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AZOBENZENE INTERCALATES OF MONTMORILLONITE

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Abstract—A study has been made of the interaction of azobenzene vapor with a series of cation-exchanged montmorillonites. Cu^{2+}- and Ag^{+}-clays give basal spacings $\geqslant$ 20Å. The azobenzene retains its *trans* conformation in the clay and can be extracted with ether. If the intercalate is heated above 120°C then there is catalytic decomposition leaving a black product. Infrared spectra of an extract from this product suggests that it might be made up of a mixture of amines. A photo-electron spectroscopic study shows that the nitrogen is in two distinct chemical environments both in the initial and in the blackened intercalates. The C:N ratio remains at 6:1 throughout.

INTRODUCTION

Recently there has been considerable interest in specific reactions occurring with organic molecules absorbed on the interlamellar surfaces of certain cation-exchanged montmorillonites (e.g. Tricker *et al.*, 1975). This study, with azobenzene, was undertaken initially to explore further the potential of layered silicates as catalytic agents. Although 14 different cation-exchanged clays were studied (see Table 1), the investigation was restricted mainly to Cu^{2+}-, Ag^{+}-, and Na^{+}- exchanged montmorillonites since the first two exchangeable cations have previously shown high reactivity, e.g. with *trans*-stilbene, which is dimerized (Tennakoon, 1974) and has a formal similarity to azobenzene, and the Na^{+}-clay appears typical of the remaining, larger, group of cation-exchanged clays usually employed.

EXPERIMENTAL

The montmorillonite used in this study was supplied by Volclay of Wallasey, Cheshire and was sedimented to obtain the fraction with particle size $< 2\ \mu$m. The cation-exchange capacity of the clay was determined as 66 mequiv./100 g of air-dry clay (interlayer Na^{+} ions were diplaced by Ca^{2+} and measured using a flame photometer). Cation-exchange was effected by washing with an excess of 0.3 M solution of an appropriate salt and then, after 24 hr, repeatedly washing with deionized water until the filtrate was free of the anion of the salt used. Thin ($< 25\ \mu$m), well-oriented clay films were prepared by drying an aqueous suspension spread on a polyethylene film (Farmer and Russell, 1964). Intercalation was accomplished by introducing supported clay films into a branched tube, the other branch containing azobenzene crystals (BDH). The apparatus was evacuated (10^{-2} torr), sealed and placed in an oven for 4 days. Identical films were used for infrared (i.r.), X-ray powder diffraction and X-ray photoelectron spectroscopy (XPS). There were no special precautions to prevent oxidation of the organic in thermogravimetric analysis runs (TGA) which were recorded at a heating rate of 15 deg/min on a Stanton-Redcroft TG750 instrument.

RESULTS AND DISCUSSION

On intercalation the Cu^{2+}- and Na^{+}-montmorillonites became brown and yellow-brown, respectively, whereas the Ag^{+}-montmorillonite retained its brown-black coloration. Each of the different metal-exchanged clays, with the exception of the Cu^{2+}-exchanged samples, gave only one, quite distinct, basal spacing with azobenzene (Table 1). The intensity of the diffraction peak due to the intercalate increased as the peak due to unintercalated clay decreased, until the clay was completely intercalated. The Cu^{2+}-montmorillonite differed in that the 20.0 Å basal spacing was formed after the sharpening of a broad peak, covering a range from 14.5 to 20.0 Å, with increasing

Table 1. Basal spacings of the cation-exchanged montmorillonites and their intercalates

Cation	d_{001} (Å) Air-dry clay	d_{001} (Å) Intercalate	* Δd_{001} (Å)	Max. 001 reflection observable
Ag^{+}	12.6	22.4	12.9	009
Cu^{2+}	12.6	20.0	10.5	00,11
Mg^{2+}	15.0	15.5	6.0	005
Sr^{2+}	15.0	15.5	6.0	005
Ba^{2+}	12.5	15.5	6.0	001
Mn^{2+}	15.0	15.5	6.0	001
Co^{2+}	14.1	15.0	5.5	005
Ni^{2+}	15.0	15.0	5.5	001
Zn^{2+}	15.0	14.7	5.2	001
Cr^{3+}	13.3	14.1	4.6	001
Na^{+}	12.3	14.0	4.5	001
Li^{+}	12.5	13.1	3.6	001
NH_4^{+}	11.9	12.3	2.8	001
Fe^{3+}	12.9	11.9	2.4	001

* Difference in basal spacing between the fully collapsed clay (9.5 Å) and the intercalate basal spacing.

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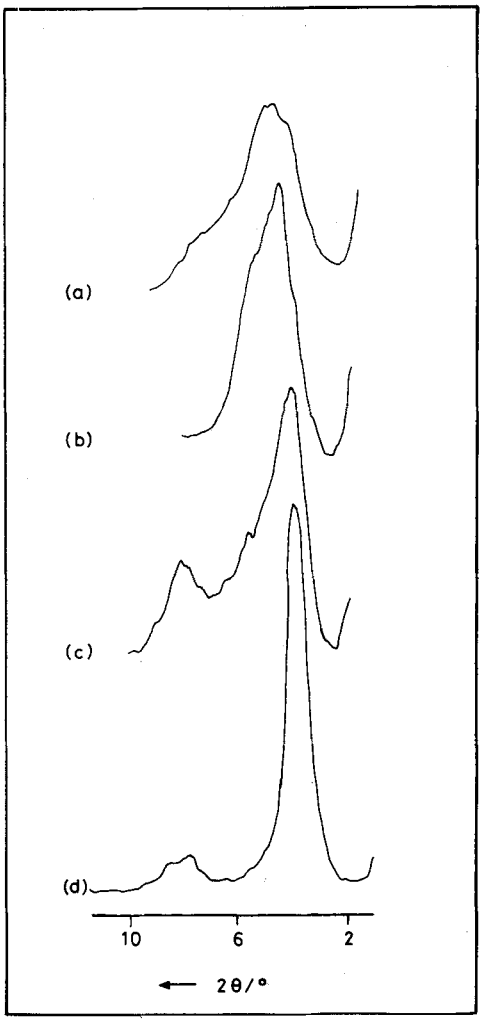


Fig. 1. X-ray powder diffraction traces of the low 2θ region for the Cu^{2+}-montmorillonite intercalate with time: (a) 1 day, (b) 2 days, (c) 3 days, (d) 4 days.

reaction time (Figure 1). This process has been examined in several samples and in each case the increase in basal spacing was smooth and continuous with no intermediate peaks. Cu^{2+}, Ag^{+}- and Na^{+}-montmorillonite:azobenzene intercalates have been left for periods of up to 4 weeks exposed to air before further X-ray examination. No decrease in basal spacings or peak broadening was observed when compared with freshly intercalated specimens; it can be concluded therefore that the intercalates are air stable and are not affected by moisture (r.h. generally $\sim$ 50%). It is interesting to see that the two cations (Cu^{2+}- and Ag^{+}-) which have been shown to confer catalytic activity to clays (Tennakoon, 1974) give very large basal spacings when intercalated. There is a large step between these two intercalates and the next group with basal spacings of around 15.5 Å. Unfortunately, one-dimensional structure analysis could not be carried out since the best resolution attainable from diffraction off thin oriented samples was of the order of 2 Å.

Infrared spectra were obtained of the parent clay and intercalates using a Pye Unicam SP1000 spectrophotometer. Comparisons of the spectra with those of the azobenzene isomers (von Kübler *et al.*, 1960) indicate that the organic molecules adopt their *trans* configuration when intercalated (the main differences being an intense peak at 1300 cm^{-1} for the *trans* conformation absent for *cis* and a peak at 1223 cm^{-1} which is much weaker for the *cis* conformation and shifted to 1259 cm^{-1}). Complete extraction of this azobenzene from between the clay sheets was effected by immersion in ether for 2 hr. Subsequent i.r. examination of the flakes showed no trace of azobenzene or indeed any organic—the ether does not penetrate into the interlamellar space in these conditions. Transmission ultraviolet spectra of the extract (in ether) showed exclusively the *trans* isomer of azobenzene (Jaffé and Orchin, 1962).

Similarities between the Cu^{2+}- and Ag^{+}-clay intercalates were apparent from thermogravimetric analysis results, with weight losses occurring in three distinct steps. The low temperature loss (< 100°C) is probably of water and azobenzene loosely bound on the surface of the clay particles. The weight change at the intermediate temperature (200–350°C) corresponds to the loss of organic species and the high temperature loss (> 550°C) to the removal of water from the hydroxyl groups of the clay structure (Mackenzie, 1957). Some problems arise when trying to assign an absolute stoichiometry since the Cu^{2+}-montmorillonite intercalate turns black and remains so even to the highest temperature and the corresponding Ag^{+}-clay intercalate remains black throughout—it is therefore somewhat misleading to equate the observed weight loss with the total amount of azobenzene in the intercalate. However, approximate stoichiometries are: (a) Cu^{2+}-exchanged sample, $Al_4Si_8O_{20}(OH)_4 \cdot (C_{12}H_{10}N_2)_{0.8}$, and (b) Ag^{+}-exchanged sample, $Al_4Si_8O_{20}(OH)_4 \cdot (C_{12}H_{10}N_2)_{0.9}$.

It was observed that if the intercalation was carried out either at about 80°C for periods exceeding 9 days, or at temperatures > 120°C for more than 5 hr, then the azobenzene catalytically decomposed and a black product was obtained for each of the three clays (Na^{+}-, Cu^{2+}- and Ag^{+}-). X-ray powder diffraction gave basal spacings of 15.5 Å for the Cu^{2+}- and Ag^{+}-clays and 14.4 Å for the Na^{+}-analogue, i.e. no reduction in the sodium case and, although the spacings are considerably reduced for the Cu^{2+}- and Ag^{+}-cases, the spacings remain appreciably greater than those found for the clays alone (12.6 Å). Since no more than six orders of diffraction could be observed, structural evaluation was not possible. Infrared spectra of the black products suggested that in all three cases a similar product was formed. When such heated intercalates were refluxed for 48 hr in redistilled pyridine an examination of the clay flakes by i.r. showed that the pyridine had entered the interlamellar space of the clay, displacing most of the azobenzene. This caused the Cu^{2+}- and Na^{+}-clays to

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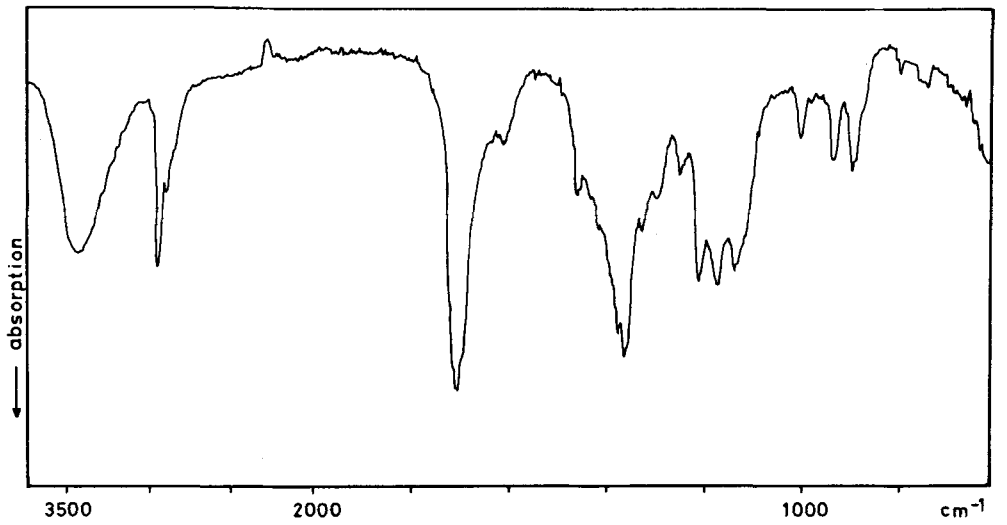


Fig. 2. Infrared spectrum of an acetone extract of the red oil extracted from the Cu^{2+}-montmorillonite:azobenzene intercalate.

lighten in color appreciably and the Ag^{+}-exchanged sample to take on a grey-green coloration. Upon filtering the pyridine solutions and removing the solvent, a deep red oil and a deep orange oil were left for the Cu^{2+}- and Ag^{+}-clay complexes, respectively. Acetone extraction of both oils (after evaporation) left a thick orange oily residue. Infrared spectra of these oils (Figure 2) suggested they might be made up of a mixture of amines.

An investigation of the extract from a Cu^{2+}-montmorillonite intercalate did not show any fragments with masses greater than that of azobenzene itself, and the major peaks (apart from those of azobenzene) were at 77 (C_6H_5) and 43 and 40, none of which indicated that any novel type of catalysis had occurred.

An XPS study of the intercalates shows that for both the heated (black) and unheated intercalates the C1*s* and N1*s* peaks are split. The double carbon signal can be assigned to one component from the organic in the clay and one component due to surface contamination of the sample. The split nitrogen, however, signifies that the nitrogen atoms are in two chemically distinct environments. Area measurements were made of the C1*s*, N1*s* and Si2*p* peaks and using procedures developed in these Laboratories (Cadman *et al.*, 1975; Adams *et al.*, 1977) stoichiometries were derived of C:N (6:1) and C:Si (2.2:1). Thus the C:N ratio is not altered upon intercalation nor upon heating to give the black product. The C:Si ratio also leads to an overall stoichiometry, for the intercalate, close to $Al_4Si_8O_{20}(OH)_4 \cdot (C_{12}H_{10}N_2)_{1.4}$ which is somewhat higher in organic than the values obtained from the TGA where, however, not all of the organic was liberated upon heating.

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