MECHANISM AND KINETICS OF THERMAL DECOMPOSITION OF NICKEL(II) SULFATE(VI) HEXAHYDRATE

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Abstract

This work presents results of research on thermal decomposition of nickel(II) sulfate(VI) hexahydrate in air and in helium atmosphere. On the base of TG and XRD results a mechanism of thermal decomposition of $NiSO_4$ hydrate was established. For calculations of kinetic parameters of the Arrhenius equation, the Coats–Redfern approximation was applied. Choice of $g(\alpha)$ function and thus of a mechanism best describing given stage of decomposition was performed by testing 12 kinetic models.

Keywords: Coats–Redfern's approximation, kinetics of thermal decomposition, nickel(II) sulfate(VI) hydrates

Introduction

Heterogeneous catalysts for dimerization and oligomerization of olefins, consisting mainly of nickel compounds supported on oxides, have been known for many years. In many papers [1–4], it has been shown that $NiO-TiO_2$, $NiO-ZrO_2$ and $NiO-\gamma-Al_2O_3$ modified with sulfate or tungstate ions are very active for ethylene dimerization. High catalytic activities in reactions are related to acidic properties of modified catalysts, which originated from the inductive effect of S=O or W=O bonds of the complex formed by the interaction of oxides with sulfate or tungstate ions.

Thermal decomposition of d-electron metal sulfates has also been used as an important reaction in chemical and metallurgical industries. The reaction has also been under recent investigation for many potential applications, e.g. possible storage of solar energy or nuclear heat. One of suggested applications is hydrogen production by a thermochemical water-splitting process [5].

The basic kinetic equation describing the rate of thermal dissociation of solids (Arrhenius equation) can be written in a form:

$$\frac{d\alpha}{dT} = \frac{A}{\alpha}\exp\left(-\frac{E}{RT}\right)f(\alpha) \tag{1}$$

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where T – is the current temperature of sample, A – pre-exponential factor, E – activation energy, R – universal gas constant, α – conversion degree.

By integrating the Eq. (1) a solution can be obtained in the form:

$$g(\alpha) = \frac{A}{\beta} \int_{T_0}^{T_\alpha} \exp\left(-\frac{E}{RT}\right) \mathrm{d}T \qquad (2)$$

This integral has no analytical solution and therefore in the kinetics theory of non-isothermal decomposition of solids some approximate dependence formulas are used [6]. One of convenient forms of them is the Coats–Redfern approximation [6] written as:

$$\ln\left(\frac{g(\alpha)}{T^2}\right) = \ln\left[\left(\frac{AR}{\beta E}\right)\left(1 - \frac{2RT_\mathrm{m}}{E}\right)\right] - \frac{E}{RT} \qquad (3)$$

where T_m – is the temperature corresponding to maximum rate of conversion for a given stage, β – the rate of heating a sample.

The dependence 3 is a basic equation making it possible, on the base of experimental data, to establish the reaction mechanism by determining the $g(\alpha)$ function as well as to find the values of parameters in the Arrhenius equation.

Thermal decomposition of hydrates of many d-electron metal sulfates (also $NiSO_4 \cdot 6H_2O$) was studied by many investigators [7–10]. Unfortunately, many publications on a decomposition of nickel(II) sulfate(VI) hexahydrate do not contain kinetic data for an inert atmosphere. In this work, thermal decomposition of $NiSO_4 \cdot 6H_2O$ was studied in two different atmospheres (air and helium). For calculations of kinetic parameters of the Arrhenius equation, the Coats–Redfern approximation was applied.

Experimental

A reagent used for research was nickel(II) sulfate(VI) hydrate $NiSO_4 \cdot 6H_2O$ obtained by a slow crystallisation from a saturated solution of nickel(II) sulfate(VI) (pure, product of POCh Gliwice, Poland). The obtained crystals of hydrate were dried in acetone and ground in an agate mortar. DTA/TG investigations were carried out by means of a SDT 2960 apparatus, product of TA Instruments. The measurements were performed in corundum crucibles in the atmosphere of air or helium (gas flow 110 mL min^{-1}), at heating rates of 2, 4, 6, 8 and 10 K min^{-1}. The mass of $NiSO_4 \cdot 6H_2O$ portions were within the 16–40 mg range. The final and intermediate solid products of $NiSO_4 \cdot 6H_2O$ decomposition in air and in helium atmosphere were identified by XRD. Investigations by this method were conducted with the use of an X-ray diffractometer DRON-3, the radiation CoK_α ($\lambda = 0.179021$ nm). Solid products of reaction were identified by comparing the X-ray powder diffraction patterns of the investigated samples with the data contained in the PDF cards of the JCPDF database [11].

Results and discussion

The investigations were begun with trying to establish the number of water molecules contained by the obtained nickel(II) (VI) hydrate. For this purpose the prepara-
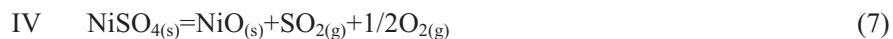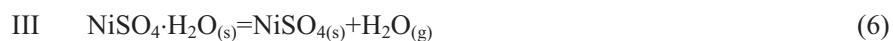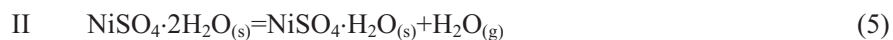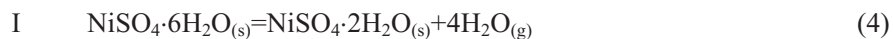
tion obtained by crystallisation was subjsulphateected to DTA/TG and XRD examination. On the base of the mass change and the XRD analysis it was found that the hydrate of $NiSO_4$ contained 6 water molecules.

Figure 1 presents the DTA/TG curves recorded while heating the samples of $NiSO_4 \cdot 6H_2O$ in the atmosphere of air and of helium, at a heating rate of 10 K min^{-1}. In each DTA curve four endothermic effects were recorded. In order to determine the characteristic of these effects, the samples of $NiSO_4 \cdot 6H_2O$ were heated for 4 h, in a flow furnace, in the following temperatures: 383, 423, 473, 533, 773 and 1173 K. These temperatures were established on the base of DTA curves. After the required heating time the samples were rapidly cooled to ambient temperature and subjected to XRD investigations. The results of such investigations for 'frozen' samples are showed in Table 1.
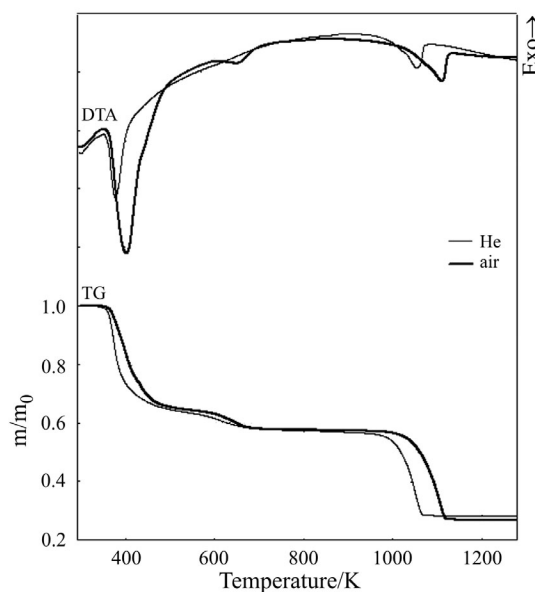
Fig. 1 DTA/TG curves of $NiSO_4$ hydrate (air and helium atmosphere, β=10 K min^{-1})

On the ground of the mass changes recorded in the TG curves, the results of XRD analysis and literature information [12–20], it was established that the mechanism of thermal decomposition of $NiSO_4 \cdot 6H_2O$, in air and helium atmosphere, can be described by the following equations:

I $NiSO_4 \cdot 6H_2O_{(s)} = NiSO_4 \cdot 2H_2O_{(s)} + 4H_2O_{(g)}$ (4)

II $NiSO_4 \cdot 2H_2O_{(s)} = NiSO_4 \cdot H_2O_{(s)} + H_2O_{(g)}$ (5)

III $NiSO_4 \cdot H_2O_{(s)} = NiSO_{4(s)} + H_2O_{(g)}$ (6)

IV $NiSO_{4(s)} = NiO_{(s)} + SO_{2(g)} + 1/2O_{2(g)}$ (7)

Table 1 Conditions of constant-temperature treatment and XRD results for $NiSO_4 \cdot 6H_2O$ samples heated in a flow furnace

Measurement No.	'Freezing' temp./K	Identified phases (air atmosphere)	Identified phases (helium atmosphere)
1	ambient temperature	$NiSO_4 \cdot 6H_2O$ (tetragonal)	$NiSO_4 \cdot 6H_2O$ (tetragonal)
2	383	$NiSO_4 \cdot 2H_2O$	$NiSO_4 \cdot 2H_2O$
3	423	$NiSO_4 \cdot 2H_2O$ $NiSO_4 \cdot H_2O$	$NiSO_4 \cdot H_2O$
4	473	$NiSO_4 \cdot H_2O$	$NiSO_4 \cdot H_2O$
5	533	$NiSO_4 \cdot H_2O$	$NiSO_4 \cdot H_2O$

Tables 2 and 3 list individual stages of thermal treatment conducted in air and in helium, applied heating rates, temperature ranges in which the individual stages of decomposition occur (ΔT) and maximum temperatures of peaks recorded in DTA curves (T_m). The calculated values of the Arrhenius equation parameters (A and E) and the values of correlation coefficient r as well as the kinetic model best describing given stage are also presented there. The kinetic model for given stage was established on the base of the best values of the correlation coefficient and identical courses of the $k(T)$ dependence for five applied heating rates. This last criterion determined the selection of kinetic model. The course of the dependence of rate constant for $NiSO_4 \cdot 6H_2O$ thermal decomposition on the temperature, concerning the IV stage of this reaction, at the applied heating rates, both in air and in helium atmosphere, is presented in Fig. 2.
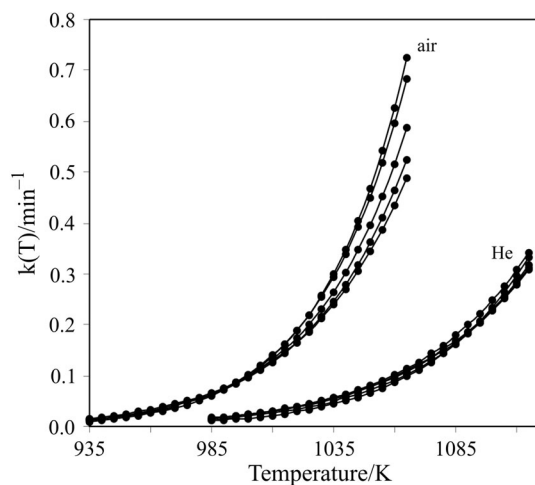
Fig. 2 Dependence of reaction rate constant k on temperature for IV stage of $NiSO_4 \cdot 6H_2O$ thermal decomposition (air and helium atmosphere)

Table 2 Results of kinetic calculations of $NiSO_4 \cdot 6H_2O$ thermal decomposition in air atmosphere

Stage	β/K min^{-1}	Kinetic model	E/kJ mol^{-1}	A/min^{-1}	r	T_m/K	ΔT/K
I	2		198.35	3.5747E+27	−0.99640	372.6	352–389
	4		191.30	3.3942E+26	−0.99566	377.7	355–394
	6	F2	148.31	4.7765E+20	−0.99235	385.1	360–409
	8		119.54	5.6088E+16	−0.98747	388.8	365–423
	10		113.18	8.5872E+15	−0.98277	390.8	366–427
II	2		59.12	2.2245E+07	−0.98908	457.4	394–560
	4		66.95	1.4288E+08	−0.98367	471.5	400–568
	6	F3	82.53	4.6698E+09	−0.98663	493.1	416–571
	8		82.78	4.9762E+09	−0.98069	503.1	427–579
	10		80.59	1.9998E+09	−0.97370	503.6	432–586
III	2		295.27	5.8894E+24	−0.98962	602.7	570–627
	4		254.23	4.0023E+21	−0.99199	611.7	576–649
	6	F2	224.63	1.7430E+19	−0.99108	615.2	581–659
	8		223.28	1.4603E+19	−0.98829	621.5	590–670
	10		226.77	2.7741E+19	−0.99174	626.4	595–677
IV	2		242.54	7.7930E+10	−0.99629	1053.9	987–1064
	4		223.85	9.8446E+09	−0.99717	1064.1	990–1078
	6	A2	205.84	1.3844E+09	−0.99752	1091.6	1004–1103
	8		208.34	1.7995E+09	−0.99621	1104.5	1017–1116
	10		218.15	5.7502E+09	−0.99575	1104.3	1018–1112

Table 3 Results of kinetic calculations of $NiSO_4 \cdot 6H_2O$ thermal decomposition in helium atmosphere

Stage	β/K min^{-1}	Kinetic model	E/kJ mol^{-1}	A/min^{-1}	r	T_m/K	ΔT/K
I	2		246.97	6.8759E+34	−0.99309	360.7	348–380
	4		243.92	2.5980E+34	−0.99145	365.4	347–377
	6	F2	226.83	1.0326E+32	−0.99393	369.6	350–380
	8		244.17	2.7084E+34	−0.99309	370.3	350–381
	10		237.29	3.2687E+33	−0.98412	372.8	352–381
II	2		127.78	2.4455E+15	−0.98827	416.9	385–466
	4		110.92	2.3651E+13	−0.98827	417.0	389–447
	6	F2	102.36	2.5445E+12	−0.98979	429.1	400–465
	8		101.73	2.1029E+12	−0.98970	429.4	400–466
	10		114.12	6.0489E+13	−0.98866	437.4	407–470
III	2		159.12	1.0446E+13	−0.98781	608.2	565–666
	4		162.21	1.7822E+13	−0.98766	618.4	570–672
	6	F2	168.95	6.2609E+13	−0.98904	618.2	575–676
	8		170.68	9.0305E+13	−0.98926	628.5	580–681
	10		182.91	9.3802E+14	−0.99223	634.5	585–685
IV	2		257.27	2.8771E+12	−0.99675	984.4	935–1003
	4		270.11	1.2978E+13	−0.99705	1004.4	595–1025
	6	A2	228.29	1.0987E+11	−0.99808	1023.2	965–1045
	8		241.51	4.5998E+11	−0.99776	1027.0	971–1052
	10		218.06	2.4418E+10	−0.99743	1037.9	977–1064

The results of calculations presented in Tables 2 and 3 indicate that both in air and in helium atmosphere the I stage of decomposition is best described by the kinetic model F2 (second-order reaction $g(\alpha)=[(1-\alpha)^{-1}-1]$), the II stage of decomposition in air atmosphere – the model F3 (third-order reaction $g(\alpha)=[(1-\alpha)^{-2}]$), and in helium atmosphere – the model F2. On the other hand, the stages III and IV, regardless of the kind of gas atmosphere, are best described by the models F2 and A2 (random nucleation – I Avrami equation $g(\alpha)=[-\ln(1-\alpha)]^{1/2}$), respectively.

Conclusions

It has been established on the ground of DTA/TG and XRD investigations that the process of thermal decomposition of nickel(II) sulfate(VI) hydrate both in air and in helium atmosphere occurs in four endothermic stages. First three stages are associated with the salt dehydration, while the last one – with decomposition of anhydrous $NiSO_4$.

For each stage of decomposition and for each heating rate the dependence of conversion degree on temperature has been determined. By applying the Coats–Redfern approximation the respective kinetic model expressed in terms of the $g(\alpha)$ function has been established and the Arrhenius equation parameters A and E have been calculated.

References

1 J. R. Sohn and D. C. Shin, J. Catal., 160 (1996) 314.
2 J. R. Sohn, H. W. Kim, M. Y. Park, E. H. Park, J. T. Kim and S. E. Park, Appl. Catal. A: Gen., 128 (1995) 127.
3 J. R. Sohn and S. Y. Lee, Appl. Catal. A: Gen., 164 (1997) 127.
4 J. R. Sohn and W. C. Park, Appl. Catal. A: Gen., 239 (2003) 269.
5 J. E. Funk and R. M. Reinstrom, Ind. Eng. Chem. Process Des. Dev., 5 (1966) 336.
6 A. W. Coats and I. P. Redfern, Nature, 201 (1964) 68.
7 H. Tagawa and H. Saijo, Thermochim. Acta, 91 (1985) 67.
8 H. Tagawa, Thermochim. Acta, 80 (1984) 23.
9 G. A. Kolta and M. H. Askar, Thermochim. Acta, 11 (1975) 65.
10 R. V. Siriwardane, J. A. Poston, E. P. Fisher, M. S. Shen and A. L. Miltz, Appl. Surf. Sci., 152 (1999) 219.
11 JCPDF PDF No: 77-0682, 17-0483, 81-0021.
12 M. E. Brown, D. Dollimore and A. K. Galwey, Reactions in the Solid State, Comprehensive Chemical Kinetics, Vol. 22, Elsevier, Amsterdam 1980.
13 E. Ingier-Stocka, J. Therm. Anal. Cal., 65 (2001) 561.
14 V. Jordanovska, B. Boyanow and Lj. Pejov, J. Therm. Anal. Cal., 71 (2003) 629.
15 V. Petkova and Y. Pelovski, J. Therm. Anal. Cal., 64 (2001) 1037.
16 V. Petkova and Y. Pelovski, J. Therm. Anal. Cal., 64 (2001) 1025.
17 Y. Pelovski, V. Petkova and S. Nikolov, Thermochim. Acta, 274 (1996) 273.
18 V. Jordanovska, B. Boyanow and Lj. Pejov, J. Therm. Anal. Cal., 71 (2003) 629.
19 B. V. L'vov and V. L. Ugolkov, J. Therm. Anal. Cal., 74 (2003) 583.
20 E. Tomaszewicz and M. Kotfica, J. Therm. Anal. Cal., 74 (2003) 583.