

Thermal Properties of Cu²⁺-Montmorillonite After Interaction with Aromatic Compounds

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Abstract: In this article has been study an influence of Cu²⁺-montmorillonite to accept various organic compounds based on benzene ring with -OH group and -NH₂ group (benzene, phenol, aniline). These organic compounds are mainly used in industry as by-product, but on the other hand, there are used in pharmacy, too. Preparation of samples was different because state of organic compound was different, too. Prepared samples had been investigated by X-ray powder diffraction, infrared spectra and by thermal analysis (thermogravimetry and derivate thermogravimetry). Results show some differences which could be assigned to different type of interaction of organic molecule and also their volume and their arranging in structure of montmorillonite. These results confirm that Cu²⁺-montmorillonite (MMT) is able to accept these compounds.

Keywords: aniline, benzene, instrumental analytic methods, montmorillonite, phenol

I. INTRODUCTION

Montmorillonite (MMT) is chemically (Na, Ca)_x(Al)₂(Si₄O₁₀)(OH)₂ · n H₂O [1]. After the adsorption of organic molecules, interlayer space of montmorillonite can change from hydrophilic to hydrophobic and the resulting materials also known as organoclays, has been used as efficient adsorbens for hydrophobic organic contaminants [2]. Clay and organically modified clays are considered as a widely used mineral as a raw material as well as their uses in other different industrial applications. Montmorillonite mineral is the major constituent of bentonite clay.

Intercalation of organic cations into the interlayer space of montmorillonite is considered as a route to modify such clay with organic compounds. This will lead to structural changes of the clay as well as the surface chemistry from hydrophilic to organophilic. The quantity and type of acid sites on the respective organoclay can be determined from the study of thermal decomposition of the bases intercalated into interlayer space of the clay [3].

Organo-montmorillonites are montmorillonites that have been modified with organic pollutants as components in the synthesis of clay-based polymer nanocomposites and as precursors in the preparation of mesoporous materials [4]. Clay minerals with a negative charge are neutralized by inorganic exchange cations such as Na⁺ or Cu²⁺ [5]. Polar organic molecules, as phenol can replace the water which normally occupies the interlayer space of montmorillonite [6]. The adsorption of specific organic contaminants by high valence metal cation-saturated montmorillonite was found to be obviously improved because of stronger H-bonding between more polar water molecule associated with high valence metal cations than low valence cations and polar organic compounds [7].

For investigation of prepared samples, XRD diffraction, IR study and thermal analysis which are very important for characterization [6].

II. EXPERIMENTAL

1. Preparation of material

The monoionic form of montmorillonite (Cu²⁺-MMT) was prepared from Ca²⁺-montmorillonite in the following way: The stock of CuCl₂ solution with concentration $c = 1 \text{ mol.dm}^{-3}$ and water were added to Ca²⁺-MMT and this suspension was mixed for five hours every day during five days (the mixing process was repeated after 24 hour). After sedimentation, solution of CuCl₂ and water was poured and then, the same solution of CuCl₂ and water were added to the suspension again. This mentioned process was repeated five times.

Finally, Cu²⁺-MMT was washed by water until Cl⁻ was eliminated completely. A presence of Cl⁻ was investigated by solution of 2% AgNO₃. After this process, Cu²⁺-MMT was dried by heating at 60°C.

After drying, this sample was crushed to a powder and prepared for pre-determined analysis.



Fig. 1: Preparation of Cu^{2+} -montmorillonite.

2. Synthesis of samples

Benzene (B = 0.18 ml) and phenol (P = 8.4 g) were added separately to 1 g of Cu^{2+} -MMT (for each one organic compounds) and this solution were mixed with 100 ml of distilled water. Solutions were mixed until MMT was completely solvated and when the reaction was ended. It was indicated by changed of colour of original and mixing solution. When the samples were sedimented then were removed and the water from solution was evaporated. Aniline (A = 5 ml) in its clear liquid state was poured into small beaker and then it was placed into desiccator to preserve the vacuum. Cu^{2+} -MMT (the weight of MMT was 1g) was also added into the same desiccator in its powder form. The beaker with aniline solution was in the centre and Cu^{2+} -MMT were around the aniline while all these three MMT form were placed separately in Petri bowls during 21 days.

Merck Millipore provided benzene and aniline which were in a liquid form and phenol in the form of powder and these organic compounds were used for interaction with Cu^{2+} -MMT.

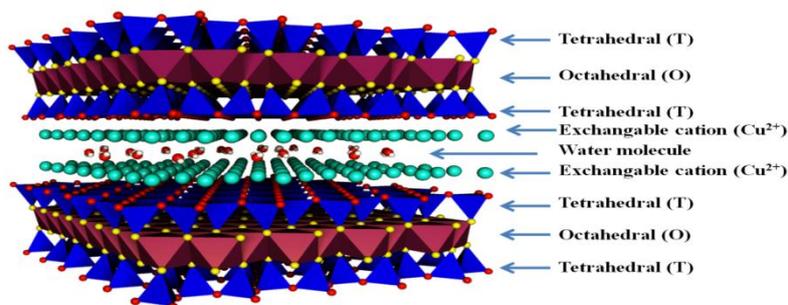


Fig. 2: Structure of MMT.

3. Analytical methods and equipments

Diffractometer Bruker D8 Discover was used for X-ray powder diffraction, using:

- $\text{CuK}\alpha$, range = 3 – 30 2θ ,
- power = 12 kW,
- heating rate = 0.05 degree
- time of measurement = 1 sec.

Using Nicolet 5700 FTIR, ATR method (Attenuated Total Reflectance) and KBr pellet method were used for analysis of IR spectra and Derivatograph Q-1500 D with digital output, heating rate $10^\circ\text{C}\cdot\text{min}^{-1}$ and weight 0.1 g was used for thermal analysis.

III. RESULTS AND DISCUSSION

Probably, based on different size of molecules of organic compounds, the results are more different in all area of measurement. Studied samples were measuring by X-ray powder diffraction, infrared spectra and finally by thermal analysis.

Phenol is a weak acid. When adsorbed by montmorillonite, phenols reveal their amphiprotic nature. They may donate or accept protons [8].

1. Diffraction properties of studied samples

After interaction of Cu^{2+} -MMT with organic compounds were changed an basal spacing.

Figure 3 show that at Cu^{2+} -MMT + B (red curve) basal spacing increased about 0.23 nm, at Cu^{2+} -MMT + P (blue curve) about 0.28 nm and at Cu^{2+} -MMT + A (green curve) basal spacing increased about 0.26 nm. The observed changes were based on different values of interlayer distance and different colour indicate, that organic compounds with benzene ring, like benzene, phenol and aniline were successfully intercalated into interlayer space of Cu^{2+} -MMT.

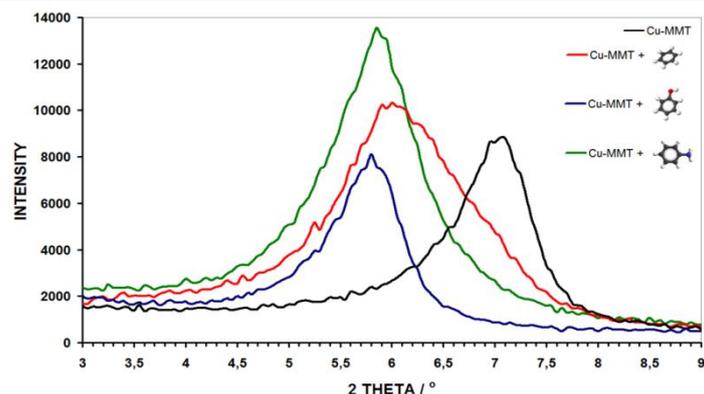


Figure 3. XRD diffraction peaks of studied samples with Cu^{2+} -montmorillonite. Prepared samples changed colour and also interlayer distances. These changes are summarized in Table 1.

Tab. 1: Diffraction data and colour changes of studies samples from X-ray powder diffraction.

| Sample | $2\theta / ^\circ$ | d_{001} / nm | $\Delta d_{001} / \text{nm}$ | colour |
|---------------------------|--------------------|-----------------------|------------------------------|-------------|
| Cu^{2+} -MMT | 7.1 | 1.25 | - | turquoise |
| Cu^{2+} -MMT + B | 6.0 | 1.48 | ↑ 0.23 | light-green |
| Cu^{2+} -MMT + P | 5.8 | 1.53 | ↑ 0.28 | gold |
| Cu^{2+} -MMT + A | 5.85 | 1.51 | ↑ 0.26 | green-black |

2. Spectral (IR) properties of studied samples

Spectral data of Cu^{2+} -MMT and Cu^{2+} -MMT with organic compounds shows some characterization peaks which could be assigned at specific group. Based on literature [9] we can divide these peaks and their vibration to three groups - asymmetric, valence and deformation. Infrared spectra of Cu^{2+} -MMT with benzene, phenol and aniline are shown in Fig. 2 and spectral data of these samples are presented in table II.

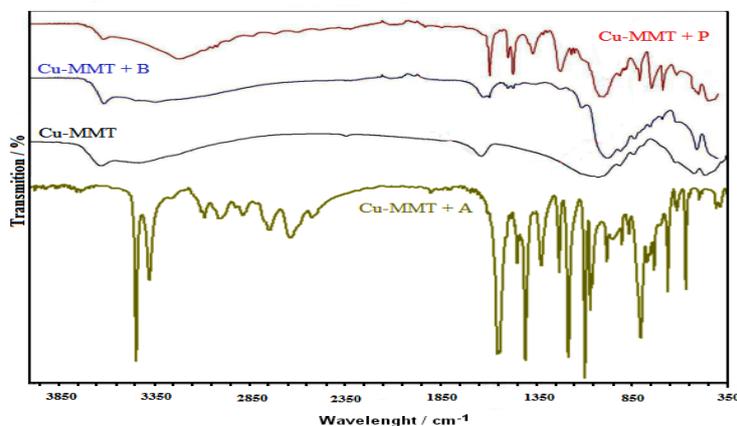
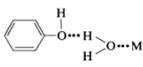
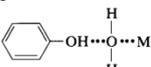
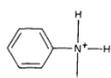
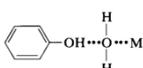
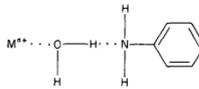
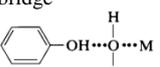


Fig. 4: Infrared spectra of studied samples with Cu^{2+} -MMT.

Table 2 shows concrete vibrations of some groups, typical for each one sample and its observed frequencies. At Cu^{2+} -MMT + B are frequencies in range $1500 - 1450 \text{ cm}^{-1}$ which could be assigned to asymmetric vibration of benzene ring, at Cu^{2+} -MMT + P are more frequencies, indicated that phenol was intercalated into interlayer space of Cu^{2+} -MMT. There are frequencies $1595, 1498$ and 1473 cm^{-1} which could be assigned to asymmetric vibration of skeleton of aromatic ring, or at 1228 cm^{-1} (valence vibration of C - O) and 1151 cm^{-1} (deformation vibration of C - OH). Sample of Cu^{2+} -MMT + A shows mainly typical vibration of NH^+ , valence or deformation (2962 cm^{-1} and 3361 cm^{-1}) and valence vibration of C - N (1259 cm^{-1}).

Tab. 2: Spectral data of studied samples.

| Sample | Wavelength [cm ⁻¹] | Adsorption mechanism | Type of vibration | | |
|------------|--------------------------------|--|---------------------------|-----------------|-----------------|
| | | | asymmetric | valence | deformation |
| Cu-MMT | 3612 | none | none | H – O – H | none |
| | 1631 | | | none | H – O – H |
| | 1024 | | | Si – O | none |
| | 910 | | | none | Al – Al – OH |
| | 835 | | | | Al – Fe – OH |
| 515 | Si – O – Al | | | | |
| Cu-MMT + B | 1500 – 1450 | | benzene ring | | |
| Cu-MMT + P | 1595 1498 1473 | Indirect coordination by H-bond with the molecule of H ₂ O by accepting a proton from acidic species  | skeleton of aromatic ring | none | none |
| | 1151 1228 | Indirect coordination through H ₂ O bridge  | none | C – O | |
| | | none | | | C – OH |
| Cu-MMT + A | 2962 | Protonation  | none | NH ⁺ | none |
| | 3361 | Indirect coordination through water bridge  | | N – H | |
| | 1521 | Protonation  | | none | NH ⁺ |
| | 1259 | Indirect coordination through water bridge  | | C – N | none |

3. Thermal properties of studied samples

TG and DTG curves of Cu²⁺-MMT and Cu²⁺-MMT with benzene, phenol and aniline are presented at Fig. 4. and steps of some processes are summarized in Table III.

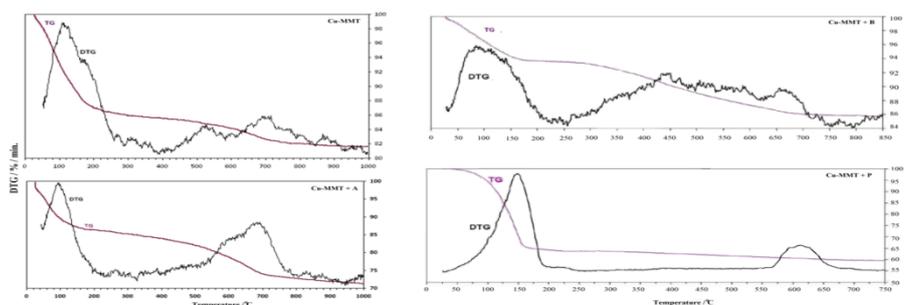


Fig. 4: TG and DTG curves of Cu²⁺-MMT with benzene, phenol and aniline.

Tab. 3: Thermal properties of studied samples.

| Sample | Step / TG: m% | | | | Step/ DTG: Tp / °C | | | |
|-----------------------|---------------|-----|------|-----|--------------------|-----|------|-----|
| | I. | II. | III. | IV. | I. | II. | III. | IV. |
| Cu ²⁺ -MMT | 8 | - | 7 | 3.5 | 105 | - | 510 | 705 |

| | | | | | | | | |
|---------------------------|----|---|----|---|-----|-----|-----|-----|
| Cu ²⁺ -MMT + B | 6 | - | 7 | 1 | 96 | - | 440 | 670 |
| Cu ²⁺ -MMT + P | 36 | 2 | - | 2 | 160 | 225 | - | 675 |
| Cu ²⁺ -MMT + A | 10 | - | 11 | 5 | 100 | - | 600 | 690 |

First peak at Cu²⁺-MMT + B decreased and other peaks increased in relative to Cu²⁺-MMT. These changes indicate that in first step (96°C) has evaporated water and benzene molecule simultaneously and at third step (440°C) and at fourth step (670°C) is possible that has evaporated only benzene and last step is assigned to dehydroxylation.

The curve of thermal decomposition of Cu²⁺-MMT + P is different completely, because it is visible only one big peak, but the curve is slowly decreased and exhibit three steps (160, 225 and 675°C. Peaks at 160°C could be assigned to evaporating of phenol, which could be:

- a) bound H⁺ and H₂O into interlayer space of Cu²⁺-MMT and created hydrogen bonds with water molecule or,
- b) added H⁺ and created hydrogen bonds with water molecules into interlayer space of Cu²⁺-MMT.

Peaks at 225°C shows thermal decomposition of adsorbed phenol which could be direct coordinated to exchangeable cations of interlayer space [8].

Thermal decomposition of Cu²⁺-MMT+ A going on in three steps (100, 600 and 690°C) divided into two visible peaks. First step shows evaporating of water and adsorbed aniline at surface of Cu²⁺-MMT while second and third steps shows evaporating of direct coordinated aniline into interlayer space of Cu²⁺-MMT.

IV. CONCLUSION

The obtained results from X-ray powder diffraction, infrared spectroscopy and thermal analysis confirmed that toxic aromatic organic compounds (benzene, phenol and aniline) are successfully intercalated into interlayer space of Cu²⁺-MMT.

X-ray powder diffraction confirmed positive differences of interlayer space of organo-montmorillonite. This change shows that organic compounds are intercalated into interlayer space of montmorillonite.

Spectra study of prepared samples shows some new peaks which could be assigned just for competed group of organic compound.

Thermal analysis confirmed statement that benzene, phenol and aniline are intercalated into interlayer space of montmorillonite. This fact is based by thermal curves.

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