgetauschten Ions abhängen. Die Anwesenheit von Zwischenschichtpolymeren ist die Ursache, daß der Ton stark hydrophobe Eigenschaften annimmt.

Résumé—L'examen à la spectroscopie infra-rouge, à la diffraction aux rayons-X, à la réflechissance diffuse, et à la résonance de spin d'électrons d'une bentonite homoionique de Sardaigne traitée au diazométhane indique que le polyméthylène a été formé dans la position intercouche. La polymérisation peut être attribuée aux propriétés acides de l'eau résiduelle dans l'espace interfeuillelet, dépendant de la nature de l'ion échangé. L'argile prend des propriétés fortement hydrophobiques à cause de la présence d'un polymère intercouche.