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Purification of Kiln Gas Formed in the Synthesis of Lithium Iron Phosphate

YU. V. OSTROVSKIY[1], G. M. ZABORTSEV[1], A. A. MATVEEV[2], N. N. MASLOV[2], V. A. KOCHNEV[2], S. A. REZVOV[2] and N. B. EGOROV[3]

[1]EYDOS Ltd.,
Ul. B. Khmelnitskogo 2, Novosibirsk 630075 (Russia)

E-mail: ost@vnipiet-nsk.ru

[2]JSC “Novosibirsk Chemical Concentrates Plant”,
Ul. B. Khmelnitskogo 94, Novosibirsk 630110 (Russia)

[3]Tomsk Polytechnic University,
Pr. Lenina 30, Tomsk 634050 (Russia)

Abstract

The composition of kiln gas from the synthesis of lithium iron phosphate ($LiFePO_4$) is considered. The catalytic oxidation of the mixture of ammonia vapour and carbon monoxide is studied. The apparatus and technological scheme of purification of kiln gas of the synthesis of lithium iron phosphate is proposed.

Key words: synthesis of lithium iron phosphate, kiln gas, ammonia vapour, carbon monoxide, gas purification, catalytic oxidation

INTRODUCTION

In 2010, the ROSNANO JSC and the Thunder Sky Chinese Co. decided to establish a Russian-Chinese joint venture in Novosibirsk for the production of lithium ion rechargeable batteries for electric vehicles using lithium iron phosphate ($LiFePO_4$) as the cathode material. For the purpose of implementation of the program of import substitution, the production of cathode material based on lithium iron phosphate is to be established at the Novosibirsk Chemical Concentrates Plant (NCCP) [1].

To master the technology of $LiFePO_4$ synthesis at the department of the production of commercial lithium products at NCCP, it is planned to make an experimental industrial unit for the production of lithium iron phosphate by means of high-temperature sintering of the mixture containing Li_2CO_3, Fe_2O_3, $(NH_4)\,HPO_4$, and carbon (molar ratio of 1 : 1 : 2 : 1.5) with the capacity up to 20 t/year (about 70 kg/day).

The kiln gas of $LiFePO_4$ synthesis contains toxic ingredients (dust of the mixture and $LiFePO_4$ gaseous components), so their release into the atmosphere without purification is unacceptable. Purification of kiln gases is assumed to be carried out through the removal of solid admixtures and subsequent catalytic purification from toxic gaseous impurities without the formation of secondary pollutants.

EXPERIMENTAL

Composition of the kiln gas of lithium iron phosphate synthesis

Thermodynamic calculations and thermogravimetric studies with the identification of the products of thermal decomposition of the mixture were carried out to predict the composition of the mixture formed in the synthesis of $LiFePO_4$.

Thermodynamic calculations were performed using the ASTRAL automated system of thermodynamic calculations and algorithms, developed in MEPhI (Moscow) [2]. The calculation algorithm is based on the method of characteristic functions extremum (MCFE), which is a generalization of the Gibbs' equilibrium criteria [3].

Thermogravimetric (TG) studies were performed using the SDT Q600 analyzer within temperature range 20–1000 °C in the inert atmosphere (argon). The sample heating rate was 10 °C/min.

Identification of the products of thermal decomposition was performed using XRD, and the mass spectra of absorption. The gases released during thermal decomposition were analyzed using a Trace DSQ gas chromatograph-mass spectrometer.

The X-ray diffraction patterns of the samples were recorded using a Shimadzu XDR 6000 diffractometer (CuK_α radiation). The X-ray diffraction patterns were recorded for samples aged after appropriate endoeffect within 3 h in vacuum.

Purification of kiln gases from the synthesis of lithium iron phosphate

It is expected to carry out purification of the kiln gas from the synthesis of $LiFePO_4$, containing NH_3, CO and CO_2, by mixing the outgoing gases with the ambient air, removing solid impurities and carrying out the subsequent catalytic oxidation of NH_3 and CO without the formation of secondary pollutants according to equations [4, 5]

$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$

$2CO + O_2 \rightarrow 2CO_2$

The dilution of outgoing kiln gases from the synthesis of $LiFePO_4$ is necessary to provide the possibility to purify the gases from the solid phase and to ensure the explosion safety of the catalytic oxidation of NH_3 and CO.

An integrated thermostated glass reactor was used to study the kinetics of the process of ammonia and carbon monoxide oxidation. The stable concentration of ammonia vapour was provided by supplying a small amount of air into the saturator filled with ammonia water; then the working concentrations were obtained by mixing the resulting gases with air. Carbon monoxide and dioxide were supplied from balloons.

Ammonia was determined through its interaction with Nessler reagent with the help of the KFK-2 photoelectric colorimeter; a Testo 335 electronic analyzer was used to measure the concentration of nitrogen dioxide (NO_2). The concentrations of carbon monoxide and dioxide were determined using the chlromatographic method.

Industrial catalysts were used in the studies: iron oxide (STK-05-3(F), PC AZK I OS, Angarsk, Russia) and aluminium-vanadium (AOK-78-55, PC KATKOM, Novosibirsk, Russia).

Before experiments, the catalysts were crushed; the fraction with grain size 1.0–1.2 mm was used. Each weighted portion of catalysts was blown with the air for 2–3 h at the experiment temperature before the experiments.

The degree of ammonia and carbon monoxide oxidation was calculated using equation

$\alpha = (C_{ini} - C_{fin})C_{ini} \cdot 100\ \%$

where α is the oxidation degree, %; C_{ini} and C_{fin} are the initial and final concentrations of NH_3 (CO) vapour, respectively, g/m^3.

Experiments on the catalytic oxidation of the mixture of gaseous ammonia, carbon monoxide and dioxide by atmospheric oxygen at the mixture of catalysts STK-05-3(F) (upper layer) and AOK-78-55 (lower layer) were carried out under the following conditions: the cata-

TABLE 1

Oxidation of the mixture of CO, CO_2 and NH_3 on the mixture of STK-05-3(F) and AOK-78-55 catalysts

T, °C	C_{CO}, g/m^3		CO conversion degree, %	C_{CO_2}, g/m^3		C_{NH_3}, g/m^3		NH_3 conversion degree, %	C_{NO}, mg/m^3
	Input	Output		Input	Output	Input	Output		
260	6.719	0	100.0	14.246	19.843	8.125	0.0375	99.5	83.44
285	5.443	0	100.0	18.571	21.115	7.500	1.0000	86.7	27.42
300	4.763	0	100.0	14.246	21.370	3.900	0.0325	99.2	34.68
310	3.799	0	100.0	14.246	16.790	3.593	0.0109	99.7	16.60
315	7.938	0	100.0	–	13.229	10.000	0.0750	99.3	84.80
330	5.557	0	100.0	15.264	26.458	3.645	0.0000	100.0	1053.0

lysts volume ratio 1 : 2, temperature 260–330 °C, the concentration of ammonia vapour 3.5–10.0 g/m^3, carbon monoxide 4.0–8.0 g/m^3, carbon dioxide 14.0–18.0 g/m^3, volume rate 5000 h^{-1}. The concentrations of pollutants were maximal taking into account mixing of the outgoing gases with air. The humidity of gases was 15–20 g/m^3. The results of experiments are presented in Table 1.

RESULTS AND DISCUSSION

In the course of thermodynamic calculations at a pressure of 0.1 MPa, the temperature of oxidation process was varied from 300 to 700 °C (the temperature range of mixture agglomeration). The results of calculations are shown in Fig. 1.

Such toxic gases as ammonia or carbon monoxide can be present in the kiln gas from the synthesis of lithium iron phosphate; in addition, the thermodynamic probability of the formation of carbon monoxide increases with an increase in temperature.

The derivatogram of the mixture used to obtain lithium iron phosphate is shown in Fig. 2. One can see that the mass decreases in several stages while temperature is increased to 1000 °C; the endothermic thermal effects occur at the temperature of 147, 196 and 701 °C.

According to the data of mass spectrometry, the ions with mass numbers 17, 18 and 44 are present in the thermolysis products of the original mixture. These ions are the molecular ions NH_3^+, H_2O^+ and CO_2^+, respectively.

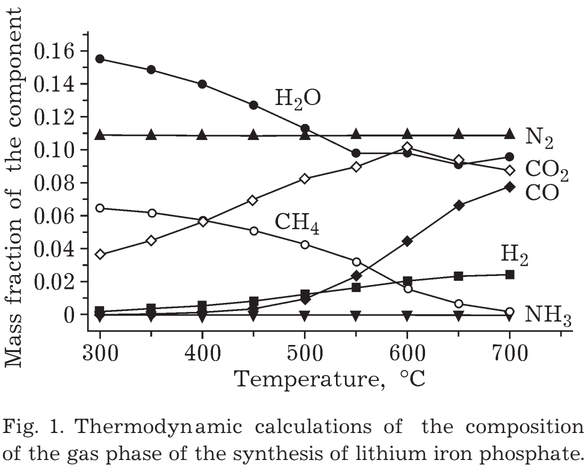

Fig. 1. Thermodynamic calculations of the composition of the gas phase of the synthesis of lithium iron phosphate.

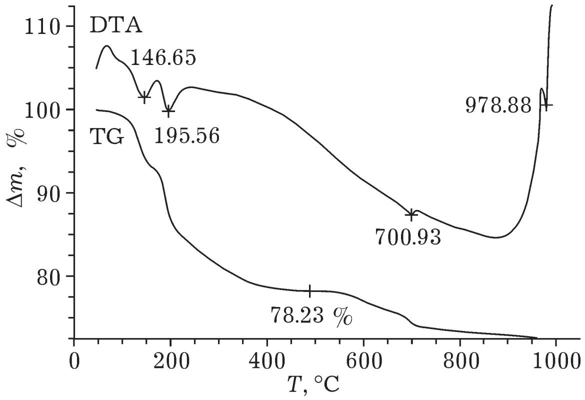

Fig. 2. Derivatogram of the mixture used to obtain lithium iron phosphate.

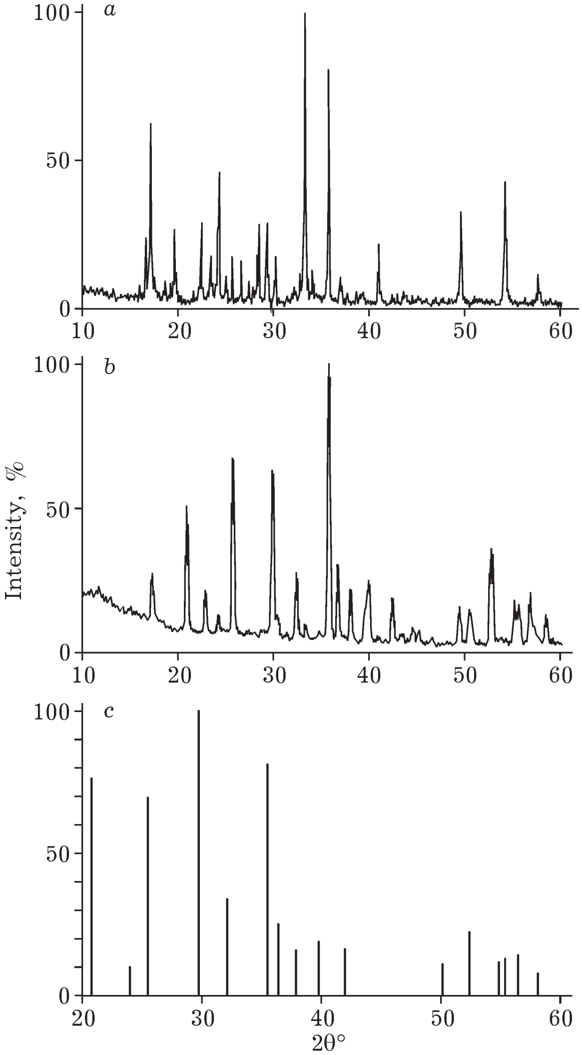

Fig. 3. X-ray diffraction patterns of the initial mixture for obtaining lithium iron phosphate (*a*) and the mixture kept at 300 °C (*b*), as well as the line diffraction pattern of $LiFePO_4$ (JCPDS 40-1499) (*c*).

TABLE 2

Oxidation of the mixture of CO, CO_2 and NH_3 in a two-reactor catalytic set-up

T_1, °C	T_2, °C	C_{CO}, g/m^3 Input	Output	CO conversion degree, %	C_{CO_2}, g/m^3 Input	Output	C_{NH_3}, g/m^3 Input	Output	NH_3 conversion degree, %	C_{NO}, mg/m^3
290	320	7.824	0.015	99.8	6.105	18.381	3.5	0.09	97.4	1.5
280	300	6.350	0.027	99.6	3.816	12.211	3.25	0	100.0	3.5
280	290	7.825	0	100.0	5.596	17.808	2.92	0	100.0	3.0
290	290	8.108	0.040	99.5	4.579	14.755	1.5	0	100.0	0.8

Note. T_1, T_2 are temperatures of the catalysts of the first reactor (STK-05-3(F)) and the second reactor (AOK-78-55), respectively.

The diffraction patterns of the initial mixture and the mixture annealed at 300 °C in vacuum are shown in Fig. 3 along with the line X-ray diffraction pattern of lithium iron phosphate (JCPDS 40-1499). We can see that the X-ray diffraction pattern of the initial mixture exposed in vacuum at 300 °C contains a seet of reflections including the basic reflections of lithium iron phosphate.

Relying on the data of XPA and TA, the following scheme can be proposed to describe the formation of lithium iron phosphate during heating the mixture containing Fe_2O_3, Li_2CO_3, $(NH_4)_2HPO_4$ and C in the inert atmosphere to 300 °C:

$$(NH_4)_2HPO_4 \rightarrow NH_4H_2PO_4 + NH_3\uparrow$$

$$2NH_4H_2PO_4 + Li_2CO_3 \rightarrow 2LiH_2PO_4 + 2NH_3\uparrow + CO_2\uparrow + H_2O$$

$$4LiH_2PO_4 + 2Fe_2O_3 + C \rightarrow 4LiFePO_4 + CO_2\uparrow + 4H_2O$$

The endothermic effect observed on the DTA curve (see Fig. 2) at $T = 701$ °C is due to the decomposition of $LiFePO_4$ according to reaction

$$8LiFePO_4 + 9C \rightarrow 4Fe_2P + 2Li_4P_2O_7 + 9CO_2\uparrow$$

The formation of carbon monoxide is likely to occur in the interaction CO_2 with excess carbon according to reaction

$$C + CO_2 \rightarrow 2CO\uparrow$$

It follows from the data obtained that within temperature range 310–315 °C deep oxidation of ammonia vapour and carbon monoxide in the presence of carbon dioxide occurs (up to CO_2 concentration 25 g/m^3) with the minimal generation of nitrogen oxides.

Substantial heating of the catalysts (320–330 °C) is observed during the oxidation of ammonia vapour and carbon monoxide, which leads to a sharp increase in the yield of nitrogen oxide (see Table 1). To decrease the effect of adiabatic heating on the characteristics of ammonia oxidation, a two-reactor set-up was used in which the catalysts (STK-05-3(F) and AOK-78-55) were placed in separate reactors. This allowed us to control the temperature of each catalyst layer individually.

The results of the oxidation of a mixture of ammonia vapour, carbon monoxide and dioxide by atmospheric oxygen on the STK-05-3(F) and AOK-78-55 catalysts in the two-reactor laboratory set-up within temperature range 280–320 °C at the volume ratio of catalysts in the reactor 1 : 2 are presented in Table 2. One can see that at the temperature of 280–290 °C in the first reactor and at the temperature of 290–320 °C in the second reactor almost complete oxidation of ammonia vapour and carbon monoxide is observed. Thus, a two-reactor set-up allows one to achieve the minimal generation of nitrogen oxides during the oxidation of a mixture of CO, CO_2 and NH_3.

To purify the outgoing gas of the process of $LiFePO_4$ synthesis from solid and gaseous admixtures, a scheme was proposed that includes the following stages: mixing of the gases formed in the synthesis of $LiFePO_4$ (not more than 10 m^3/h) with air (total gas flow rate 500 m^3/h); separation of the solid phase in a bag filter; subsequent oxidation of ammonia vapour and carbon monoxide in the catalytic reactor of the KROT-500 type [6].

A scheme of integrated purification of kiln gas of $LiFePO_4$ production from solid and gaseous admixtures (Fig. 4) includes the following units: gas mixing unit, into which the gases enter from the rotating drum-type furnaces and with periodic mixture loading, bag filter, catalytic reactor, ventilators. The operation of the unit proceeds as follows: kiln gases at a tem-

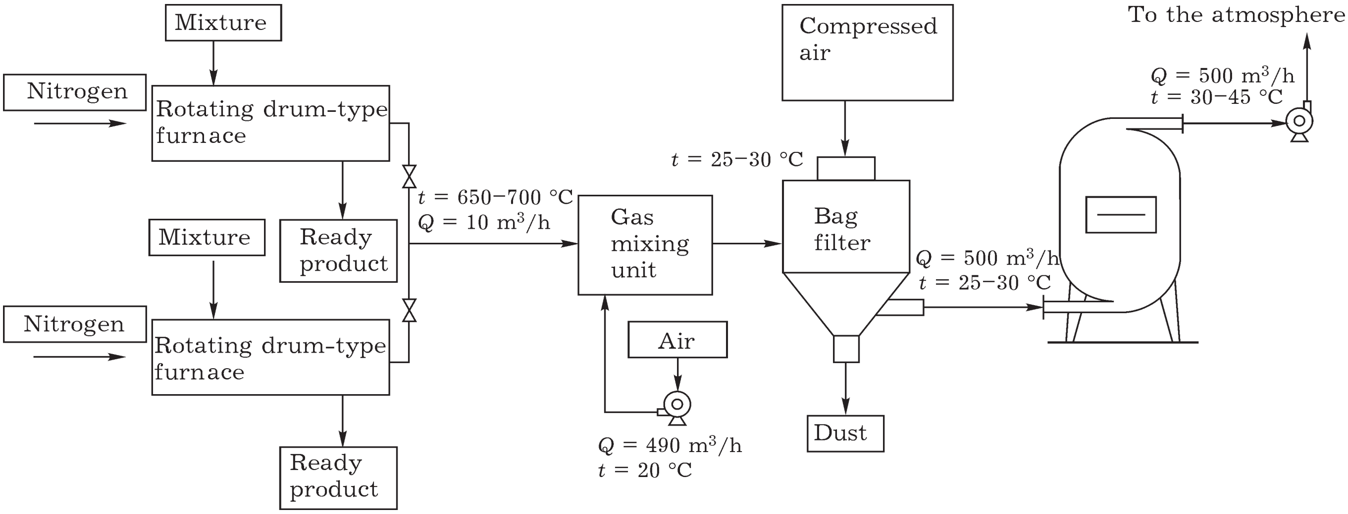

Fig. 4. Apparatus technological scheme of the purification of kiln gases from the experimental industrial production of $LiFePO_4$. See text for designations.

perature up to 700 °C enter the mixing unit where sharp cooling of the gases occurs and temperature decreases to 25–30 °C. Dust is separated in the bag filter.

The purification of gases from ammonia vapour and carbon monoxide is performed by means of thermocatalytic oxidation with atmospheric oxygen using a mixture of AOK-78-55 and STK-05-3(F) catalysts.

The gas under purification is fed into the catalytic reactor KROT-500. The gas flow rate is 500 nm^3/h, temperature in the reactor is 300–320 °C, the volume rate is 5000 h^{-1}.

The concentrations of ammonia vapour and carbon monoxide at the outlet of the catalytic reactor reach 5.0 and 2.0 mg/m^3, respectively. Purified gases are emitted into the atmosphere with the help of the ventilators.

CONCLUSION

The following parameters were achieved as the result of the implementation of proposed technology of gas purification.

1. The losses of mixture components and $LiFePO_4$ (due to dusting in the furnace) are decreased as these components are trapped and returned into production.

2. Gaseous emissions are purified (the concentrations of ammonia vapour and carbon monoxide in the gas emitted from the reactor do not exceed 5 mg/m^3).

Passing to the industrial production of lithium iron phosphate, it is necessary to perform utilization of gaseous admixtures too (ammonia vapour and carbon monoxide) by means of their processing either into initial components of the mixture for the synthesis of $LiFePO_4$ or into other commercial products.

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