

A STUDY OF THE INTERACTIONS OF Co(II)–MONTMORILLONITE WITH HETEROCYCLIC COMPOUNDS

M. SAPIETOVÁ¹, E. JÓNA¹, V. LUPTÁKOVÁ², K. JESENÁK² AND Ľ. KUČHTA²

¹*Department of Chemistry and Technology of Inorganic Materials, Faculty of Industrial Technologies, Trenčín University of Alexander Dubček in Trenčín, Púchov Slovakia, sapietova@spt.tnuni.sk, jona@spt.tnuni.sk*

²*Department of Inorganic Chemistry, Faculty of Natural Sciences, Komenius University in Bratislava, Bratislava, Slovakia, jesenak@fns.uniba.sk, kuchta@fns.uniba.sk*

ABSTRACT: In this paper diffraction and spectral analysis have been used to study the influence of different conditions of the preparation of the Co(II)–montmorillonite with imidazole and benzimidazole (different pH of the solutions) on the character of the interactions. The obtained results indicated, that in the acid solution a ionic exchange takes place, while in a neutral and basic solution imidazole and benzimidazole molecules are coordinated to exchanged cations.

KEY WORDS: Co–montmorillonite, imidazole, benzimidazole, IR spectroscopy, X–ray diffraction analysis

1. INTRODUCTION

It is well known that smectite minerals, which can be exchanged by various cations, can accommodate in their interlayer space a great variety of intercalation coordination compounds [9,12]. They attract considerable attention from both fundamental and practical viewpoints. The shape and size selectivities of the clays exchanged by various cations have been used the stereochemical control of several organic catalytic reactions [13] and play an important role as adsorbents of hazardous organic pollutants in the soil [10].

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 [11]. Polar organic molecules can replace the water molecules which occupy the interlayer spaces in the montmorillonite. In introducing transition metal ions and adding suitable ligands, coordination – intercalation compounds may be formed in the interlayers of montmorillonite [9, 12].

Imidazole (IM) and benzimidazole (BIM) are of interest for a variety of reasons. They act as a ligands in a variety of biological molecules and are used as in model compounds for metalloproteins. Coordination ability of imidazole and benzimidazole are strongly dependent on the pH of the reaction solutions. In near – neutral environments unprotonated IM and BIM are usually coordinated to the central atom. In sufficiently basic media the conjugate base of imidazole (IM⁻) and benzimidazole (BIM⁻) may be formed and they react as anionic ligands. In acid media, both electron pairs on a nitrogen are occupied imidazolium and benzimidazolium ions are formed.

Although knowledge of the coordination chemistry of transition metal ions with imidazole and benzimidazole are extensive [1, 2], no Co(II) complexes with imidazole and benzimidazole intercalated in clay minerals have been studied. In this paper the type of interactions of Co(II) with imidazole and benzimidazole in the interlayer space of montmorillonite (at various pH values) has been studied.

2. EXPERIMENTAL

2.1 Synthesis

Montmorillonite from Jelšovský Potok (Slovakia) with a composition $\text{Ca}_{0,48}(\text{Si}_{7,59}\text{Al}_{0,41})(\text{Al}_{3,06}\text{Fe}_{0,34}\text{Mg}_{0,63})\text{O}_{20}(\text{OH})_4$ [6, 8] has been used as a carrier for intercalated Co(II) complexes.

The $< 2 \mu\text{m}$ fraction was obtained by sedimentation. The cation exchange capacity (CEC), determined according to the method [7] was $0,98 \text{ mmol.g}^{-1}$ (Co-MMT).

Imidazole (IM) and benzimidazole (BIM) was supplied by Merck and the other chemicals of analytical grade were purchased from Lachema.

The Co(II)-exchanged montmorillonite (MMT) was prepared by repeated immersion (five times) of 1g of Ca-MMT in 100 cm^3 water solution with a concentration of $0,1 \text{ mol.dm}^{-3}$ of CoCl_2 at room temperature. The excess salt was removed by washing with deionised water until the Cl^- tests were negative. The interlayer spacing of Co-montmorillonite was $1,47 \text{ nm}$.

The reaction of imidazole and benzimidazole with Co(II)-montmorillonite was performed by suspending 1g of Co-clay in 100 cm^3 of aqueous solution of IM and BIM with a concentration of $0,03 \text{ mol.dm}^{-3}$ and $0,06 \text{ mol.dm}^{-3}$. The appropriate pH value was adjusted with aqueous solution of HCl or NaOH. The suspensions were stirred at room temperature for 48 h. The solids were separated from the solution by filtering, washed with 200 cm^3 of water and dried at $50 \text{ }^\circ\text{C}$. The amount of Co(II), which was released from Co(II)-montmorillonite in the reaction with imidazole and benzimidazole, was determined by complexometric titration.

2.2 Characterization

Powder diffraction data were collected on a Philips PW 1050 X-ray diffractometer in the range $4\text{--}40^\circ 2\theta$ using CuK_α radiation.

Infrared spectra were measured in nujol mulls and KBr pellets on a Nicolet 750 Magna spectrometer in the $400\text{--}4000 \text{ cm}^{-1}$ range.

3. RESULTS AND DISCUSSION

The analytical characteristics of the samples prepared, together with their interlayer distances are summarised in the Table 1.

Table 1: The concentration (c) and pH values of imidazole and benzimidazole reaction solutions, the number of released Co^{2+} ions (Co^{2+} rel.) and montmorillonite interlayer space (d_{001}).

Sample	c [mol.dm^{-3}]	pH	Co^{2+} rel. [mmol.g^{-1}]	d_{001} [nm]
Co-MMT	0	0	0	1,47
Co-IM 1	0,03	2,1	0,49	1,27
Co-IM 2	0,03	9,3	0	1,63
Co-IM 3	0,03	11,99	0	1,69
Co-BIM 1	0,06	2,04	0,49	1,38
Co-BIM 2	0,06	9,2	0	1,57
Co-BIM 3	0,06	12,1	0	1,59

The various ways in which imidazole and benzimidazole form bonds in the interlayer space of the Co(II)–montmorillonite can be deduced from IR spectra of the prepared samples. The fundamental vibrational modes of IM and BIM have been given by several authors [3,4]. Assignments for the interlayer complexes were based on the spectra of the different transition metal complexes [5]. The IR spectra of the samples show bands characteristic of heteroaromatic nitrogen compounds. However, the number, position and relative intensities of the bands depend upon the type of interactions of IM and BIM with Co(II)–montmorillonite.

The IR spectra of the samples in which the reaction of Co(II)–montmorillonite with IM and BIM was performed in nearly neutral solution (Table 1) and in basic solution (Table 1) illustrate that the IM and BIM ligand vibrations are shifted from those of the free ligand. The presence of NH–stretching and NH–bending mode peaks indicates that the ligand proton remains bound at the N2 position. Thus, the Co(II) to ligand bonding takes place through the N1 donor atom. The vibration spectra of samples Co–IM 2 (Co–BIM 2) and Co–IM 3 (Co–BIM 3) are very similar to each other suggesting that imidazole and benzimidazole are coordinated in the same way in the interlayer space of these samples. When the neutral medium of reaction was changed on the basic medium, the quantity of adsorbed IM and BIM and also the interlayer distance d_{001} increased (Table 1).

When the reaction of Co(II)–exchanged montmorillonite with IM and BIM solution was performed in acid medium (Table 1), an ionic exchange of Co^{2+} for imidazolium and benzimidazolium ion took place. This is shown by the fact that, according to the analysis ($\text{Co}^{2+} \text{ re} \approx 0,49 \text{ mmol.g}^{-1}$), these samples practically contains no Co^{2+} ions. The IR spectra show the bands of NH groups at 3164 (3150) and 625 (622) cm^{-1} . The bands at 1541 cm^{-1} , which is typical of imidazolium chloride and benzimidazolium chloride [1, 2], can also be observed. This band may be regarded as the bending mode of the NH groups protonated imidazole and benzimidazole ring. The bands of the C–C and C–N stretching vibrations in the range 1200–1500 cm^{-1} are remarkably reduced in intensity, which indicates a strong interaction of the organic molecule with the environment.

Thus, the use of complexes with imidazole and benzimidazole as ligands which are able to change their functionality depending on the synthetic conditions, are a promising means of synthesis of intercalated complexes with a wide variety of structures.

4. CONCLUSIONS

X–ray powder diffraction and infrared spectra shown that imidazole and benzimidazole was successfully intercalated into interlayer spaces of Co(II)–montmorillonite. The formation of Lewis and/or Brönsted type of interaction of imidazole and benzimidazole to Co(II) in the silicate interlayers are expressively influenced by the reaction conditions. In a nearly neutral and basic solution, imidazole and benzimidazole are coordinated to Co(II) as neutral ligands. In a strongly acid solution, a nearly stoichiometric ionic exchange of imidazolium ion and benzimidazolium ion for Co(II) ions take place in the interlayer space of montmorillonite.

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