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THERMAL TRANSFORMATIONS OF SELECTED TRANSITION METALS OXYHYDROXIDES

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Abstract

The results of investigation of thermal dehydroxylation of freshly precipitated iron(III) oxyhydroxide, α-FeO·OH (goethite) and titanium(IV) oxyhydroxide, $TiO(OH)_2$ are reported. The measurements have been carried out by thermogravimetric method in static air atmosphere at different heating rates. The crystal structure of intermediate products has been identified by X-ray powder diffractometry. The JMAEK model A3 has been used as the adequate equation representing the dehydroxylation process of precipitated goethite. The third order model F3 has been used for description the rate of dehydroxylation reaction of titanium(IV) oxyhydroxide. The products of thermal dehydroxylation of mentioned oxyhydroxides can be used as precursors for preparation of ferrites or titanates.

Keywords: dehydroxylation, iron(III) oxyhydroxide, oxyhydroxides of transition metals, titanium(IV) oxyhydroxide

Introduction

Mixed transition metals oxides are used for preparation of many compounds which are numbered to functional or advanced materials. As examples can be mentioned ferrites, titanates, electroceramics, combustion catalysts, electrochemical materials and others [1, 2]. These materials are most frequently prepared using high temperature route by thermal treatment a mixture of metals oxides or carbonates. In low temperature procedure are used metal oxalates which are however expensive.

The aim of our work was to determine the rate of dehydroxylation process of iron and titanium oxyhydroxides proceeding at different heating rates as well as to investigate the crystal structure and reactivity of obtained at different temperature products. The well established reactivity and properties of intermediate products that are formed during thermal dehydroxylation of transition metals oxyhydroxides can give essential information about possibility of preparing the functional materials using low temperature procedure.

The oxyhydroxides of transition metals can be taken into account as precursors for preparing many functional materials. The most important members of this group

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of compounds are iron(III) and titanium(IV) oxyhydroxides which are produced on industrial scale. This work is the first part of the planed more extensive investigation of thermal transformations of mixtures of transition metals oxyhydroxides and carbonates. The idea of these investigation is to explain the possibility of preparing of such materials as ferrites and titanates of transition metals having spinel structure by the low temperature way. The knowledge of thermal transformations of iron and titanium oxyhydroxides as well as the rate of occurring transformations should be helpful for the proper selection of condition for such kind syntheses.

Oxyhydroxides of transition metals are compounds in which the coordination group around the central metal cation is composed of O and OH ligands. Most metal oxyhydroxides, $MO_x(OH)_y$ consists of extended arrays of the component atoms having layer or three dimensional structure in which the structural layers are connected by hydrogen bonds.

The largest class of compounds of which the layer structure are known are of the type MO·OH, formed among others by Fe, V, Cr, Mn and Co oxyhydroxides. These oxyhydroxides can exist in α and β forms. For example the goethite has α-FeO·OH structure and is similar to α-MnO·OH (groutite) and α-VO·OH (montroseite). The titanium(IV) oxyhydroxide, $TiO(OH)_2$ has the three dimensional structure formed by octahedral coordination groups and resembles in its configuration the distorted structure of anatase [3].

The thermal transformations of precipitated goethite and hydrated titanium dioxide at temperature range from 293 to 1273 K have been investigated and reported previously [4–6]. The investigation of mechanism of the thermal transformation from goethite to hematite has been carried out for commercial Bayferrox yellow pigment by Walter *et al*. [7]. Results of examination of kinetics of the thermal dehydroxylation of goethite have been reported by Grygar *et al*. [8] and Frost *et al*. [9]. The results of emanation thermal analysis used for examination of hydrous titania and hydrous titania containing 10% ruthenia have been reported Balek *et al*. [10]. The investigation of thermal decomposition of hydrated titanium dioxide has been carried out by Żmijewski *et al*. [11].

This report is focused on rate of thermal dehydroxylation of freshly precipitated iron(III) and titanium(IV) oxyhydroxides in order to establish the most adequate kinetic equations as well as to explain the influence of heating rate on properties of obtained as products partially amorphous oxides.

During thermal treatment of goethite or titanium(IV) oxyhydroxide occurs the process of their dehydroxylation. As the products in the solid state are formed amorphous metal oxides having very evolved surface area which at higher temperature can crystallize and form crystal structure of hematite, α-Fe_2O_3 or anatase. These intermediate amorphous phases are very reactive and can easily form at relatively low temperature compounds with other metal oxides forming the structures characteristic for mixed oxides of transition metals as spinel, perowskite or corundum lattice or almost continuous series of these oxides solid solutions.

It is evident that oxyhydroxides of iron(II) and titanium(IV) can be among others the important precursors which can be used for the preparation of many functional materials. These compounds are produced in a large industrial scale and are commonly used as the inorganic pigments.

Experimental

Materials and sample preparation

The iron(III) oxyhydroxide, α-FeO·OH (goethite) has been precipitated from aqueous solution of iron(II) sulphate using precipitating oxidation procedure. As a raw material was used waste iron(II) sulphate originating from titanium dioxide production. This salt was purified by its re-crystallization from acidic aqueous solution which was reduced by metallic iron. The precipitation of goethite has been carried out at temperature 333 K and at pH=3.5±0.2. The solution of iron(II) sulphate was slowly oxidized by air oxygen at almost pH-static conditions. The precipitated yellow iron oxyhydroxide was filtered out, washed few times by distilled water and dried at temperature 353 K.

The titanium(IV) oxyhydroxide, $TiO(OH)_2$ has been precipitated from acidic solution of titanium(IV) sulphate by hydrolytic procedure. The solution of titanium(IV) sulphate concentration of 180 g TiO_2/dm^3 was diluted by hot water used in proportion 5:1 and next the obtained milk-white suspension was boiled by several hours until the degree of titanium precipitation exceeds 98%. The precipitated titanium(IV) oxyhydroxide, which is frequently also called 'hydrous titanium dioxide' was filtered out and washed few times by distilled water. The obtained product was next dried through the period of 24 h at temperature 378 K.

Methods

The composition of used iron(II) sulphate heptahydrate, precipitated goethite and titanium(IV) oxyhydroxide have been determined using X-ray fluorescence spectrometry on Philips PW 1480 spectrometer equipped with rhodium lamp. The measurements were carried out at voltage 40–100 kV and current 30–75 mA using as the diffraction crystals Ge-C, Ge111, LiF200, LiF220, PE-C and PX1.

The crystal structure of iron(III) and titanium(IV) oxyhydroxides as well as the structure of intermediate products formed during their thermal treatment were identified by X-ray diffractometry on the Philips PW 1410 goniometer using CuK_α radiation at voltage 45 kV and current 40 mA.

The kinetic investigations of the thermal dehydroxylation of investigated compounds have been carried out by the thermogravimetric method on MOM 1500 thermoanalyser at temperature range from 293 to 773 K. The measurements have been carried out in static air atmosphere using standard ceramic crucibles containing 400 mg samples of investigated material. It has been established that such relatively high mass of samples did not disturb the recorded process rate by evacuation of gaseous product (water vapour) because it is evolved slowly and at relatively wide temperature range. The used higher mass of samples enabled however their direct further investigation using powder X-ray diffractometry.

Results and discussion

The thermogravimetric curves for dehydroxylation of goethite were recorded at temperature range from 293 to 773 K and at heating rate equal 5, 10 and 20 K min^{-1}. The influence of heating rate on dehydroxylation kinetics is shown in Fig. 1. The experimental curves are drawn using solid lines. The dehydroxylation of goethite begins at temperature 480 K and at temperature range from 620 to 650 K the conversion is almost complete.

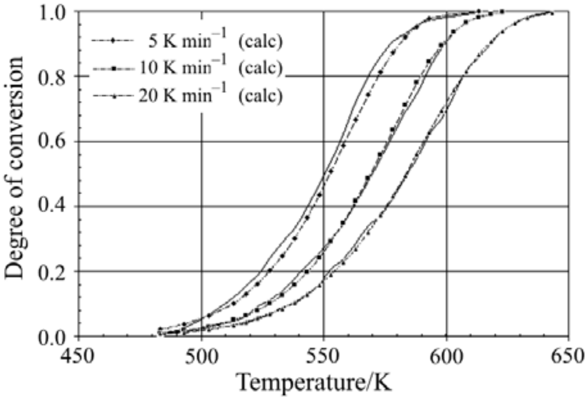

Fig. 1 Thermokinetic curves of goethite dehydroxylation

The thermogravimetric curves for titanium(IV) oxyhydroxide were recorded at temperature range from 293 to 773 K and at heating rate equal 1.25, 5, 10 and 20 K min^{-1}. At this temperature range occurs progressive dehydroxylation of this compound. The process of sample dehydroxylation begins at temperature range from 320 to 390 K in dependence on heating rate. The degree of conversion higher than 0.8 is attained at wide temperature range from 440 to 540 K and this process is continued almost to 1000 K. The influence of heating rate on the process rate is shown in Fig. 2. The experimental curves

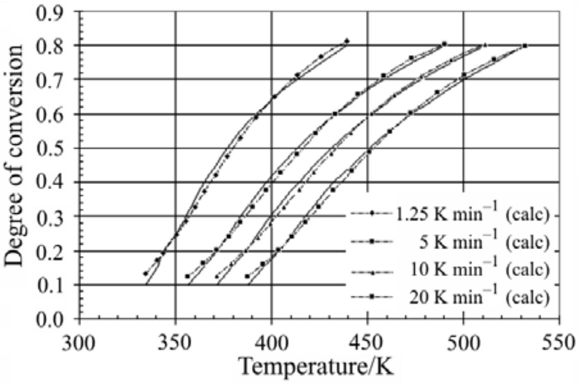

Fig. 2 Thermokinetic curves of titanium(IV) oxyhydroxide dehydroxylation

are drawn using solid lines. The kinetic analyse of titanium(IV) oxyhydroxide dehydroxylation has been evaluated for experimental data including degree of conversion from 0.1 to 0.8.

The experimental results have been preliminary elaborated using the Coats–Redfern method. The applied integral Coats–Redfern equation has following form

$$\ln\left[\frac{g(\alpha)}{T^2}\right]=\ln\left[\left(\frac{AR}{\beta E}\right)\left(1-\frac{2RT}{E}\right)\right]-\frac{E}{RT} \tag{1}$$

where $g(\alpha)$ is the integral form of rate equation (kinetic model). This equation has been used for the preliminary choosing the kinetic models describing properly thermal dehydroxylation or dehydration of investigated compounds. The calculation has been carried out for each heating rate using the experimental data sets including (α_i,T_i) values. The most important rate equations $g(\alpha)$ commonly used in kinetic analyses of solid state reaction [12] have been tested in calculations. As the first criterion for model selection was taken the value of R^2 calculated using linear regression for Eq. (1). By this way have been selected few models having the largest R^2 values equal in all cases more than 0.9. In next step were calculated the values of standard deviation for these selected models

$$s=\sqrt{\frac{\sum_i(\alpha_{\text{exp,i}}-\alpha_{\text{calc,i}})^2}{n-1}} \tag{2}$$

where α_{exp} denotes the experimental degree of conversion and α_{calc} – corresponding value resulting from kinetic model and n – the number of experimental points. The model giving the least standard deviation was selected as the best rate equation. The results recorded at different heating rates were also elaborated using isoalpha method.

The results of kinetic analyse of goethite thermal dehydroxylation are shown in Table 1. There are given activation parameters E_a and A, correlation coefficient R^2 and standard deviation s calculated for JMAEK model A3. These values have been calculated for each applied heating rate. The mean value of activation energy for the investigated range of heating rate is about 27.56 kJ mol^{-1} and pre-exponential coefficient equals 49 min^{-1}. Figure 1 shows the comparison of experimental and calculated values of degree of conversion.

Table 1 Kinetic parameters for goethite dehydroxylation – model A3

No.	β/K min^{-1}	E_a/kJ mol^{-1}	A/min^{-1}	R^2	s
1	5	28.26	34.15	0.9441	0.0327
2	10	28.76	61.47	0.9965	0.0129
3	20	25.67	51.40	0.9983	0.0940

The diffractometric investigations proved that obtained product forms the amorphous hematite phase (protohematite) [13]. Figure 3 shows, respectively, the diffraction patterns of precipitated goethite (a), hematite formed at temperature 773 K (b) and the standard diffraction pattern of hematite phase taken from the JCPDS data base (c).

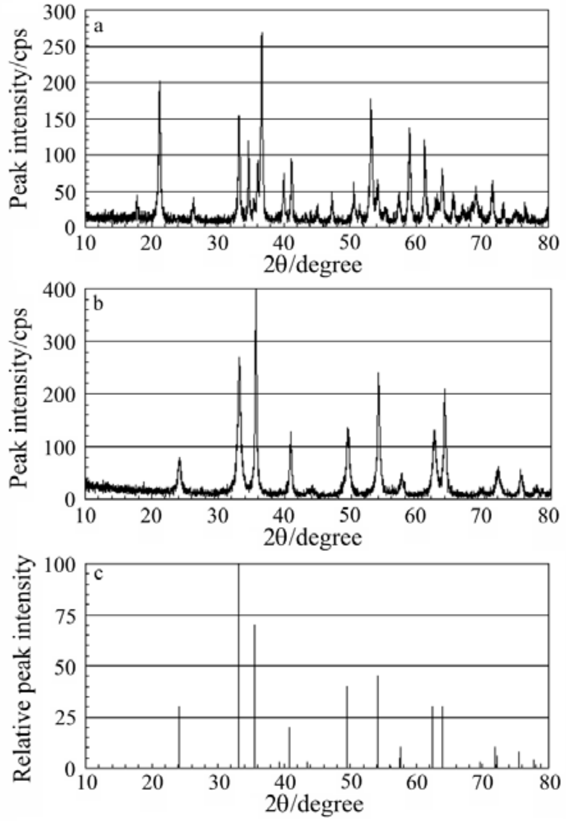

Fig. 3 Diffraction patterns of investigated samples: a – precipitated goethite, b – product of goethite dehydroxylation at temperature 773 K, c – standard diffraction pattern of hematite

The results of kinetic investigation of thermal dehydroxylation of titanium(IV) oxyhydroxide shown in Fig. 2 have been elaborated using identical as shown above method. The results of kinetic analyse for the selected third order equation F3 are given in Table 2.

The mean value of activation energy for the investigated range of heating rate is about 43.21 kJ mol^{-1} and pre-exponential coefficient equals $1.71 \cdot 10^5$ min^{-1}. Figure 2 shows the comparison of experimental and calculated values of degree of conversion. The value of activation energy calculated using isoalpha method is 51.8 kJ mol^{-1}.

Table 2 Kinetic parameters for dehydroxylation of titanium(IV) oxyhydroxide – model F3

No.	β/K min^{-1}	E_a/kJ mol^{-1}	A/min^{-1}	R^2	s
1	1.25	44.95	2.44E5	0.9856	0.0199
2	5	41.20	0.77E5	0.9916	0.0155
3	10	42.45	1.27E5	0.9916	0.0151
4	20	44.25	2.37E5	0.9922	0.0148

The obtained after thermal treatment product investigated by X-ray diffractometry shown that at investigated temperature range one can observe the systematic increase of crystallinity of dehydrated titanium dioxide but at temperature 773 K the obtained titanium dioxide reveals still the diffuse structure of anatase. This is illustrated by diffraction patterns shown in Fig. 4.

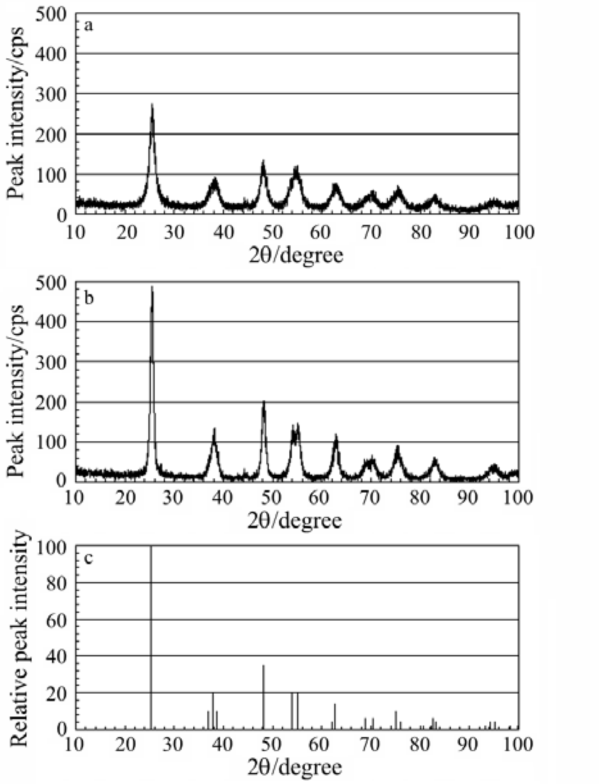

Fig. 4 Diffraction patterns of investigated samples: a – precipitated titanium(IV) oxyhydroxide, b – product of titanium(IV) oxyhydroxide dehydroxylation at temperature 773 K, c – standard diffraction pattern of TiO_2 (anatase)

Conclusions

From the shown above results it may be concluded that as a product of dehydroxylation of precipitated iron(III) oxyhydroxide (goethite) is obtained amorphous hematite. The dehydroxylation of titanium(IV) oxyhydroxide ('hydrated titanium dioxide') leads to formation of titanium dioxide phase with diffuse anatase structure.

The JMAEK model A3 has been used as the adequate equation describing the dehydroxylation reaction of goethite. The third order model F3 has been selected as the rate equation for reaction of dehydroxylation of titanium(IV) oxyhydroxide.

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