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THERMAL BEHAVIOUR OF SYNTHETIC PYROAURITE-LIKE ANIONIC CLAY

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Abstract

Thermal behaviour of synthetic pyroaurite-like anionic clay with molar ratio Mg/Fe=2 was studied in the range of 60–1100°C during heating in air. TG/DTA coupled with evolved gas analysis, emanation thermal analysis (ETA), surface area measurements, XRD, IR and Mössbauer spectroscopy were used. Microstructure changes characterized by ETA were in a good agreement with the results of surface area measurements and other methods. After the thermal decomposition of the pyroaurite-like anionic clay, which took place mainly up to 400°C, a predominantly amorphous mixture of oxides is formed. A gradual crystallization of MgO (periclase) and Fe_2O_3 (maghemite) was observed at 400–700°C by XRD. The $MgFe_2O_4$ spinel and periclase were detected at 800–1100°C. The spinel formation was also confirmed by Mössbauer spectroscopy.

Keywords: ETA, layered double hydroxide, Mg–Fe hydrotalcite, pyroaurite-like anionic clay, thermal decomposition

Introduction

The naturally occurring minerals of chemical composition $Mg_6Fe_2(OH)_{16}CO_3{\cdot}4.5H_2O$ are known as pyroaurite and sjögrenite, exihibiting the rhombohedral (3*R*) and hexagonal (2*H*) symmetry, respectively. They belong to the layered minerals known as anionic clays, which are also reported as layered double hydroxides or hydrotalcite-like compounds. Although anionic clays are found in nature, the synthetized ones are used for most applications, e.g. in heterogeneous catalysis, ion-exchange and adsorption processes, polymer processing, etc. Many catalysts based on mixed oxides can be obtained by a controlled thermal decomposition of these compounds [1–3]. The preparation and characterization of synthetic pyroaurite was reported by Hansen and Koch [4]. Pyroaurite-like compounds intercalated by organic anions were described by Raki *et al.* [5]. The calcination and rehydration behaviour of Mg–Fe hydrotalcite-like compounds were studied by Hibino and Tsunashima [6]. The calcined hydrotalcite-like compounds con-

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taining iron were used for removal of humic substances [7] and in heterogeneous catalysis as catalysts in alkylation of phenol with methanol [8] and in reduction of aromatic nitro compounds with hydrazine hydrate [9]. Shen *et al*. [10] prepared Fe/MgO catalysts by thermal decomposition of Mg–Fe hydrotalcite-like precursors with various Mg/Fe molar ratios followed by reduction of Fe^{3+} to Fe by hydrogen and used these catalysts in Fischer–Tropsch synthesis. The thermal decomposition of Mg–Al–Fe hydrotalcite-like compounds and the effect of iron on the crystalline phases formed were studied by Fernandez *et al.* [11].

In view of the importance of oxide catalysts obtained from hydrotalcite-like precursors, it is of interest to understand in detail the thermal behaviour of these compounds. Several authors [8, 9, 11] reported about the formation of poorly crystallized MgO after the decomposition of Mg–Fe hydrotalcite-like precursor with Mg/Fe molar ratio of 3 and higher followed by the $MgFe_2O_4$ spinel crystallization at high temperatures. This study aims to describe the thermal behavior of the synthetic pyroaurite-like anionic clay with relatively high iron content (Mg/Fe molar ratio equal to 2). TG/DTA/EGA, BET surface area measuments, XRD, IR and Mössbauer spectroscopy were used to characterize the thermal decomposition process and its products. The emanation thermal analysis (ETA) [12, 13] based on the measuring of the radon release from sample previously labeled was used to characterize the microstructure changes during heating of the sample. The ETA was already used to monitor the microstructure development during thermal decomposition of various chemical compounds such as oxalates, sulphates or carbonates used as precursors for catalysts preparation [14, 15].

Experimental

Sample preparation

Pyroaurite-like anionic clay was prepared by coprecipitation. An aqueous solution (300 mL) of $Mg(NO_3)_2{\cdot}6H_2O$ and $Fe(NO_3)_3{\cdot}9H_2O$ with Mg/Fe molar ratio of 2 and total metal ion concentration of 1.0 mol L^{-1} was added dropwise under vigorous stirring into 300 mL of 0.5 M Na_2CO_3 solution. The addition took about 1 h. During the synthesis, the temperature was maintained at 40°C and pH at about 10.5 by a simultaneous addition of a 3 M NaOH solution. The resulting suspension was then maintained at 40°C, with stirring, for 18 h. The obtained product was filtered off and washed several times with distilled water and dried at 60°C in air. The dried product was heated at chosen temperatures in the range 100–1100°C in air for 2 h and then cooled to the room temperature. These calcined samples were used for the XRD, IR, Mössbauer spectroscopy and BET surface area measurements.

The initial sample of pyroaurite-like anionic clay for the ETA measurement was labeled by adsorption of the radionuclides of ^{228}Th and ^{224}Ra from acetone solution on the surface of the product dried at 120°C. After the labeling, the acetone was evaporated at 80°C. The atoms of ^{228}Th adsorbed at the sample surface served as a source of ^{224}Ra and ^{220}Rn.

Experimental techniques

TG/DTA/EGA measurements were carried out using a Netzsch STA 409 apparatus equipped by the quadrupole mass spectrometer QMS 403/4 (Balzers) for analysis of gases evolved during sample heating. The heating rate of 6°C min^{-1} in air with flow rate of 75 mL min^{-1} and 50 mg of sample were used. The furnace and mass spectrometer were connected by stainless steel capillar of inner diameter 0.1 mm which was heated to about 200°C to prevent a condensation of evolved gases. Gaseous products were continually monitored for chosen mass numbers m/z (18–H_2O^+ and 44–CO_2^+).

Powder X-ray diffraction patterns were recorded using a Seifert XRD 3000P instrument with CoK_α radiation (λ=0.179 nm, graphite monochromator, goniometer with Bragg–Brentano geometry) in 2θ range 12–75°, step size 0.05°.

Surface area measurements were carried out by nitrogen adsorption using Coulter SA 3100 equipment and evaluated by one point BET method.

Fourier-transform infrared absorption spectra were recorded using the KBr pellet technique on the spectrometer Nicolet Avatar 320 in the range 4000–400 cm^{-1} and the resolution of 4 cm^{-1}.

Mössbauer spectra were measured at room temperature using a Mössbauer spectrometer in the constant acceleration mode. The measurements were carried out using a ^{57}Co(Rh) source with an activity $3.8\cdot10^8$ Bq.

ETA consisted in the measurement of the radon release rate from samples previously labeled [12, 13, 15]. Radon atoms ^{220}Rn have been formed by the spontaneous α-decay of ^{228}Th and ^{224}Ra. The thorium nuclide ^{228}Th used for sample labeling has a suitable long enough half-life (1.9 years) to serve as a quasi-permanent source of radon ^{220}Rn (half-life 55 s). The half-life of ^{220}Rn ensured that the radioactive steady state between ^{224}Ra and ^{220}Rn was established within several minutes and therefore it was possible to study even rapid changes in the solid and on its surface. The specific activity of the labeled sample was 10^5 Bq per gram. The labeled sample was stored more than three weeks prior to the ETA measurement under dry conditions to allow the radioactive equilibrium between the ^{228}Th and ^{224}Ra nuclides to be established. It was determined by means of TRIM code [16] that the maximum depth of the labeling by ^{224}Ra and ^{220}Rn recoiled atoms is 80 nm.

The apparatus used for the ETA measurements was constructed on the basis of the Netzsch DTA 409 Equipment in the Nuclear Research Institute Řež. During the ETA measurements, the labeled sample was situated in a furnace and heated in the temperature range 20–1200°C at the rate of 6°C min^{-1} in the air with flow rate 50 mL min^{-1}. The flowing air carried the radon released from the sample into the measuring chamber of radon radioactivity. The resulting ETA curve is presented as a temperature dependence of the radon release rate E (in relative units); $E=A_\alpha/A_{\mathrm{total}}$, where A_α is the α-radioactivity of radon released in a time unit from the labeled sample and A_{total} is the total γ-radioactivity of the labeled sample. The A_{total} value is proportional to the rate of radon formation in the sample. Semiconductor and NaI(Tl) detectors were used for the α- and γ-radioactivity measurements, respectively.

Results and discussion

The results of elemental chemical analysis of the dried product (Table 1) confirmed the Mg/Fe molar ratio equal to 2. Based on the chemical analysis and thermogravimetry results, the chemical composition of the prepared pyroaurite-like anionic clay corresponded approximately to the theoretical formula $Mg_4Fe_2(OH)_{12}CO_3{\cdot}3H_2O$.

Table 1 Chemical composition of the prepared pyroaurite-like anionic clay as synthetized and dried at 60°C/mass%

Mg	Fe	CO_3^{2-}	Na	Mg/Fe*	Fe/CO_3^{2-}*
18.10	20.84	10.72	0.030	1.996	2.089

*molar ratio

Thermal analysis results

Thermal treatment of hydrotalcite-like compounds can give mixed metal oxides with interesting properties as heterogeneous catalysts. It was reported by other authors [17–20] that following main processes are usually observed during the heating of hydrotalcites: release of interlayer water, thermal decomposition followed by formation of oxides and finally spinel crystallization.

The DTA curve of the prepared pyroaurite-like anionic clay exhibited two characteristic effects (Fig. 1). The first one with minimum at 200°C indicated sample dehydration accompanied by the loss of interlayer water. The evolved gas analysis confirmed the water release from the sample. The small effect on the EGA curve at about 100–120°C was ascribed to the release of humidity adsorbed at the sample surface. The second DTA endothermic peak at 350°C was accounted to the dehydroxylation of the hydroxide layers and decomposition of the interlayer carbonate anions. The EGA results confirmed the sample decomposition at 350–400°C accompanied with the maximum release rate of CO_2 and H_2O at 370–375°C.

From TG results (Fig. 1) it followed that the mass loss of the sample started at room temperature and was completed at 600–650°C. Two steps of the mass loss were observed during heating, as it is usual for hydrotalcite-like compounds [17–20]. The first one, up to 200–230°C, corresponded to a removal of water physisorbed on the external surface of sample particles, and a release of water molecules from the interlayers. In the temperature range 20–230°C the mass loss of 17.5% of the initial sample mass was observed. The second mass loss, almost completed at 600°C, corresponded to the removal of water released from the hydroxide layers due to their dehydroxylation as well as of carbon dioxide released from the sample during the decomposition of interlayer carbonate anions. The total mass loss up to 600°C was 39.7% of the initial sample mass. No mass loss above 600°C was observed. A humidity free sample of $Mg_4Fe_2(OH)_{12}CO_3{\cdot}3H_2O$ pyroaurite-like clay should show the total mass loss of 39.1% of the initial sample mass. The diffrerence of 0.6% could be explained by the presence of some residual free water

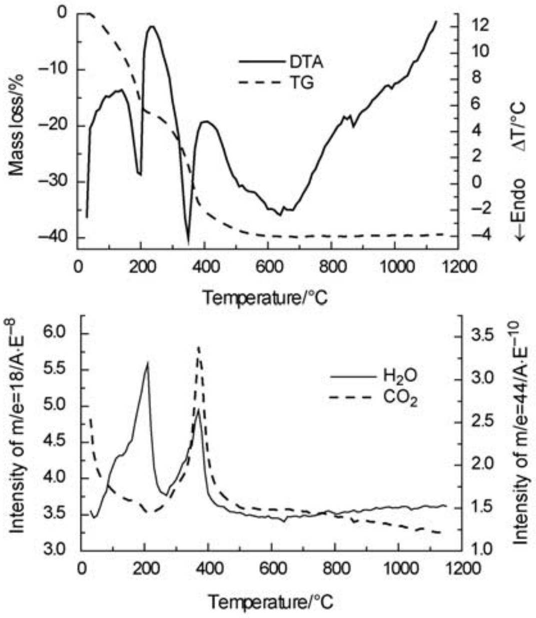

Fig. 1 Characterization of thermal behaviour of synthetic pyroaurite-like anionic clay during heating in air by TG/DTA and evolved gas analysis (H_2O and CO_2)

in the pores of the dried product which was not released at 60°C or which was re-adsorbed during handling of the dried sample.

XRD and IR spectroscopy results

A well-crystallized hydrotalcite-like phase was present in the dried product. No other crystalline phases were detected in the XRD pattern of the prepared pyroaurite-like anionic clay (Fig. 2). After the release of interlayer water, XRD patterns showed the worse crystallinity of dehydrated sample (200°C) but this sample still had the hydrotalcite structure. During the subsequent heating, the hydroxyl and carbonate groups were simultaneously transformed into water and carbon dioxide, respectively. The layered crystal structure of hydrotalcite collapsed. The sample heated to 300°C was rather amorphous. Based on XRD results, MgO (periclase), Fe_3O_4 (magnetite) and/or Fe_2O_3 (maghemite) may be present at higher temperatures (400–700°C). The diffractograms of magnetite and maghemite are very similar, there are only low differences between XRD lines positions. The sample heating was carried out in air and therefore the presence of Fe(III) oxide (maghemite) could be rather expected. The $MgFe_2O_4$ spinel together with periclase were detected at high temperatures (800–1100°C).

The infrared spectra of heated samples showed in Fig. 3 confirmed the gradual dehydroxylation and decarboxylation of the prepared pyroaurite-like anionic clay

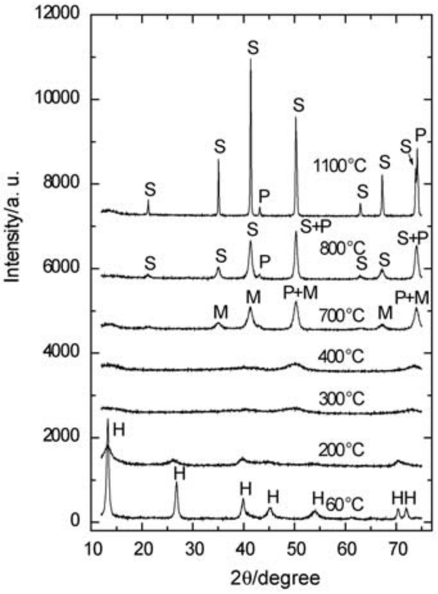

Fig. 2 Powder X-ray diffraction patterns of synthetic pyroaurite-like anionic clay in dependence on heating temperature; H – hydrotalcite-like phase; M – Fe_3O_4 (magnetite) and/or Fe_2O_3 (maghemite); P – MgO (periclase); S – $MgFe_2O_4$ spinel

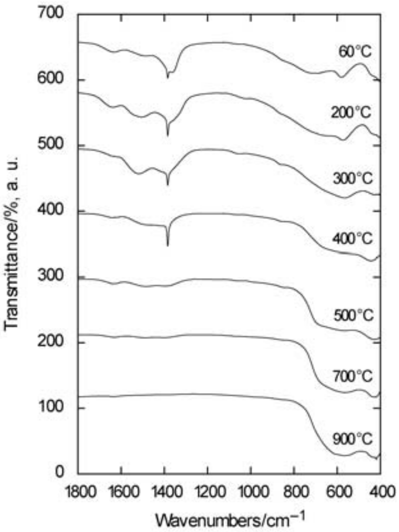

Fig. 3 FTIR spectra of synthetic pyroaurite-like anionic clay heated at various temperatures

and the formation of oxides. A decrease of intensity of the hydroxyl stretching bands in the interval 4000–3000 cm^{-1} and H_2O bending band at 1640 cm^{-1} was observed up to about 450°C. Similarly, the two strong carbonate bands at about 1500 and

1360 cm^{-1} diminished in intensity up to 500°C. A sharp band at 1384 cm^{-1} attributed to stretching vibration of NO_3^- disappeared completely at 500°C Changes in the IR spectra of samples heated to 500–900°C can be explained as follows: the absorption band at 570 cm^{-1} in the range 400–700°C could be assigned to the lattice vibration of Fe_3O_4 and/or Fe_2O_3. The shape of this band was asymmetric to higher wavenumbers which could correspond to the simultaneous presence of nanoparticles of Fe_3O_4 and/or Fe_2O_3 and MgO. The band at 440 cm^{-1} indicated the formation of MgO. The new bands at 564 and 432 cm^{-1} were detected in samples heated to 700°C and higher temperatures. These bands were accounted to the formation of spinel.

Mössbauer spectroscopy results

The Mössbauer spectra are presented in Fig. 4. The Mössbauer spectrum of the synthetic pyroaurite-like anionic clay heated to 200°C consisted of Fe^{3+} doublet with isomer shift related to iron IS=0.33 mm s^{-1} and quadrupole splitting QS=0.72 mm s^{-1}. These hyperfine parameters corresponded with parameters of similar samples reported by Raki *et al.* [5]. The additional broad doublet with IS=0.29 mm s^{-1} appeared in Mössbauer spectra of samples heated to 400 and 600°C (Fig. 4). The Mössbauer spectra of samples heated to 800 and 900°C already consisted of only two broad sextets with identical IS=0.29 mm s^{-1} and QS=0.01 mm s^{-1} however with different hyperfine magnetic fields B=45.2 and 41.9 T. From the Mössbauer spectra of the samples heated above 700°C it followed that two different Fe^{3+} sites, probably spinel arrangement, were present in the structure. The broad doublet characterizing the samples heated to 400 and 600°C splitted into sextets measured for the samples heated above 800°C. Therefore it was assumed that new spinel structure was developed in

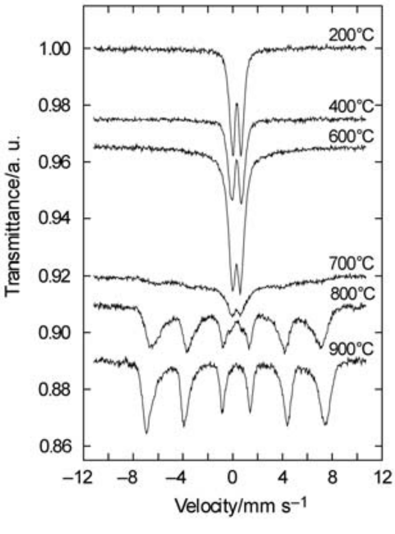

Fig. 4 Mössbauer spectra of synthetic pyroaurite-like anionic clay heated at various temperatures

the sample heated to 700°C and that the particles were of poor crystallinity. However, the particles with better crystallinity were formed by the heat treatment to 800 and 900°C. Consequently, the magnetic behaviour of these particles changed and sextets appeared in Mössbauer spectra.

Emanation thermal analysis and surface area measurements results

During the ETA measurements, a part of the radon atoms formed by the spontaneous α-decay of radium was directly released from the sample by recoil. Another part of the radon atoms was trapped at lattice defects, such as vacancy clusters, grain boundaries, and pores, and could be released from the sample via diffusion. It was supposed that the structure defects in solids can serve both as traps and diffusion paths for radon atoms. As it follows from theories of diffusion and recoil processes [14], the radon release rate, E, depends on the surface area and on the radon diffusion parameters in the solid. The radon release rate, E (also called the emanating rate), can be expressed as

$$E=E_R+E_D=S[K_1+(D/\lambda)^{1/2}K_2] \tag{1}$$

where E_R is the part of the radon release due to recoil, E_D is the diffusion part of the released radon, S is the surface area, K_1 is the temperature independent constant, proportional to the penetration depth of radon recoiled atoms, D is the coefficient of radon diffusion in the sample, λ is the decay constant of radon, and K_2 is a constant dependent on temperature.

Consequently, an increase in the radon release rate, E, indicated an opening of the structure and/or an increase of the surface area of the interfaces, whereas a decrease in E reflected the annealing of structure irregularities serving as paths for radon migration, a densification of structure, closing pores, and/or a decrease in the surface area of the interfaces. Therefore, the changes in radon release rate give an information about transport properties of the samples labeled with radon atoms.

The ETA results in Fig. 5 indicated that the radon release was facilitated by the water release from the interlayer space in the range 20–200°C. From the break on the ETA curve observed at 200°C it can be assumed, that at this temperature a stacking of water free interlayer space started, affecting the radon mobility from the sample. Thus, it was assumed that the interlayer space could serve as radon diffusion channels. The stacking of the interlayer space occurred at 200–230°C as indicated the sharp decrease of the radon release rate in this temperature range. This was in a good agreement with the TG/DTA/EGA measurements, which showed the maximum interlayer water release at 200°C.

From TG/DTA/EGA, X-ray diffraction and IR spectroscopy measurements it followed that in the range 250–400°C the sample decomposition took place and the layered hydrotalcite crystal structure of the sample is transformed into amorphous. It can be assumed that interface boundaries of the oxides formed during the thermal decomposition served as new additional diffusion channels for radon migration and that the increase of the surface area took place. In the range 250–400°C, the ETA results showed the increase

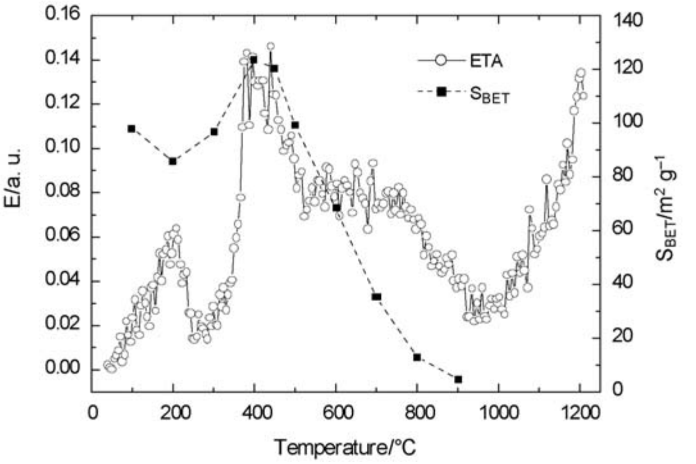

Fig. 5 ETA results of synthetic pyroaurite-like anionic clay obtained on heating in air compared with BET surface area values of the samples prepared from this compound by heating at various temperatures

of radon release rate, which was ascribed to the increase of the surface area of the sample. The values of surface area of samples heated at different temperatures determined by nitrogen adsorption at 77 K confirmed this assumption. As it follows from Fig. 5, the value of surface area of as dried pyroaurite-like anionic clay was about 100 m^2 g^{-1} and changed only a little during interlayer water release of the sample on heating to 300°C. The values of 125 and 123 m^2 g^{-1} were measured for samples heated to 400 and 450°C, respectively. This considerable increase in surface area indicated the decomposition of sample. The surface area decreased with increasing temperature in the range 450–900°C. From Fig. 5 it follows that in the range 450–600°C the radon release rate decreased similarly with the temperature dependence of surface area.

The ETA results characterized the microstructure development under in situ conditions of the sample heating, based on the measurement of the radon release. The break observed on the ETA curve at 400°C can be ascribed to the onset of the structure irregularities annealing, the decrease of the surface area, and the oxide formation. The most intense decrease of the radon release rate was observed in the range 450–500°C and it was in a good agreement with sharp decrease of surface area (123 and 101 m^2 g^{-1} at 450 and 500°C, respectively).

The surface area continually decreased with increasing temperature (69 and 5 m^2 g^{-1} at 600 and 900°C, respectively), probably due to changes in internal arrangement of the heated product caused by crystallization of oxides. The gradual crystallization of MgO (periclase) and iron oxides (magnetite and/or maghemite) with increasing temperature was confirmed by the XRD analysis (Fig. 2). The decrease of radon release rate observed on the ETA curve in the range 780–950°C indicated the annealing of grain boundaries, which served as radon diffusion paths from the sample labeled.

It is of interest to point out that results of ETA and BET surface area measurements characterized in the different way the microstructure changes of the sample preheated to the temperatures 600–800°C. The differences are due to the principal characteristic of the methods, namely that the BET surface area values were obtained by nitrogen adsorption, whereas the ETA results indicated the permeability of radon along the diffusion paths in the near surface layer of the sample at the respective temperature.

The decrease in the radon release rate observed in the temperature range 700–900°C could be ascribed to the crystallization of $MgFe_2O_4$ spinel which resulted in the structure ordering of the sample and the decrease of the interphase boundaries, serving as radon diffusion paths. The spinel formation at 700–900°C was confirmed also by the Mössbauer spectroscopy (Fig. 4). The ETA results gave an additional information about the thermal behaviour of the pyroaurite-like anionic clay. The increase of the radon release rate observed on heating at 1000–1200°C characterized the radon permeability of the sample by the bulk diffusion mechanism.

Conclusions

Information about thermal decomposition of the synthetic pyroaurite-like anionic clay and about subsequent microstructure changes was obtained by TG/DTA/EGA and ETA, BET surface area measurements, XRD, IR and Mössbauer spectroscopy. After the thermal decomposition of the sample on heating to 350–400°C, the predominantly amorphous oxide phases were formed which gradually crystallized (MgO, Fe_3O_4 and/or Fe_2O_3) in temperature range 400–700°C. The crystallization of $MgFe_2O_4$ spinel was detected at 800°C and higher temperatures.

The ETA gave following additional information about the surface and microstructure changes under in situ conditions of heating of the synthetic pyroaurite-like anionic clay: the decrease of the radon release rate observed in the range 400–500°C monitored the decrease of the surface area of the sample and in the range 700–900°C characterized the annealing of structure irregularities and structure ordering due to the crystallization of $MgFe_2O_4$ spinel, respectively.

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