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INFLUENCE OF ENCAPSULATION ON THE MECHANISM OF THERMAL DESTRUCTION OF CYANIDE TRANSITION METAL COMPLEXES

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Abstract

The results of investigation of the influence of encapsulation on the mechanism of thermal decomposition of cyanide transition metal complexes, based on data obtained by methods of differential thermal analysis (inert atmosphere) and thermodesorption (mass-spectral monitoring of gaseous products) are represented. It was established, that encapsulation of cyanide iron(II) and cobalt(III) complexes in faujasite type zeolite results in the hydrolytic mechanism of thermal destruction of complexes, unlike to bulk analogues, which is determined by essential decreasing of the temperature of complex anions encapsulated destruction beginning, up to temperatures while zeolite water molecules are saved; the gaseous products of thermal destruction composition is determined by the peculiarities of localization of cations of different nature in inclusion compounds.

Keywords: cyanide transition metal complexes, differential thermal analysis, encapsulation of complexes in faujasite, localization of cations in faujasite, thermal destruction mechanism, thermodesorption with mass-spectral monitoring of products

Introduction

Methods of encapsulation in zeolites of positively charged complex ions and neutral complexes are sufficiently well elaborated upon [1], whereas encapsulation in negatively charged carrier framework of complex anions (which include cyanide transition metal complexes) presents a topical scientific problem [2–7].

The encapsulation of cyanide transition metal complexes in the large cages of faujasite (FAU) results in an essential modification of a porous structure and geometry of FAU inner-crystalline space, that should have an effect on reactivity of such inclusion compounds as a whole, and complexes encapsulated.

The formation of anionic cobalt cyanide complexes inside zeolite Y as result of the reaction of Co-exchanged faujasite with NaCN in methanol or formamide represents the first example of a synthesis of anionic complex inside zeolite framework [2–3]. The monoionic distribution of cobalt(III) cyanide complexes in faujasite framework can be achieved by using amine cobalt(III) complexes as initial substances: the reaction with NaCN in boiling ethanol or *i*-propanol of $[Co(NH_3)_6]^{3+}$-ex-

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changed zeolite NaY leads to formation of Na[Co$(CN)_6$]FAU [4, 6, 7]. We admitted that approach proposed by Drago and co-workers [2] can be applicable to syntheses of iron(II) hexacyanide complexes in faujasite framework. In fact, the reaction of Fe-exchanged NaY with NaCN in boiling *i*-propanol leads to formation of Na[Fe$(CN)_6$]FAU with practically monoionic distribution of complex species in faujasite framework [4–7].

The present work is devoted to clearing up the influence of encapsulation on the mechanism of thermal decomposition of cyanide iron and cobalt complexes, as well as to establish the correlation between such processes and the peculiarities of localization of cations of different nature in inclusion compounds.

It is known, that the mechanism of bulk cyanoferrates thermal decomposition is determined in a main by the nature of inner-spheric cations in complexes [8]. The mechanism of decomposition of alkaline, alkaline-earth, transition metal cyanoferrates is non-hydrolytic, whereas cyanoferrates of aluminium, scandium and some other metals are decomposed on the hydrolytic one [8] which, unlike the non-hydrolytic one, is characterized by the presence of HCN in gaseous products and overlapping temperature intervals of separation of thermal decomposition products [8].

Experimental

Synthesis of faujasites with encapsulated cyanide transition metal complexes (CN-FAU) with unit cell formula $M_{a1n1}...M_{aknk}[M_b(CN)_6]_8\ [(AlO_2)_{64}\ (SiO_2)_{128}]\cdot nH_2O$, designated in accordance to [4–5] as $M_{a1}...M_{ak}[M_b(CN)_6]$FAU ($M_a$=Na, K, Cs, Ni, Cu, Co; M_b=Fe, Co), were carried out according to [4–5].

The characterization of samples was carried out by the powder X-ray diffraction (XRD) data (automated diffractometer DRON-3M, CuK_α radiation) and infrared spectra (‘Specord 75IR’ spectrometer, pellets with KBr, region 4000–400 cm^{-1}).

The thermal researches were carried out by using Q-1000 device (MOM; Paulik, Paulik, Erdey system) in helium atmosphere (volumetric velocity: 60 ml min^{-1}), temperature 293–1273 K, velocity of heating: 10 K min^{-1}. For the investigation of the samples by thermodesorption method with mass-spectral monitoring of gaseous products MX-1310 mass-spectrometer was used (vacuum 10^{-7} torr, velocity of heating: 5 K min^{-1}, ionization of products – by electronic impact method: energy: 40 eV, accelerating voltage: 5 kV).

The PEAKFIT program was applied to select components of complicated absorption bands in IR spectra (ν_{CN} region) and nitrogen-containing products thermodesorption curves.

Results and discussion

The results obtained from application to investigation of thermal destruction of encapsulated in faujasite cyanide complexes of the combination of differential thermal analysis and thermodesorption method with mass-spectral monitoring of gaseous products are presented in Table 1.

Table 1 Composition of gaseous products of CN-FAU thermal transformations

Sample (cations per unit cell)	Temperature/K	Gaseous products, molecules per unit cell			
		H_2O	HCN	C_2N_2	N_2
Na[Co(CN)$_6$]FAU ($88Na^+$)	up to 550	11	16	–	–
	550–650	4	–	–	–
	650–900	1	4	2	4
	900–1050	–	–	–	8
Na[Fe(CN)$_6$]FAU ($96Na^+$)	up to 675	7	24	4	–
	675–725	2	–	–	–
	725–925	1	4	1	5
NaK[Fe(CN)$_6$]FAU ($9Na^+$, $87K^+$)	up to 575	10	32	–	–
	575–775	3	–	–	–
	775–900	2	16	–	–
NaNi[Fe(CN)$_6$]FAU ($74Na^+$, $11Ni^{2+}$)	up to 575	19	16	4	–
	575–675	4	2	2	1
	675–775	2	4	3	3
NaCu[Fe(CN)$_6$]FAU ($6Na^+$, $45Cu^{2+}$)	up to 525	12	2	8	3
	525–600	3	4	–	2
		1	–	–	8

Table 2 The influence of cationic composition of CN-FAU and bulk cyanoferrates on composition of gaseous products of their thermal transformations

Sample	Cations[a]				Products[a]		
	Na^+	K^+	Ni^{2+}	Cu^{2+}	HCN	C_2N_2	N_2
Na[Fe(CN)$_6$]FAU	96	–	–	–	28	–	5
$Na_4[Fe(CN)_6]$	32	–	–	–	–	–	8
NaK[Fe(CN)$_6$]FAU	9	87	–	–	48	–	–
$K_4[Fe(CN)_6]$	–	32	–	–	–	–	8
NaNi[Fe(CN)$_6$]FAU	74	–	11	–	22	9	4
$Ni_2[Fe(CN)_6]$	–	–	16	–	–	4	20
NaCu[Fe(CN)$_6$]FAU	6	–	–	45	6	8	13
$Cu_2[Fe(CN)_6]$	–	–	–	16	–	8	16

[a] For CN-FAU – per unit cell; for bulk cyanoferrates – per 8 $[Fe(CN)_6]^{4-}$-anions

Main stages of thermodestruction processes and corresponding mass losses were established from the thermal analysis in inert atmosphere data, and analysis in detail of gaseous products composition on each stage was carried out by thermodesorption method with mass-spectral monitoring of gaseous products data (the examples of thermodesorption curves of water and different nitrogen-containing products are presented in Figs 1–3). The data presented unambiguously show that processes under consideration for all investigated CN-FAU possess by hydrolytic mechanism (presence of HCN in gaseous products; overlapping of temperature intervals of separation of nitrogen-containing products), as against. massive analogs (bulk cyanoferrates of such cationic composition were shown to be decomposed by non-hydrolytic mechanism [8], Table 2).

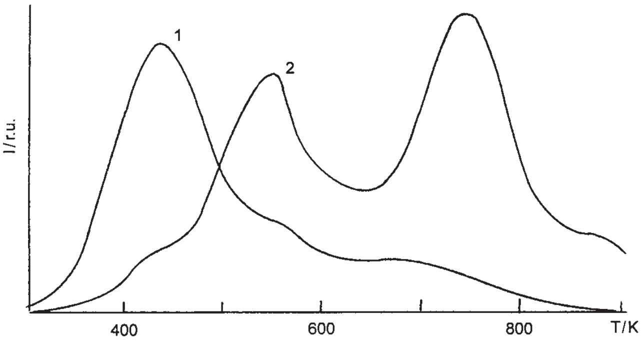

Fig. 1 Thermodesorption curves of H_2O and HCN for $Na[Fe(CN)_6]FAU$

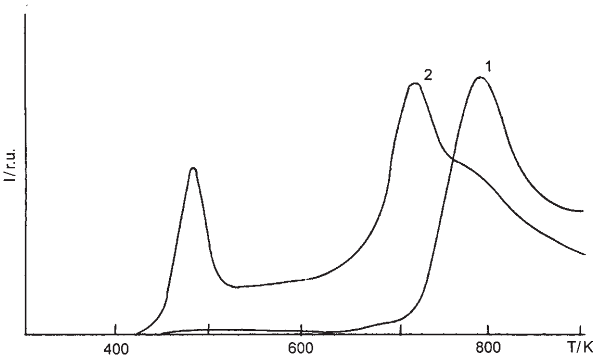

Fig. 2 Thermodesorption curves of C_2N_2 for $Na[Fe(CN)_6]FAU$ (1) and $NaNi[Fe(CN)_6]FAU$ (2)

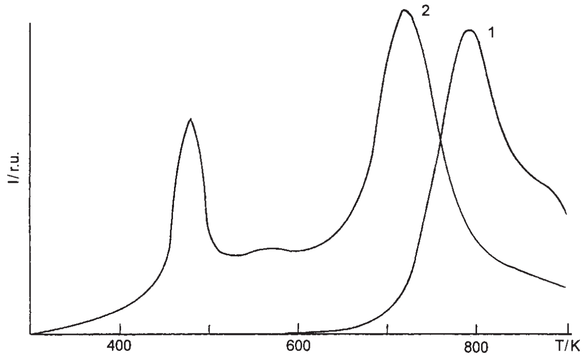

Fig. 3 Thermodesorption curves of N_2 for $Na[Co(CN)_6]FAU$ (1) and $NaCu[Fe(CN)_6]FAU$ (2)

Such influence of encapsulation on the mechanism of cyanide complexes thermal destruction may be caused in main by the significant decrease in temperature of encapsulated complex anion destruction beginning (in comparison with bulk analogues: for $K_3[Co(CN)_6]$ such temperature is shown to be near 700 K [9]), up to temperatures while zeolite water molecules are saved (Table 1, Fig. 1). In our opinion, the possible reasons for this phenomenon are as the monoionic distribution (one anionic complex per large cage) of encapsulated complexes in faujasite, as the stoichiometry of encapsulated substance and peculiarities of complex – cations interactions in large cages of inclusion compounds.

The peculiarities of gaseous products of encapsulated complexes thermal destruction processes composition (Table 2) and temperature intervals of thermodesorption of nitrogen-containing products (Figs 1–3) may be explained from the peculiarities of localization of cations of different nature in inclusion compounds [4–7].

The encapsulation of complexes, especially anionic ones, in FAU is rather an essential factor, which, in particular, excludes localization of cations in S_{IV} positions in large cages (Fig. 4), and leads to the redistribution of intensities of reflexes with (hkl) (220), (311), (331) on diffractograms of inclusion compounds [10–11].

It is known [10–11 that the relationship $I_{331}>I_{220}>I_{311}$ corresponds approximately to a random distribution of cations in crystalline space, whereas $I_{331}>I_{311}>I_{220}$ testifies to increase the contents of cations in $S_{I'}$ positions (sodalite cages) and S_{II} positions in large cages. The data presented in Table 3 show as the predominant localization of transition metal cations in CN-FAU large cavities (with creation of $-Fe(CN)_5-CN-M_a(S_V)-NC-Fe(CN)_5-$ or $-Fe(CN)_5-CN-M_a(S_{II})$ fragments [5]), as the essential increase of the amount of alkali metal cations in sodalite cages for CN-FAU, containing only such cations.

Table 3 Cationic composition and relative peaks intensity in diffractograms of CN-FAU

Sample (cations per unit cell)	hkl						I_{311}/I_{220}
	111	220	311	331	333	533	
NaFAU ($64Na^+$)	100	22	16	83	25	71	0.73
$Na[Fe(CN)_6]$FAU ($96Na^+$)	49	8	32	100	14	63	4.00
$NaK[Fe(CN)_6]$FAU ($9Na^+$, $87K^+$)	49	10	31	93	22	100	3.10
$NaNi[Fe(CN)_6]$FAU ($74Na^+$, $11Ni^{2+}$)	35	7	19	100	21	65	2.71
$NaCu[Fe(CN)_6]$FAU ($6Na^+$, $45Cu^{2+}$)	35	9	15	100	29	69	1.67
$NaCo[Fe(CN)_6]$FAU ($54Na^+$, $21Co^{2+}$)	31	8	17	100	27	73	2.13
$Na[Co(CN)_6]$FAU ($88Na^+$)	57	10	34	100	16	77	3.40
$NaK[Co(CN)_6]$FAU ($8Na^+$, $80K^+$)	47	10	30	86	20	100	3.00
$Na[Co(NH_3)_6]$FAU ($40Na^+$)	100	18	16	79	48	89	0.89

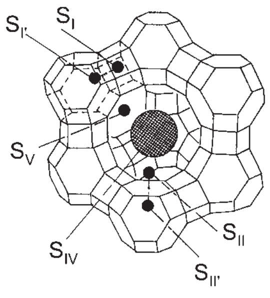

Fig. 4 The positions of localization in CN-FAU of encapsulated anionic complex and cations

The main groups of encapsulated cyanide complexes thermal decomposition processes for investigated CN-FAU are:

– low-temperature (maximum of thermodesorption peak T_m<450 K) HCN thermodesorption (for Na[Fe(CN)$_6$]FAU and NaK[Fe(CN)$_6$]FAU, Fig. 1), which is connected with the existence in such CN-FAU of the encapsulated cyanide complexes with distortion in octahedral symmetry, [4, 6, 7] unlike the Na[Co(CN)$_6$]FAU one (in this case no low-temperature HCN thermodesorption was observed);

– low-temperature C_2N_2 thermodesorption (for Na[Fe(CN)$_6$]FAU, NaNi[Fe(CN)$_6$]FAU and NaCu[Fe(CN)$_6$]FAU; T_m<450 K, Fig. 2), connected with the formation of –Fe(CN)$_5$–CN–M$_a$(S$_V$)–NC–Fe(CN)$_5$– (M_a=Fe, Ni, Cu) fragments – analogues of main structural fragments in bulk cyanoferrates framework in inner-crystalline FAU space; [5, 7] the absence of such fragments in NaK[Fe(CN)$_6$]FAU supports such a conclusion;

– low-temperature N_2 thermodesorption for NaCu[Fe(CN)$_6$]FAU (T_m<450 K, Fig. 3), connected with the formation of –Fe(CN)$_5$–CN–Cu(S$_{II}$) fragments [5] the absence of such fragments in NaNi[Fe(CN)$_6$]FAU (which contains only Ni^{2+}(S$_V$), but no Ni^{2+}(S$_{II}$) cations [7]) supports such a conclusion;

– high-temperature processes (including simultaneous HCN, C_2N_2, N_2 thermodesorption at T>700 K, Table 1), connected with decomposition of encapsulated Fe(CN)$_2$– or Co(CN)$_2$-particles (on the basis of the thermal analysis data, for all investigated CN-FAU in inner-crystalline space there are only such encapsulated particles at T>700 K), that determined by interactions of encapsulated species with Na$^+$(S$_{II}$) cations [12] and active sites of FAU framework, and, in common, by the effect of FAU large cages as nanoreactors (such representations are well elaborated upon by Ozin and co-workers [12, 13]), the existence of water in zeolite at such temperatures, indicated by mass-spectrometry data, supports such a conclusion.

Conclusions

The data obtained allow us to state as follows:

– encapsulation of cyanide iron(II) and cobalt(III) complexes in FAU results in the hydrolytic mechanism of thermal destruction of the complexes (gaseous products contains HCN), unlike the bulk analogues, which is determined by the essential decreasing of the temperature of complex anions encapsulated destruction beginning, up to temperatures while zeolite water molecules are saved;

– the gaseous products of thermal destruction composition is determined by the peculiarities of localization of cations of different nature in inclusion compounds;

– the main peculiarities of the structure of inner-zeolite substance in inclusion compounds studied reflects on the gaseous nitrogen-containing products separation: low-temperature production of HCN is determined by the existence of encapsulated complexes with octahedral symmetry distortion, C_2N_2 and N_2 – by formation of the bulk cyanoferrate structure fragments of the type $–Fe(CN)_5–CN–M_a(S_V)–NC–Fe(CN)_5–$ (M_a= Ni, Cu) or $–Fe(CN)_5–CN–M_a(S_{II})$ (M_a=Cu), respectively, in FAU inner-crystalline space.

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