

Thermal, spectral, and diffraction properties of Co-exchanged montmorillonite with 2-, 3-, and 4-hydroxyphenol

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Abstract The influence of the 2-, 3-, and 4-OH phenols on the type of interaction with Co-exchanged montmorillonite and thermal properties of these materials were studied. The results of XRD, IR, and thermal (TG, DTG) analysis show that organic species are intercalated into the interlayer space of montmorillonite. Thermal decomposition in the temperature interval 20–700 °C of studied samples with 2- and 3-hydroxyphenol proceeds in three steps (the release of adsorbed H₂O molecules, combustion/desorption of protonated hydroxy phenols and dehydroxylation), while the sample with 4-hydroxyphenol decompose in four steps (the new peak at ~222 °C corresponds to directly coordinated organic species). The effect of different position of the hydroxyl groups on the phenol ring on the thermal decomposition is evident.

Keywords Co-exchanged montmorillonite · 2-, 3-, and 4-hydroxyphenols · TG · DTG · IR-spectroscopy · X-ray diffraction

Introduction

During the last 60 years much study of the interactions between clays and organic pollutants (especially phenol derivatives) was carried out with the purpose of determining the structures and thermal stability of the organo-clay complexes [1–4]. The clay surface and its interlayer space are populated by Brönsted and Lewis acidic and basic sites. The main interactions between the clay and the adsorbed organic species are of the acid–base type [1, 5]. In the interlayer space of montmorillonite adsorbed water molecules which are coordinated to exchangeable metallic cations serve as proton donors (Brönsted acid). The organic base may be protonated by accepting a proton from a water molecule, thus gaining a positive charge. The exchangeable cations may also serve as Lewis acids and adsorbed organic species become coordinated directly to the cations (organic base may as well form a hydrogen bond with a polar water molecule).

Phenol and substituted phenols are important chemicals in the manufacture of synthetic resins, pharmaceutical, dyes, and agrochemicals. Their toxicity is high and they may accumulate in the environment [6]. This study is part of a global research on the adsorption of different organic substances by clay minerals [7–9]. The purpose of the present investigation was to study the adsorption of 2-, 3-, and 4-hydroxyphenols by Co-exchanged montmorillonite.

One of the characteristic features of montmorillonite is its layered structure. The layers are formed by two tetrahedral sheets linked with an octahedral sheet. Isomorphous substitution in the octahedron (or tetrahedron) generates a negative

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charge on the layers, which is balanced by hydrated exchangeable cations in the interlayer (mostly Na^+ , Ca^{2+} , but also Co^{2+}). Polar organic molecules, as phenol and phenol derivatives can replace the water which normally occupies the interlayer spaces in the montmorillonite.

Thermal, X-ray, and spectral analyses are very useful methods for materials characterization. Therefore, many authors have applied these techniques for various materials characterization [10–30]. In this paper, thermal analysis (TG, DTG), IR-spectra, and the X-ray diffraction studies have been used to study the effect of different phenol derivatives (2-, 3-, and 4-hydroxyphenols) on the type of interactions with Co-exchanged montmorillonite (Co-MMT) and thermal decomposition of prepared samples.

Experimental

Syntheses of the samples

Less than 2 μm fraction of bentonite from Jelšový Potok (bentonite deposit in the central part of Slovakia) was separated from a bulk sample and converted into the monoionic Ca-form using standard method [2]. The crystallochemical formula of Ca-MMT is as follows: $\text{Ca}_{0.48}(\text{Si}_{7.59}\text{Al}_{0.41})(\text{Al}_{3.06}\text{Fe}_{0.34}\text{Mg}_{0.63})(\text{OH})_4\text{O}_{20}$.

The monoionic form of Co-MMT was prepared from the Ca-MMT in a way that 450 cm^3 of a CoCl_2 solution ($c = 1 \text{ mol dm}^{-3}$) were added to 3 g Ca-MMT, the mixture was stirred for a short time and left to stand for 24 h. After decantation CoCl_2 solution was added again to the solid phase, stirred and left to stand as before. This procedure was repeated four times. The solid product was then washed by water to remove the Cl^- anions and finally dried at 60 °C. The monoionic form Co-MMT was added to the water solution of pyrocatechol (2-hydroxyphenol); resorcinol (3-hydroxyphenol) and hydroquinone (4-hydroxyphenol) and their mixtures were stirred for a 48 h at pH 6.

Analytical methods and equipments

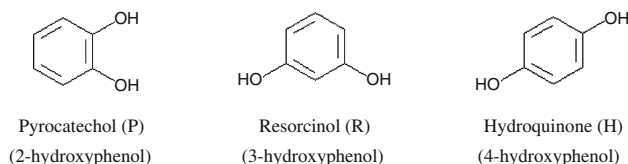
The analytical methods used have been described elsewhere [2]. The thermal properties (TG, DTG) were studied on a Derivatograph MOM 1500. The measurements were carried out in nitrogen atmosphere using platinum crucible. A sample mass of 20–25 mg and heating rate 10 °C min^{-1} were used.

The infrared absorption spectra were recorded with Nicolet Magna 750 Fourier transform IR spectrometer in the range of 400–4,000 cm^{-1} .

The X-ray diffraction patterns for pressed powder samples were recorded on a Philips PW 1050 diffractometer using CuK_α radiation.

Results and discussion

As reported previously [31], thermal analysis (TG, DTG) combined with measurement of IR spectra and diffraction properties can provide a precious information about the character of bonds between the adsorbed phenol and monoionic forms of montmorillonite. In this paper, we directed the attention on the hydroxy-derivatives of phenol:



Diffraction and spectral properties of studied samples

The interlayer distances from the X-ray diffraction patterns and color of studied samples are summarized in Table 1. After the interactions with phenol derivatives, the basal spacing increased from 1.48733 to 1.57996 nm.

Since the basal spaces are close for all studied products, we suppose that the arrangement of phenol derivatives in the interlayer space is similar. The observed changes indicated that the hydroxy-phenols are intercalated into the interlayer spaces of montmorillonite [2, 7].

The decrease of basal spacing is partly due to the different hydration of montmorillonite. In order to exclude this possibility, the products were heated at 60 °C. It was observed that basal spaces of all products did not change during the heat treatment. From these observations, we have concluded that the observed increase of the basal space was due to the intercalation of the hydroxy-phenols into the interlayer space of montmorillonite [31].

The changes in color of studied samples suggest the changes in the coordination sphere of the interlayer Co^{2+} cations. Since these cations were surrounded by water molecules at ambient conditions, the increase in the basal spaces may be due to the intercalation of the phenol derivatives into the interlayer spaces of montmorillonite.

The various ways in which hydroxy-phenols form bonds in the interlayer space of the Co-MMT can be studied by means of IR-spectra of the prepared samples. For Co-MMT in the studied region (400–4,000 cm^{-1}) several peaks can be observed that were attributed to the stretching vibration of OH-groups ($\sim 3,428$ – $3,624 \text{ cm}^{-1}$) and water (3,429–3,423 cm^{-1}), stretching vibration of Si–O groups (1,030–1,040 cm^{-1}), deformation vibrations of OH-groups (912–787 cm^{-1}), AlAlOH at 912–908 cm^{-1} , AlMgOH at 841–839 cm^{-1} , deformation vibrations of Al–O–Si groups at 518–515 cm^{-1} , and Si–O–Si 462–439 cm^{-1} [7–9].

Table 1 Representative diffraction data and color of Co-MMT and adsorption products

Sample	d_{001}/nm	$2\theta/^\circ$	Color
Co-MMT(I)	1.48733	5.95	Rose
Co-MMT + P(II)	1.56603	5.65	Black
Co-MMT + R(III)	1.57996	5.60	Black
Co-MMT + H(IV)	1.52566	5.8	Black

MMT montmorillonite, P pyrocatechol, R resorcinol, H hydroquinone

Significant difference between pure Co-MMT and the sample with hydroxy-phenols can be observed first of all in the region $\sim 1,639\text{--}1,200\text{ cm}^{-1}$ [1] (Table 2.). Whereas Co-MMT shows only one peak at $\sim 1,629\text{ cm}^{-1}$, assigned to the deformation vibration of H–O–H groups, the intercalated species exhibit in this region characteristic peaks at 1602–1639, 1487–1514, 1467–1469, 1342–1377, and 1186–1,216 cm^{-1} . It is known that the peaks of pure phenol derivatives at 1,597–1,608 cm^{-1} and 1,469–1,491 (ring stretching) shift to higher and lower frequencies when accept a proton from the acid species (water molecules serve as proton donors, Brönsted acid). The shift of these peaks in the studied samples (Table 2) supports the assumption that phenol derivatives form a hydrogen bond with the water molecules and exist in the protonated form. The band at 1,639 cm^{-1} in sample Co-MMT + H(IV), however, indicated the possibility of formation of the additional interactions (adsorbed phenol derivatives may be also co-ordinated directly to the Co^{2+} cations or may form a hydrogen bond with the polar water molecules [1]).

Thermal properties of studied samples

Thermal analysis results are summarized in Table 3 and the typical DTG curves of Co-MMT + P(II), Co-MMT + R(III), and Co-MMT + H(IV) are shown in Fig. 1. The thermal decomposition of Co-MMT(I) proceeds under dynamic conditions in the temperature interval 20–700 °C in two distinct steps. The first step can be assigned to the release of water molecules (adsorbed and coordinated) with maximum on the DTG curve at 104 °C (Table 3) while the second step is connected with a release of water molecules from hydroxide group with maximum on the DTG curve at 678 °C (the dehydroxylation of MMT).

The samples Co-MMT + P(II) and Co-MMT + R(III) exhibit three desorption peaks on the DTG curves with maxima in the region $\sim 92\text{--}99, 410\text{--}424,$ and $643\text{--}648\text{ }^\circ\text{C}$, respectively (Table 3). In accordance with [3], the first peak corresponds to the release of physisorbed H_2O molecules, and phenol derivatives, the second peak corresponds to the combustion/desorption of the protonated phenol derivatives while the third one is assigned to the dehydroxylation of MMT. The sample Co-MMT + H(IV) exhibit for peaks on the DTG curve (Fig. 1) with maxima at $\sim 92, 222, 431,$ and $662\text{ }^\circ\text{C}$. The second peak at $\sim 222\text{ }^\circ\text{C}$, which is absent in samples II and III is assigned to the directly coordinated hydroquinone to the Co^{2+} cation. After thermal dehydration the exchangeable cations namely may serve as Lewis acids and adsorbed species become coordinated directly to the cation [1].

The results suggest that the position of OH-groups on the benzene ring influences the type of interactions in the silicate

Table 2 Characteristic features of infrared spectra (in cm^{-1}) in the region $\sim 1,200\text{--}1,630\text{ cm}^{-1}$ of studied samples

Vibration type	P	Co-MMT + P(II)	R	Co-MMT + R(III)	H	Co-MMT + H(IV)
Ring stretching	1,597	1,602	1,606	1,608	1,608	1,639
	1,514	1,512	1,491	1,487	1,514	1,514
	1,469	1,467	/	/	1,469	1,469
OH deformation	1,361	1,342	1,375	1,377	1,325	1,350
CO stretching	1,236	1,213	1,145	1,216	1,190	1,192

Table 3 Thermal analysis results of studied samples

Sample	TG: $\Delta m/\%$				DTG: $T_p/^\circ\text{C}$			
	I	II	III	IV	I	II	III	IV
Co-MMT	8.00	x	x	1.14	104.00	x	x	678.00
Co-MMT + P 6 g/L	6.20	x	15.56	4.77	92.60	x	443.00	643.00
Co-MMT + R 6 g/L	12.34	x	23.51	8.49	99.40	x	418.70	647.30
Co-MMT + H 6 g/L	7.17	20.44	13.86	7.57	92.00	222.00	431.00	661.00

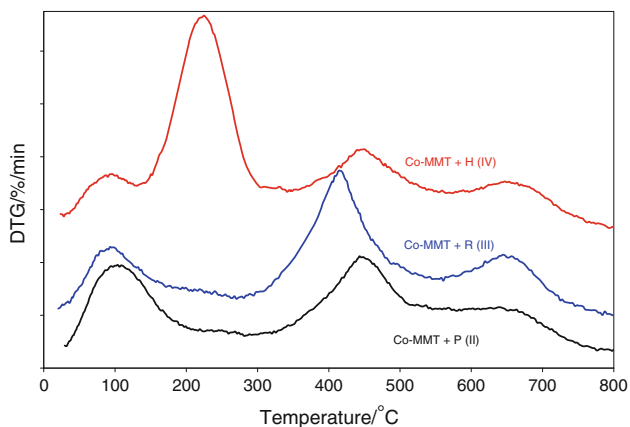


Fig. 1 DTG curves of prepared samples (Co-MMT + P, R, H 6 g/L)

interlayer: from 2-hydroxyphenol, to 4-hydroxyphenol the possibility to coordination of these species increased.

Conclusions

X-ray powder diffraction, spectral, and thermal analysis shows that 2-, 3-, and 4-hydroxy phenols are successfully intercalated into interlayer spaces of Co(II)-exchanged montmorillonite. The presence of protonated or coordinated phenol derivatives in the silicate interlayers will be connected with different position of hydroxyl groups on the benzene ring (different steric and electronic properties of individual hydroxyphenols) which also influence the stoichiometry of thermal decomposition of studied materials.

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