

Intercalation of Pyridine Derivatives and Complex Formation in the Interlayer Space of Cu(II)-Montmorillonite

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Intercalation of pyridine, 4-methylpyridine, and 4-ethylpyridine into the interlayer spaces of Cu(II)-montmorillonite was investigated. The successful intercalation of these compounds through coordination to the interlayer Cu^{2+} cations was confirmed by powder X-ray diffraction and infrared spectroscopy of the products. The presented solid-gas intercalation of pyridine derivatives and *in situ* complex formation in the interlayer spaces of montmorillonite is a feasible way to prepare clay coordination-intercalation compounds which cannot be obtained in conventional ion-exchange reactions.

Intercalation of organic compounds into layered silicates has attracted considerable attention from both fundamental and practical viewpoints. Among possible layered solids, the smectite group of layered clay minerals (especially montmorillonites) provides attractive features, such as large surface areas, swelling behaviour, and ion-exchange properties [1]. Clay minerals act as efficient catalysts for variety of organic reactions, they play an important role as adsorbents of hazardous organic pollutants in the soil and can be used as filters in some industrial processes [2].

Montmorillonite belongs to the group of expanding layer silicates (known as smectites), having the layers formed by two tetrahedral sheets linked with an octahedral one. Negative charge of the layers is balanced by hydrated exchangeable cations [3]. Polar organic molecules (*e.g.* pyridine derivatives) can replace the water molecules which occupy the interlayer spaces in the montmorillonite. On introducing transition metal ions and adding suitable ligands, coordination-intercalation compounds may be formed in the interlayers of montmorillonite [4, 5]. Since its surface and interlayer space are populated by Brønsted or Lewis acid sites, the principal interactions between the clay and organic compounds are those of the acid-base type [6, 7].

Many authors investigated heterocyclic compounds with pyridine ring due to their structural and biological properties and examined them as ligands in solid coordination compounds [8–10]. In this paper

diffraction and spectral analysis have been used to study the type of interactions between Cu^{2+} ions and the pyridine (py), 4-methylpyridine (4-Mepy), and 4-ethylpyridine (4-Etpy).

Diffraction analysis combined with measuring of IR spectra can provide a precious information about the character of interactions between the adsorbed pyridine and monoionic montmorillonite containing Co^{2+} and/or Ni^{2+} ions in its interlayer spaces [11, 12]. From this aspect, using these methods, we have focused our attention on the Cu^{2+} -exchanged montmorillonite with the aim to investigate whether the intercalation of pyridine derivatives into layered structure of Cu^{2+} -montmorillonite takes place.

EXPERIMENTAL

The analytical methods used have been described elsewhere [13]. The X-ray diffraction profiles for pressed powder samples were recorded on a Philips PW 1050 diffractometer at 2° (2θ) min^{-1} using $\text{CuK}\alpha$ radiation. The thermal properties were studied with a TA Instrument SDT 2960. The measurements were carried out in air using a platinum crucible. A sample mass of 20–25 mg and heating rate $10^\circ\text{C min}^{-1}$ were used in particular thermal decomposition. The infrared absorption spectra were recorded with Nicolet Magna 750 Fourier Transform IR spectrometer in the range of $400\text{--}4000\text{ cm}^{-1}$ in KBr tablets.

Less than 2 μm fraction of Jelšovský Potok ben-

tonite was separated from a bulk sample and converted into the monoionic Ca-form using standard methods [13]. The structural formula as calculated from the chemical analysis of the fine fraction is $\text{Ca}_{0.48}(\text{Si}_{7.59}\text{Al}_{0.41})(\text{Al}_{3.06}\text{Fe}_{0.34}\text{Mg}_{0.63})(\text{OH})_4\text{O}_{20}$.

The Cu^{2+} -exchanged montmorillonite (Cu-MMT) was prepared from the Ca-form (3 g) by the addition of a CuCl_2 solution (450 cm^3 , $c = 1 \text{ mol dm}^{-3}$) and the mixture was stirred shortly and left to stand for 24 h. After decantation CuCl_2 solution was added again to the solid phase, stirred and left to stand as previously. This procedure was repeated four times. The solid product was then washed by water in order to remove the Cl^- anions and finally dried at 60°C .

A thin layer ($\approx 250 \text{ mg}$) of monoionic forms was exposed to pyridine, 4-methylpyridine, and 4-ethylpyridine vapours for 72 h at room temperature. Intercalation products py/Cu-MMT, 4-Mepy/Cu-MMT, and 4-Etpy/Cu-MMT were obtained.

RESULTS AND DISCUSSION

As a result of the solid-gas reactions with pyridine bases, the colour of montmorillonite changed as summarized together with diffraction data in Table 1.

The X-ray diffraction patterns of studied samples are shown in Fig. 1. After the heterogeneous reactions the basal spacing increased to *ca.* 1.5 nm irrespective of the used pyridine base. Since the basal spacings are close for all studied products, the arrangement of pyridine rings of the pyridine derivatives in the interlayer space is similar. The increase of the basal spacing may be partly due to the hydration of montmorillonite. In order to exclude this possibility, the products were heated at 60°C . It was observed that basal spacing of all products did not change during the heat treatment. From these observations we concluded that the observed increase in the basal spacing was due to the intercalation of pyridine derivatives into the interlayer spaces of montmorillonite [4, 5].

The change in the colour as a result of the solid-gas reactions (Table 1) suggests the change in the coordination states of the interlayer Cu^{2+} cations of the montmorillonite which were surrounded by water molecules at ambient conditions, the increase in the basal spacings was caused by the intercalation of pyridine bases through their ligand displacement reactions with H_2O molecules.

TG curves of Cu-MMT and intercalation products are shown in Fig. 2. The thermal decomposition of Cu-MMT proceeds under dynamic conditions in two distinct steps. The first step can be assigned to the release of adsorbed water molecules while the second one is connected with a release of water molecules from hydroxide groups. The py/Cu-MMT exhibits three desorption peaks. In accordance with Breen [14] the first and second peaks correspond to the release of physisorbed and chemically bonded py, while the third

Table 1. Colour and Representative Diffraction Data of Cu^{2+} -Montmorillonite and Intercalation Products

Sample	Colour	$2\theta/^\circ$	d_{001}/nm
Cu-MMT	Pale blue	7.14	1.237
py/Cu-MMT	Blue	5.85	1.509
4-Mepy/Cu-MMT	Blue	5.96	1.482
4-Etpy/Cu-MMT	Blue	5.95	1.484

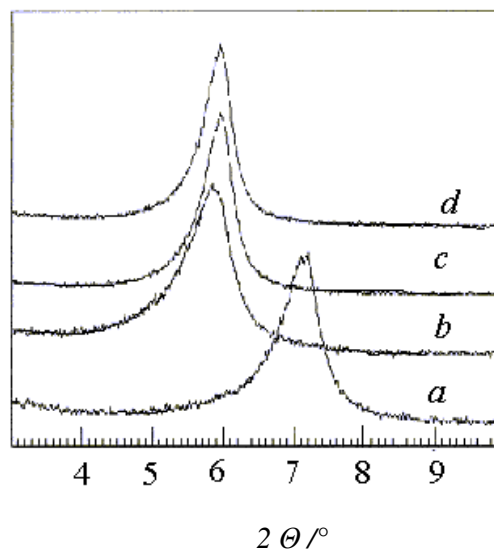


Fig. 1. Powder X-ray diffraction pattern of studied samples: a) Cu-MMT, b) py/Cu-MMT, c) 4-Mepy/Cu-MMT, d) 4-Etpy/Cu-MMT.

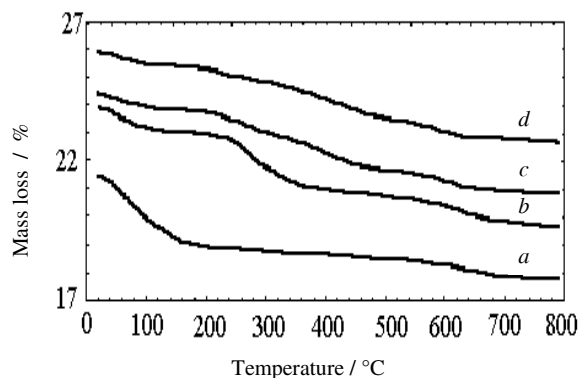


Fig. 2. TG curves of studied samples: a) Cu-MMT, b) py/Cu-MMT, c) 4-Mepy/Cu-MMT, d) 4-Etpy/Cu-MMT.

one may be assigned to lattice dehydroxylation. In the case of 4-Mepy and 4-Etpy/Cu-MMT the release of chemically bonded pyridine derivatives proceeds in the temperature interval $\approx 220\text{--}500^\circ\text{C}$ in two steps (Fig. 2). The type of intercalation between Cu^{2+} ions and pyridine derivatives was studied by means of infrared spectra.

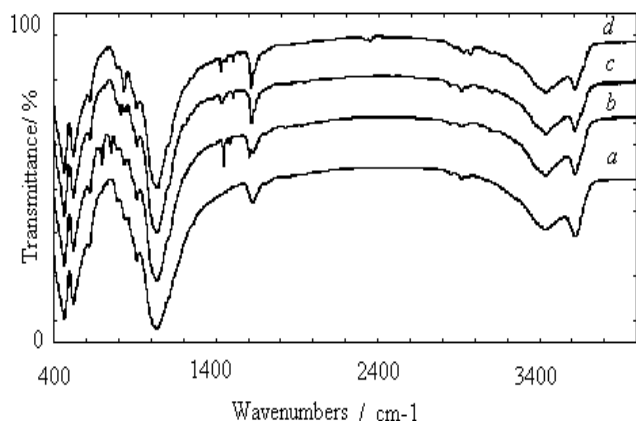


Fig. 3. Infrared spectra of studied samples: a) Cu-MMT, b) py/Cu-MMT, c) 4-Mepy/Cu-MMT, d) 4-Etpy/Cu-MMT.

The IR spectra of the studied samples are presented in Fig. 3. In the studied region ($400\text{--}4000\text{ cm}^{-1}$) several peaks can be observed that were attributed to the stretching vibrations of OH groups ($3622\text{--}3629\text{ cm}^{-1}$) and water ($3446\text{--}3448\text{ cm}^{-1}$), stretching vibrations of Si—O groups ($1024\text{--}1043\text{ cm}^{-1}$), deformation vibrations of OH groups ($800\text{--}950\text{ cm}^{-1}$): AlAlOH at $916\text{--}918\text{ cm}^{-1}$, AlMgOH at $839\text{--}845\text{ cm}^{-1}$, deformation vibrations of Al—O—Si groups at 523 cm^{-1} and Si—O—Si at $467\text{--}469\text{ cm}^{-1}$ [15]. The significant difference between Cu-MMT and the intercalated products can be observed first of all in the region $1450\text{--}1750\text{ cm}^{-1}$. Whereas Cu-MMT shows only one peak at 1635 cm^{-1} assigned to the deformation vibration of H—O—H groups, the intercalation species exhibit in this region two peaks at $1608\text{--}1624\text{ cm}^{-1}$ and $1635\text{--}1647\text{ cm}^{-1}$ (pure py exhibits in the studied region the peak at 1583 cm^{-1} and 4-Rpy at about 1604 cm^{-1} [16]). It is known [17–19] that these peaks of pure ligands shift to the higher frequencies upon complex formation. The shift of these peaks to about 1608 cm^{-1} (py) and $1624\text{--}1627\text{ cm}^{-1}$ (4-Rpy) may support the conclusion about the formation of the coordination bond between Cu^{2+} central atom and the nitrogen atom of heterocyclic ring in these samples. This assertion is also supported by the presence of the diagnostic Lewis peak at $\approx 1435\text{--}1450\text{ cm}^{-1}$.

The infrared spectra of studied samples are similar and therefore we assume that the differences in stoichiometry of thermal decomposition are not connected with different type of bond of pyridine derivatives [7].

In conclusion we can state that X-ray powder diffraction and spectral data showed that pyridine, 4-methyl-, and 4-ethylpyridine were successfully intercalated into the interlayer spaces of copper (II)-montmorillonite and were coordinated to Cu^{2+} ions. The solid-gas intercalation and the complex formation in the silicate interlayers is a specific synthetic way to the preparation of clay coordination-intercalation compounds which cannot be obtained by conventional ion-exchange methods in solutions.

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