

Mössbauer and XRD investigations of layered double hydroxides (LDHs) with varying Mg/Fe ratios

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Abstract The effects of the Mg(II)/Fe(III) ratio on the structure and Fe microenvironments in MgFe LDH substances were investigated. The LDHs were prepared by the co-precipitation method with Mg(II)/Fe(III) ratios from 2:1 to 6:1. The materials were characterized by ^{57}Fe Mössbauer spectroscopy and powder X-ray diffractometry. The ^{57}Fe Mössbauer spectra exhibited asymmetric doublet corresponding to high-spin Fe(III) microenvironments in all LDH structure. It was found that the quadrupole splitting decreased with increasing Mg(II)/Fe(III) ratio reflecting change in the electric field gradient due to the incorporation of different amounts of iron into the Mg-containing layers.

Keywords MgFe-LDH · Mg/Fe ratios · ^{57}Fe Mössbauer spectroscopy · XRD measurements

1 Introduction

Layered double hydroxides (LDHs) are inorganic lamellar compounds with the general chemical formula: $[\text{M}_{1-x}^{2+}\text{M}_x^{3+}(\text{OH})_2]_x + (\text{A}_{x/n}^{n-}) \cdot m\text{H}_2\text{O}$, where M^{2+} and M^{3+} are divalent and trivalent metal ions, and x is the ratio $\text{M}^{3+}/(\text{M}^{2+} + \text{M}^{3+})$.

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Through partial isomorphous substitution of Mg^{2+} cations by M^{3+} cations their structure can be intentionally varied leading to interesting properties that are important in industrial applications as catalysts (after calcination), catalyst supports, anion exchangers, polymer stabilizers, adsorbents, fillers, etc. [1–3].

The aim of the present work was to investigate the effect of the Mg/Fe ratio on the structure and Fe microenvironments in $[\text{Mg}_{1-x}^{2+}\text{Fe}_x^{3+}(\text{OH})_2]_x + (\text{Cl}_{x/n}^{n-}) \cdot m\text{H}_2\text{O}$ LDH substances. The Mg(II)Fe(III)-LDHs were prepared by the co-precipitation method applying aqueous NaOH with Mg(II)/Fe(III) ratios from 2 to 6 (they will be denoted as $\text{Mg}_n\text{Fe-LDH}$ in the following). For the characterization of the obtained substances ^{57}Fe Mössbauer spectroscopy, powder X-ray diffractometry and thermogravimetry were applied.

2 Experimental

All preparation steps were performed using double distilled water saturated with nitrogen to exclude CO_2 . Concentrated NaOH (~ 20 M) stock solutions were prepared from *a.r.* grade solid NaOH (Spectrum 3D) and their carbonate content was minimised. $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (Molar Chemicals, *puriss*), iron chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, Molar Chemicals, *puriss special*) were used without further purification.

The $\text{Mg}_n\text{Fe-LDHs}$ were prepared by the co-precipitation method, via dropwise addition of freshly-made NaOH solution to vigorously stirred and N_2 -blanketed solution of the two metal chloride with various (2:1, 3:1, 4:1, 5:1, 6:1) molar ratios until $\text{pH} = 9.5$. The precipitates formed were rapidly filtered until air dry in a CO_2 free atmosphere. The obtained crystals were kept at room temperature in a desiccator over dry P_2O_5 .

Powder X-ray diffraction (PXRD) patterns of the samples were registered in the $2\Theta = 3\text{--}60^\circ$ range on a computerised DRON-2 instrument, using $\text{CuK}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) radiation. The first reflection (003) was used for calculating interlayer spacing data.

^{57}Fe Mössbauer transmission spectra were measured by conventional constant acceleration type Mössbauer spectrometers (Wissel and Ranger) in transmission geometry in a bath cryostat at 80 K and 295 K. A $^{57}\text{Co}(\text{Rh})$ source of a $\sim 10^9$ Bq activity was used and the spectrometer was calibrated with α -iron at room temperature. Spectrum evaluation was carried out using the MOSSWIN[®] code [4].

3 Results and discussion

XRD measurements confirmed the formation of LDH structures. XRD patterns (Fig. 1) of the samples with different Mg(II)/Fe(III) ratio exhibit broad reflections corresponding to hexagonal LDH phase (the sharp reflections belong to the side product NaCl). Considerable (*ca.* 10 %) increase was found in the $d(003)$ basal spacing values (from 7.98 \AA to 8.82 \AA) as the Mg(II)/Fe(III) ratio was increased from 2 to 6 (Table 1, last row).

The thermogravimetry results are consistent with those characteristic of Mg-Fe LDH compounds [5].

Fig. 1 XRD patterns of Mg_nFe -LDHs with various Mg/Fe ratio (broad reflections belong to the LDH, the two sharp reflections marked with * are stemming from the side product NaCl)

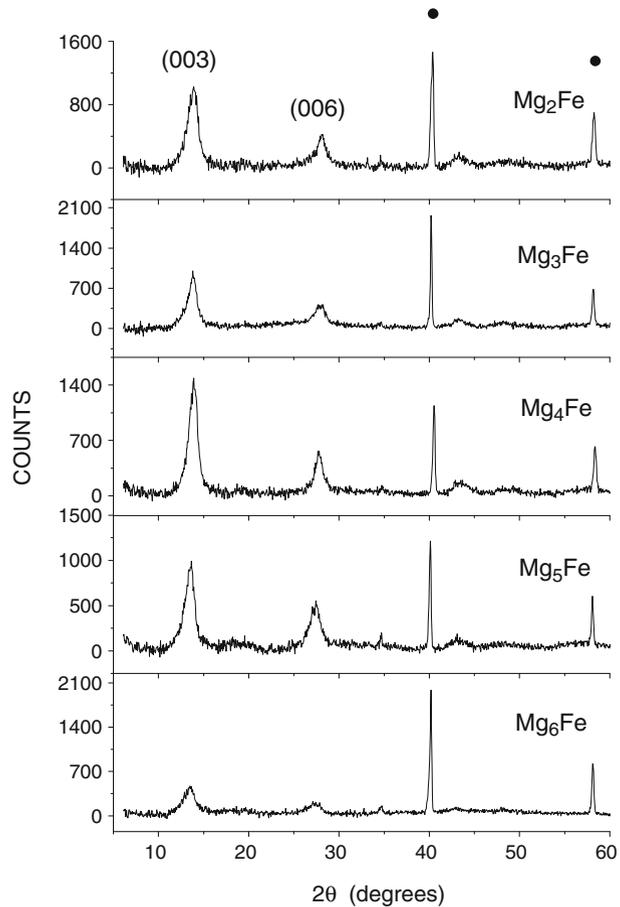


Table 1 ^{57}Fe Mössbauer parameters at 78 K and $d(003)$ interlayer spacing values

Mg/Fe	2	3	4	5	6
δ (mm/s)	0.46 ± 0.004	0.46 ± 0.003	0.46 ± 0.005	0.46 ± 0.004	0.46 ± 0.005
Δ (mm/s)	0.63 ± 0.01	0.57 ± 0.01	0.54 ± 0.01	0.52 ± 0.01	0.52 ± 0.01
W (mm/s)	0.53 ± 0.01	0.47 ± 0.01	0.46 ± 0.01	0.46 ± 0.01	0.48 ± 0.015
$d(003)$ (Å)	7.98	8.07	8.20	8.82	8.63

The ^{57}Fe Mössbauer patterns of Mg_nFe -LDH samples (Fig. 2) are asymmetric doublets. The asymmetry in the relative area of doublet lines can be attributed to the texture effect originated from the layered structure of the compounds. Decomposition of the spectra into subcomponents resulted in unusual parameters, therefore it was concluded that the simplest satisfactory evaluation of the spectra was to fit them assuming one asymmetric doublet. The ^{57}Fe Mössbauer parameters thus obtained at 78 K are given in Table 1. They ($\delta = 0.36$ mm/s and $\Delta = 0.52$ – 0.63 mm/s at room temperature) reflect high-spin Fe(III) microenvironments for all cases. ^{57}Fe

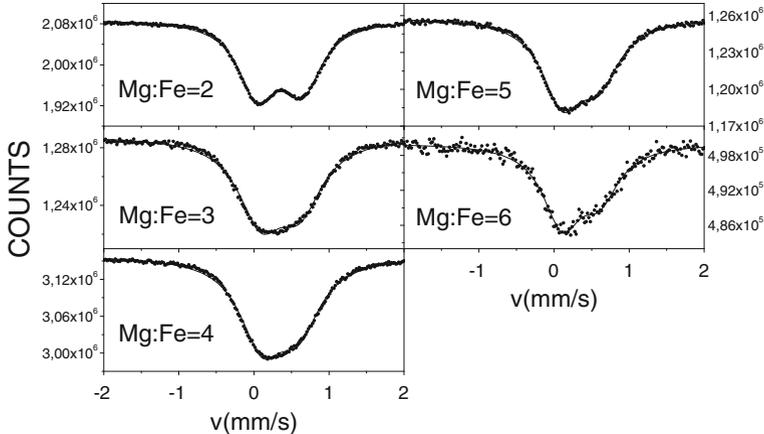


Fig. 2 ^{57}Fe Mössbauer spectra of Mg_nFe -LDHs with varying Mg/Fe ratios recorded at 295 K temperature

Mössbauer measurements were repeated on a series of freshly prepared samples cooled immediately to 78 K after their preparation to avoid structural changes due to the possible reaction with aerial CO_2 . However, spectra and parameters obtained from them were reproducible for every sample. At 295 K the Mössbauer parameters were also in excellent correspondence with those measured at 78 K, except the isomer shifts, which displayed some changes due to second order Doppler shift. No change was observed in the isomer shift with the variation of Mg(II)/Fe(III) ratio, reflecting no change in the electronic density at the site of the iron nucleus in these LDHs. This is in agreement with the ionic character of these compounds.

However, it has been found that the quadrupole splitting significantly decreased with increasing Mg/Fe ratio indicating that the electric field gradient at the iron site increased on increasing iron content. This is consistent with the variations in the spatial charge distribution around the iron. At low iron content, in Mg_6Fe -LDH, iron is situated in a layer where there are mainly Mg(II) ions in its second coordination sphere, which can supply a more symmetric charge distribution, consequently, a smaller EFG and quadrupole splitting. In Mg_2Fe -LDH, some Mg atoms in the second coordination sphere must be replaced by Fe(III) atoms increasing the EFG and the quadrupole splitting.

The results revealed that different microenvironments of iron were incorporated into Mg site in Mg_nFe -LDH structures at different Mg(II)/Fe(III) ratios.

4 Conclusions

Layered double hydroxides with varying Mg(II)/Fe(III) ratios from 2:1 to 6:1 were successfully prepared with the co-precipitation method from solutions of Mg(II) and Fe(III) salts. Hexagonal LDH phase, with basal spacings from 7.98 Å to 8.82 Å, was evidenced by XRD. The characteristic ^{57}Fe Mössbauer spectrum of the Mg_nFe -LDH compounds is an asymmetric doublet with average isomer shift $\delta = 0.36$ mm/s

and quadrupole splitting $\Delta = 0.52\text{--}0.63$ mm/s at room temperature. Gradual change in quadrupole splitting was found with varying Mg(II)/Fe(III) ratios reflecting the effect of substitution of Fe(III) with the Mg(II) site in the layered structure.

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