

Mössbauer study of pH dependence of iron-intercalation in montmorillonite

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Abstract ^{57}Fe Mössbauer spectroscopy and XRD have successfully been applied to show the incorporation of Fe ion into the interlayer space of montmorillonite via treatment with FeCl_3 in acetone. The 78K ^{57}Fe Mössbauer spectra of montmorillonite samples reflected magnetically split spectrum part indicating the intercalation of iron into the interlayer of montmorillonite via the treatment with FeCl_3 +acetone and washed with water until the initial pH=2.3 increased to pH=4.14. It was found that the occurrence of intercalated iron in the form of oxide-oxihydroxide in montmorillonite increases with the pH. Intercalation was confirmed by the gradual increase in the basal spacing d_{001} with pH.

Keywords Ca-montmorillonite · ^{57}Fe Mössbauer spectroscopy · Interlayer Fe · pH dependence

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1 Introduction

The intercalation of drugs into the interlayer space of clay minerals is one of the possible ways for controlled drug delivery. The exchange of the interlayer cations of montmorillonite with iron(III) ions is an effective approach to obtain catalysts, catalyst supports, sensors and adsorbents, too. In previous reports [1, 2], ^{57}Fe Mössbauer spectroscopy has successfully been applied to show the incorporation of Fe ion into the interlayer space of montmorillonite via treatment with FeCl_3 in acetone.

The aim of the present work was to prepare novel iron intercalated montmorillonite via treatment with FeCl_3 in acetone and washed with water at different pH's and to study the effect of pH on the incorporation of iron into the interlayers. For this study, we applied ^{57}Fe Mössbauer spectroscopy that can give reliable information about the intercalation of iron via the appearance of magnetically split spectra, as a fingerprint of intercalated irons, at low temperatures.

2 Experimental

The original Ca-montmorillonite was obtained from Ca-bentonite collected in the region of Istenmezeje, Hungary. Elemental analysis of the original Ca-bentonite resulted in the following composition: 73.29 % SiO_2 , 18.71 % Al_2O_3 , 1.48 % Fe-oxide, 2.29 % CaO and 4.23 % MgO.

In the first step, the Fe encapsulation into Ca-bentonite was carried out in the same way as reported earlier [1, 2] The mass ratio of Ca-bentonite to FeCl_3 was 1:1. For this 50.341g FeCl_3 and 50.634 g Ca-bentonite were used. The solvent was filtered by cellulose nitrate membrane filter with $0.45\text{ }\mu\text{m}$ pore size. The sample was washed with acetone to remove free salts before analyzing. Altogether about 850 cm^3 acetone was used for the solution and washing in order to get the sample entirely free from FeCl_3 . 11g of Fe-bentonite was suspended in 50 cm^3 distilled water (when pH was 2.3) and stirred for 30 minutes. The supernatant was filtered with a membrane filter having $0.45\text{ }\mu\text{m}$ pore size. Then the material was suspended again in 50 cm^3 distilled water, its pH was measured, and then filtered again. This procedure has been repeated several times until pH=5 was reached. XRF analysis revealed iron concentration of $7.24 \pm 0.65 \cdot 10^{-4}\text{ mol/g}$ bentonite for this sample, while $4.05 \pm 0.35 \cdot 10^{-4}\text{ mol/g}$ for the original Ca-bentonite. The difference between these iron concentrations can well correspond to the estimated cation exchange capacity of $2.7 \pm 0.26 \cdot 10^{-4}\text{ mol/g}$ for trivalent cations. The samples for Mössbauer and XRD measurements were obtained at pH=2.70, pH=2.78, pH=2.91, pH=3.76 and pH=4.14.

The iron concentration of each filtrate was determined by microwave plasma atom emission spectrometry (Agilent Technologies SPS 3) and we found that less than 0.2 % of iron content was dissolved during washing with water.

XRF analyses were obtained with an energy dispersive X-ray fluorescence system. The parts of the system were: radioactive source ($185\text{ MBq }^{241}\text{Am}$), Si(Li) detector with 20 mm^2 surface, 3.5 mm evaporated layer, Canberra DSA 1000 digital spectrum analyzer, Canberra Genie 2000 3.0 spectroscopy software.

XRD diffractograms were recorded using a computer controlled DRON-2 powder diffractometer equipped with a $\text{FeK}\alpha$ radiation and a beta-filter.

^{57}Fe Mössbauer measurements were performed with WISSEL spectrometer in transmission geometry at 78 K and 298 K using a JANIS He cryostat and 20 mCi activity $^{57}\text{Co/Rh}$ sources. The isomer shifts are given relatively to $\alpha\text{-Fe}$. The Mössbauer spectra were

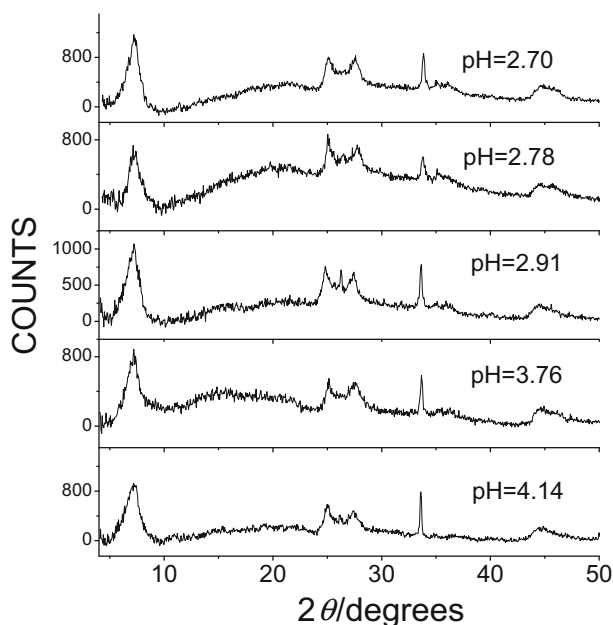


Fig. 1 XRD of montmorillonite treated with FeCl_3 + acetone and washed with water (from *top* to the *bottom*:) at pH=2.70, pH=2.78, pH=2.91, pH=3.76 and pH=4.14

evaluated by least-square fitting using the MOSSWINN program [3]. The Mössbauer spectra were analyzed by least-square fitting of Lorentzian lines by the help of the MOSSWINN code.

3 Results and discussion

Powder X-ray diffractograms of montmorillonite treated with FeCl_3 + acetone and washed with water to set pH at pH=2.70, pH=2.78, pH=2.91, pH=3.76 and pH=4.14 are shown in Fig. 1. The diffractograms correspond well to those reported earlier for Ca-bentonites [4]. The most important difference among the diffractograms was found in the difference of the d values belonging to (001) reflections. Accordingly, the basal spacing d_{001} increased with increasing pH. The increase of basal spacing d_{001} indicates the incorporation of iron in oxide or oxihydroxide form into the interlayer space. Our findings show that more effective iron oxihydroxide formation can be achieved when the pH increases. However, the slope of the dependence of iron oxihydroxide formation on pH is not uniform in the whole pH interval. An abrupt change is observed between pH=2.7 and 2.91 while the changes are much smoother between pH= 2.91 and 4.14, as illustrated in Fig. 3.

Mössbauer spectra, recorded at 298 K and 78 K, of montmorillonite treated with FeCl_3 + acetone and washed with water to set pH=2.70, pH=2.78, pH=2.91, pH=3.76, and pH=4.14 are shown in Fig. 2. The room temperature Mössbauer spectra of both the original Ca-bentonite and those treated with FeCl_3 + acetone and washed with water at different pH were decomposed into two doublets. The major doublet, with average Mössbauer parameters of $\delta = 0.32$ mm/s and $\Delta = 0.61$ mm/s for Ca-bentonite, was assigned to Fe^{III} at the

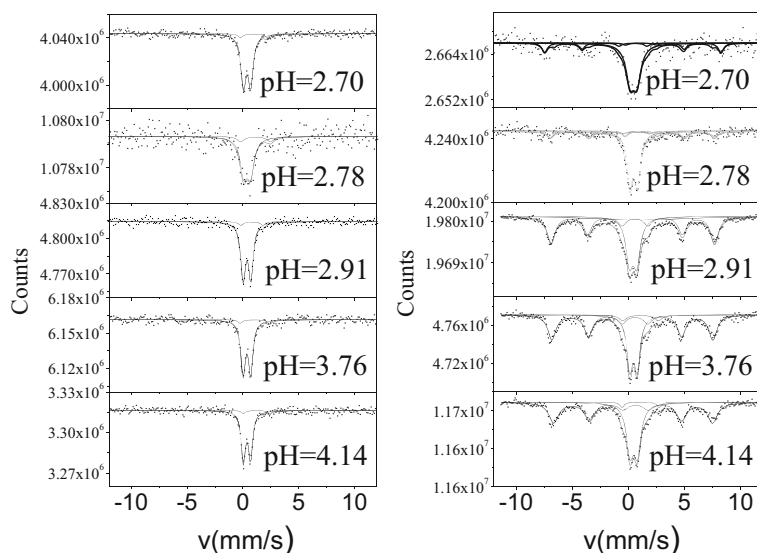


Fig. 2 298 K (*left side*) and 78 K (*right side*) ^{57}Fe Mössbauer spectra of montmorillonite treated with FeCl_3 + acetone and washed with water at pH values indicated

octahedral sites, while the minor doublet, with $\delta = 1.08$ mm/s and $\Delta = 2.65$ mm/s for Ca-bentonite, was attributed to Fe^{II} at the octahedral sites in montmorillonite; these data are in good agreement with previous literature data for the montmorillonites [4–7].

In the 78 K Mössbauer spectra (Fig. 2 on the right side) of all FeCl_3 + acetone treated and washed with water montmorillonites new magnetically split sextet components showed up besides the doublets corresponding to those found in the 293 K Mössbauer spectra. The Mössbauer parameters of sextets at 78 K were found in the range of $\delta = 0.44$ – 0.49 mm/s, $\Delta = -0.08$ – 0.12 mm/s and $B = 44$ – 48 T. We assigned the sextets to Fe^{3+} cations intercalated, in oxide or oxihydroxide form, in the interlayer space of montmorillonite based on previous studies [1, 2, 4, 8, 9]. We have found that the relative area of the sextet components increased monotonously with the pH (Fig. 3). However, the slope of the increase in the interval between pH=2.7 and 2.91 is considerably larger than that between pH= 2.91 and 4.14.

The tendency of the pH dependence of the relative amount of intercalated iron-oxide/oxihydroxide obtained from the Mössbauer spectroscopy measurements is in excellent correspondence with the pH dependence of the basal spacing obtained from the XRD results (see in Fig. 3). The latter indicates the gradual transformation of the hydrated iron to iron oxide/oxihydroxide in the interlayer space during the repeated washing with water. Since the concentration of the intercalated Fe does not change with the increasing pH during the washing, the increasing oxide/oxihydroxide ligand environment must be responsible for the demand for a larger volume resulting in increase in the basal spacing.

The Mössbauer and XRD results mutually confirm and complete each other and prove the iron oxide/oxihydroxide incorporation in the interlayer space upon the applied FeCl_3 + acetone treatment and washing with water.

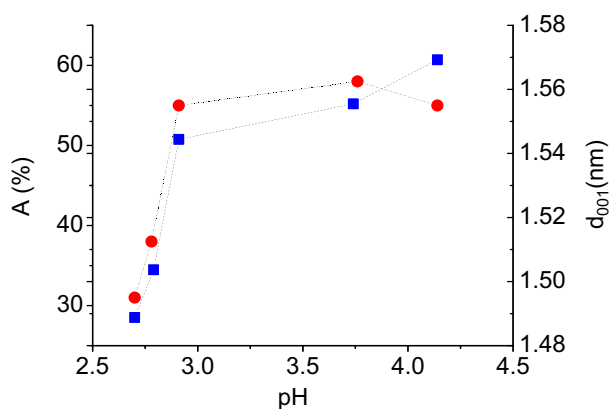


Fig. 3 pH dependence of relative spectral area of sextets related to iron intercalated (denoted with *red circles*) and basal spacing d_{001} (denoted with *blue squares*)

The abrupt change observed in the slope of pH dependence of relative spectral area of sextets related to intercalated iron as well as in the basal spacing d_{001} , can be explained by the effect of pH on the formation of different iron bearing species. Since after the treatment of montmorillonite with FeCl_3 +acetone the sample is acidic ($\text{pH}=2.3$), iron may occur in interlayer space in form of hydrated free Fe^{III} ions. By repeated washing, the hydrolysis of Fe^{III} begins at above $\text{pH}=2.7$, similarly as happens in pure water, and iron oxide-hydroxide begins to form. By taking into consideration the solubility product of Fe^{III} hydroxide being $4 \cdot 10^{-38}$ [9], we can estimate the concentration of Fe^{III} ions to be about 0.1 mol/l based on the size of the interlayer space. Accordingly, the hydrolysis will rapidly saturate with the pH [10], being well consistent with the Mössbauer results.

During the hydrolysis of Fe^{III} the negative layer charge should be balanced. We can assume that hydrogen ions released at the hydrolysis will neutralize the negative layer charge of montmorillonite; H-bentonite is produced. But, H-bentonite is known to be metastable. In our case, however, XRD revealed stable structure due to the stabilisation effect by iron-oxide-oxihydroxide formed in the interlayer space.

4 Conclusions

A gradual increase of the relative spectral area of sextets related to iron intercalated in the interlayer space was found in the ^{57}Fe Mössbauer spectra recorded at 78K as an effect of pH when Ca-montmorillonite was treated with FeCl_3 +acetone and washed with water. Simultaneously, XRD indicated an increase of the basal spacing d_{001} with the pH. These results show the formation of increasing amount of iron oxides/oxihydroxides in the interlayer space with increasing pH. The abrupt increase of these dependences in the interval between $\text{pH}=2.7$ and $\text{pH}=2.9$ can be associated with the hydrolysis of Fe^{III} ions, saturating at higher pH where iron-oxide-hydroxide stabilised H-bentonite forms.

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