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ТВЕРДОФАЗНЫЙ СИНТЕЗ ФЕРРИТА КАЛЬЦИЯ СО СТРУКТУРОЙ БРАУНМИЛЛЕРИТА

В работе с помощью методов рентгенофазового, рентгеноструктурного и синхронного термического анализа, а также сканирующей электронной микроскопии исследован процесс получения феррита кальция из оксалата железа(II) и гидроксида кальция при их твердофазном взаимодействии. Результаты рентгенофазового анализа образца, подвергнутого термической обработке при 750 °С в течение 3 ч, свидетельствуют об образовании однофазного феррита кальция со структурой браунмиллерита. Анализ кривых DTA, указывает на то, что процессы кристаллизации продолжаются до температуры >1000 °С. Расчет субструктурных параметров полученного $Ca_2Fe_2O_5$ показывает, что величина размера области когерентного рассеяния равна 198 Å, а суммарное число микродеформаций составляет 0,8%. Площадь поверхности образца не превышает 5 $м^2/г$.

Ключевые слова: феррит кальция, твердофазный синтез, условия получения

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SOLID-PHASE SYNTHESIS OF CALCIUM FERRITE WITH BROWNMILLERITE STRUCTURE

The process of calcium ferrite preparing from ferrum (II) oxalate and calcium hydroxide by solid-phase interaction was studied using data of X-ray diffraction, X-ray phase analysis, simultaneous thermal analysis, and scanning electron microscopy. X-ray phase analysis results of a sample subjected to heat treatment at 750 °C for 3 h, show formation of single-phase brownmillerite structure of calcium ferrite $Ca_2Fe_2O_5$. Analysis of the DTA shows that crystallization process continues up to 1000 °C. Calculation of substructure parameters of $Ca_2Fe_2O_5$ shows that the area of coherent X-ray scattering is 198 Å, total amount of microstrains is 0.8 %. The specific surface area of the sample is not more 5 m^2/g.

Key words: calcium ferrite, solid phase synthesis, brownmillerite structure

Calcium ferrite possesses catalytic properties in a number of different reactions and can be used as analogue of precious metals containing catalyst [1, 2]. In [3, 4] it was proposed to use massive catalyst containing calcium and copper ferrites for carrying out a carbon monoxide conversion to hydrogen by steam, and properties of the catalyst was not inferior to traditional Fe-Cr oxide catalysts. The article [5] established the correlation between the maximum density of interfacial and the grain boundaries, the presence of weakly bounded oxygen and the specific catalytic activity of the samples in the reaction of CO oxidation. The authors of [6] examined the possibility of neutralization of gas emissions containing nitrogen oxide (I) on different crystal structures of ferrite catalysts.

Analysis of published data on the manufacture of calcium ferrite shows that there are different methods: precipitation from solution, the sol-gel, ceramic, mechanochemical and others [2, 5, 7-9]. It is known that producing method has a significant effect on the properties of the finished product. For example, specific surface area, content of acid-base centers and porosity have influence on the catalytic properties. Thus, to obtain materials with predetermined properties, it is necessary to establish the correlation between the preparing conditions and catalyst's physico-chemical characteristics.

EXPERIMENTAL

Ferrum oxalate $FeC_2O_4{\cdot}2H_2O$ and calcium hydroxide $Ca(OH)_2$ were used for solid phase synthesis of calcium ferrite $Ca_2Fe_2O_5$.

X-ray phase analysis (XRD) was performed on a diffractometer DRON-3M using Cu Kα radiation.

Substructure parameters were determined using Harmonic analysis of form the X-ray line (GIRL).

Thermogravimetric analysis (TG) and Differential thermal analysis (DTA) were performed using simultaneous thermal analysis instrument STA 449 F3 Jupiter at a heating rate of 5 °C·min^{-1}.

Microscopic images were obtained with a scanning electron microscope (SEM) VEGA 3 TESCAN.

The specific surface area was determined by the BET method using Sorbi-MS.

RESULTS AND ITS DISCUSSION

Figure 1 shows the results of simultaneous thermal analysis of a mixture of ferrum oxalate and calcium hydroxide in stoichiometric ratio to form calcium ferrite.

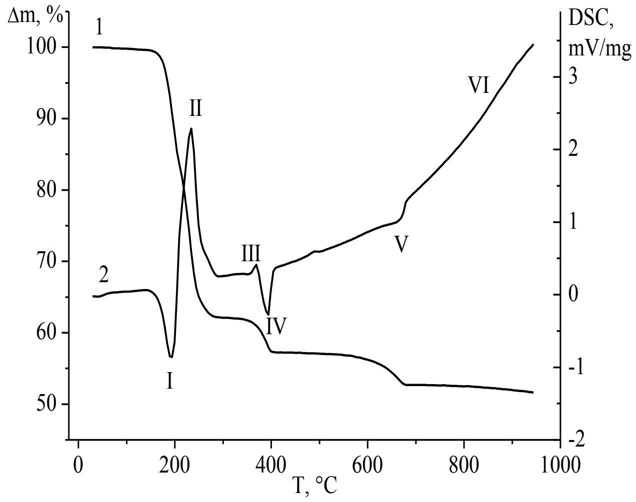

Fig. 1. Simultaneous thermal analysis of $FeC_2O_4{\cdot}2H_2O$ and $Ca(OH)_2$ mixture: 1-TG; 2- DTA
Рис. 1. Результаты синхронного термического анализа 1-TG, 2- DTA

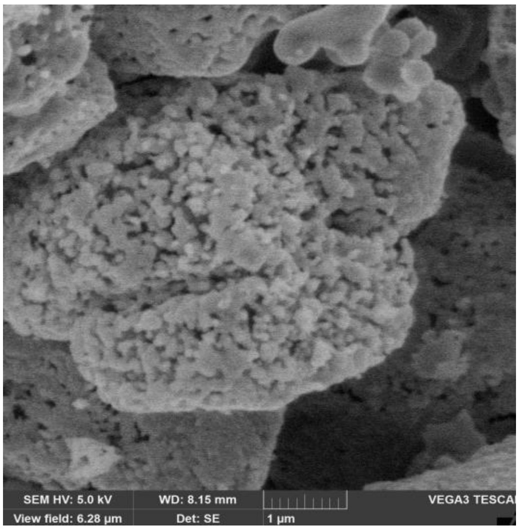

Fig. 2. The SEM images of $Ca_2Fe_2O_5$
Рис. 2. СЭМ изображения $Ca_2Fe_2O_5$

Calcination process is accompanied by 6 thermal effects (Fig.1):

I – endothermic heat effect at 130-200 °C – removal of adsorbed air and crystallization water;

II – exothermic heat effect at 200-285 °C – carbon monoxide oxidation, which is formed by the decomposition of ferrum oxalate;

III – exothermic heat effect at 360-380 °C can be caused by polymorphic transition of γ-Fe_2O_3 formed according to reaction (1) into α-Fe_2O_3;

$$2FeC_2O_4{\cdot}2H_2O \xrightarrow{t,\ 0.5O_2} \gamma\text{-}Fe_2O_3 + 2CO + +2CO_2 + 4H_2O \quad (1)$$

IV – endothermic heat effect at 380-410 °C - calcium hydroxide decomposition.

V – endothermic heat effect at 650-680 °C-calcium carbonate decomposition (which is due to calcium hydroxide carbonization during mechanical mixing of the initial reagents);

VI – exothermic heat effect is greatly extended and shows $Ca_2Fe_2O_5$ crystallization.

X-ray analysis of the sample calcined at 750 °C shows that the structure is one-phase. A set of reflections on the X-ray pattern corresponds to the brownmillerite structure of the calcium ferrite.

SEM images (Fig. 2) shows that it consists of spherical particles 0,1-0,2 size of microns, which form conglomerates of larger size (2-10 μm).

Table shows the conditions of the reaction and $Ca_2Fe_2O_5$ characteristics.

Table.
Reaction conditions and $Ca_2Fe_2O_5$ characteristics
***Таблица.* Условия получения и характеристики $Ca_2Fe_2O_5$**

Formula	Calcining temperature, °C	Calcining time, hour	Specific surface, m^2/g	Coherent X-ray scattering, Å	Total amount of microstrains, %
$Ca_2Fe_2O_5$	750	3	5	198	0,8

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ЛИТЕРАТУРА

1. **Tejuca L.G., Fierro J.L.G., Tascón J.M.D.** Structure and Reactivity of Perovskite-Type Oxides. Advances in catalysis. 1989. V. 36. C. 328-237.
2. **Исупова Л.А., Цыбуля С.В. Крюкова Г.Н.** Механохимический синтез и каталитические свойства феррита кальция $Ca_2Fe_2O_5$. *Кинетика и катализ.* 2002. Т. 43. № 1. С. 132-139.

REFERENCES

1. **Tejuca L.G., Fierro J.L.G., Tascón J.M.D.** Structure and Reactivity of Perovskite-Type Oxides. *Advances in catalysis.* 1989. V. 36. P. 237-328.
2. **Isupova L.A., Tsybulya S.V., Kryukova G.N.** Mechanochemical synthesis and catalytic properties of the calcium ferrite $Ca_2Fe_2O_5$. *Kinetics and Catalysis.* 2002. V. 43. N 1. P. 122-128.

3. **Румянцев Р.Н., Кочетков С.П., Лапшин М.А.** Влияние ферритов меди и кальция на активность и селективность катализаторов среднетемпературной конверсии CO. *Изв. вузов. Химия и хим. технология.* 2016. Т. 59. Вып. 3. С. 43-48.
4. **Ильин А.А., Ильин А.П., Курочкин В.Ю., Смирнов Н.Н.** Механохимический синтез катализатора для среднетемпературной конверсии монооксида углерода водяным паром. *Усп. в химии и хим. технологии.* 2007. Т. XXI. № 9 (77). С. 79-83.
5. **Исупова Л.А., Яковлева И.С., Цыбуля С.В.** Механохимический метод синтеза перовскитных катализаторов $La1_{-X}Ca_XFeO_{3-0.5X}$ для окислительных каталитических процессов. *Химия в интересах устойчивого развития.* 2002. Т. 10. № 1-2. С. 77-78.
6. **Rumyantsev R.N., Ilyin A.A., Babichev I.V., Ilyin A.P.** Decomposition of nitric oxide(I) on the ferrite with different crystal structures. *SITA-Journal*. 2014. V. 16. N 3. P. 1-5.
7. **Hasmonay E., Depeyrot J., Sousa M.H. et al.** Magnetic and optical properties of ionic ferrofluids based on nickel ferrite nanoparticles. *J. Appl. Phys.* 2000. V. 88. N 11. P. 6628- 6635.
8. **Tartaj P., Morales M.P., Veintemillas-Verdaguer S.** The preparation of magnetic nanoparticles for applications inbiomedicine. *J. Phys. D: Appl. Phys.* 2003. V. 36. P. 182-197.
9. **Губкин С.П., Кокшаров Ю.А., Хомутов Г.Б., Юрков Г.У.** Магнитные наночастицы: методы получения, строение и свойства. *Усп. химии*. 2005. Т. 74. № 6. С. 539-574.

3. **Rumyantsev R.N., Kochetkov S.P., Lapshin M.A.** Influence of calcium and copper ferrites on activity and selectivity of the medium temperature CO conversion catalysts. *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.* 2016. V. 59. N 3. P. 43-48 (in Russian)
4. **Il'in A.A., Il'in A.P., Kurochkin V. Yu., Smirnov N.N.** Mechanochemical synthesis of medium temperature conversion of carbon monoxide catalyst by water vapour. *Uspehi v khimii i khimicheskoiy tekhnologii.* 2007. V. XXI. N 9 (77). P. 79-83 (in Russian).
5. **Isupova L.A., Yakovleva I.S., Cybulja S.V.** Mechanochemical synthesis method of perovskite catalysts $La1\text{-}xCa_XFeO_{3-0.5X}$ for oxidizing catalytic processes. *Khimiya v interesakh ustoiychivogo razvitiya.* 2002. V. 10. N 1-2. P. 77-78 (in Russian).
6. **Rumyantsev R.N., Il'in A.A., Babichev I.V., Il'in A.P.** Decomposition of nitric oxide(I) on the ferrite with different crystal structures. *SITA-Journal.* 2014. V. 16. N 3. P. 1-5.
7. **Hasmonay E., Depeyrot J., Sousa M.H.** Magnetic and optical properties of ionic ferrofluids based on nickel ferrite nanoparticles. *J. Appl. Phys.* 2000. V. 88. N 11. P. 6628-6635.
8. **Tartaj P., Morales M.P., Veintemillas-Verdaguer S.** The preparation of magnetic nanoparticles for applications inbiomedicine. *J. Phys. D: Appl. Phys.* 2003. V. 36. P. 182-197.
9. **Gubkin S.P., Koksharov Yu.A., Khomutov G.B., Yurkov G.U.** Magnetic nanoparticles: preparation, structure and properties. *Russian Chemical Reviews.* 2005. V. 74. N 6. P. 489-520.

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