Journal of Thermal Analysis and Calorimetry, Vol. 65 (2001) 561–573

TG AND DTA EVALUATION OF COBALT SALTS AND COMPLEXES MIXED WITH ACTIVATED CARBON

E. Ingier-Stocka

Institute of Inorganic Chemistry and Metallurgy of Rare Elements, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, 50–370 Wrocław, Poland

Abstract

The thermal decomposition process of mixtures of $CoC_2O_4\cdot 2H_2O$ (COD) or $Co(HCOO)_2\cdot 2H_2O$ (CFD) or $[Co(NH_3)_6]_2(C_2O_4)_3\cdot 4H_2O$ (HACOT) with activated carbon was studied with simultaneous TG–DTG–DTA measurements under non-isothermal conditions in argon and argon/oxygen admixtures. The results show that the thermal decomposition of the studied mixtures in Ar proceeds in the same manner. It begins with the salt decomposition to Co_{met}+CoO mixture followed by (T>680 K) the simultaneous reduction of CoO to Co_{met} and carbon degasification. The final product of the thermal decomposition of COD-C and CFD-C mixtures, identified by XRD, is β-Co. Cobalt contents determined in the final products fall in the range 71–78 mass%. The rest is amorphous residual carbon. In Ar/O_2 admixtures the end product is Co_3O_4 with ash admixture.

Keywords: cobalt oxide reduction, decomposition of cobalt oxysalt-carbon mixtures, metallic cobalt as a residue, thermal decomposition

Introduction

A literature data review points out that the metal oxide–carbon systems were investigated from different points of view i.e.

- reduction processes of metal oxides to metals
- heterogeneous catalysis where metal and/or metal oxide are catalysts in the combustion of coal or carbon is used as a support for precious or less-common metals as catalysts.

Recently, the interest in the preparation of uniform metal particles of a nanometer to micrometer size has escalated because they show superior performance as catalysts and in electronic, optical, medical and other applications [1]. Goia and Matijevic's review article [1] deals with the preparation, characterization and mechanisms of formation of uniform simple and composite metal particles. Reduction of powders of some metal compounds (precursors) is one of the methods to prepare them. Since metal oxides are commonly used in such reduction processes, it is sometimes necessary to convert the original powders of different chemical compositions (such as metal carbonates, oxalates etc.) into the oxide and then treat the product with a reducing agent e.g. hydrogen. The precursors used [1–10] include oxysalts of tran-

1418–2874/2001/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

sition or noble metals e.g. nitrates, oxalates, acetates, formates, carbonates, acetyloacetonates, malonates and hydroxides. The final products of a thermal decomposition process of the above mentioned salts in an inert atmosphere are metal oxides or pure metal powders or mixtures of a metal powder and a metal oxide with different composition depending on the type of the precursor [1–13]. Sometimes, the complex metal salts with ammonia were considered as possible precursors [6, 13–15]. Rosenband *et al.* [14] present a method for the production of extra-fine cobalt powder from the cobalt ammonium halide salts. The powder is manufactured in a simple manner by the direct one-stage thermal treatment of these salts in a closed reactor at 600°C.

In practice, the most usual application of carbon in catalysis is the support for metals in several states (reduced metals, oxides, sulphides, etc.). A great deal of information exists about the behaviour of carbon-supported metal systems under both oxidizing and reducing atmospheres. On the other hand, few studies exist where the influence of a treatment under an inert atmosphere on the properties of carbon–supported catalysts is considered. However, these treatments are of a great interest in catalysis since they are sometimes necessary in catalyst preparation [11]. Several authors [10, 16–18] reported that carbon was able to reduce the metal precursor introduced during the catalyst preparation. This is also true for the reduction of CoO to Co [10, 16]. In the studied systems both graphite [16, 19–21] and activated carbon [3, 10, 11, 22] were used. The metal to carbon mass ratio was varied in a large extent [20–23]. The mechanism of the reduction of metal oxides by carbon is not well understood yet. There are many conflicting views and many aspects of the problem have not been studied comprehensively [10, 19, 21, 24–27].

The author's interests are focused on a possibility to obtain pure metallic cobalt as a final product of thermal decomposition of some precursors i.e. mixtures of some cobalt carboxylates and carbon. The results obtained can be useful in the preparation of cobalt catalysts. Previous investigations [12, 13, 28] showed that the final products of the thermal decomposition of $CoC_2O_4{\cdot}2H_2O$ (COD), $Co(HCOO)_2{\cdot}2H_2O$ (CFD) and $[Co(NH_3)_6]_2(C_2O_4)_3{\cdot}4H_2O$ (HACOT) in an inert atmosphere were Co_{met}+CoO mixtures with a different content of the metal (50–87 mol%). A survey of a large number of articles on COD decomposition is presented in [13]. Among the cited publications especially interesting are articles [29–32] by Brown and Dollimore and their co-workers. Contrary to the common opinion, it is impossible to obtain pure cobalt during the decomposition of COD under an inert atmosphere [13]. It was revealed earlier [13] that newly formed Co_{met} with a high reactivity reacted immediately with any traces of oxygen present in the system. The phase ratio of the solid products CoO:Co_{met} formed in the primary reaction of COD decomposition can be altered not only by secondary reactions with the carrier gas as it happens with oxygen but also with the decomposition gases e.g. CO, H_2 or hydrocarbons [13].

The aim of the present work is to examine the thermal decomposition process of the mixtures: COD or CFD or HACOT with activated carbon. The assumed role of the carbon is i) it acts as the reducing agent of cobalt oxides and/or ii) it catches oxygen traces from the inert gas atmosphere.

Experimental

The synthesised salts COD, CFD and HACOT used throughout the present work followed the same preparation of reactants as studied previously [12, 13, 28]. Commercial (Aldrich) activated carbon (–100 mesh, powder, Darco® G-60) was used. Intimate mixtures with the weight ratio of cobalt salt to carbon equals to 6:1 (COD, CFD) and 11:1 (HACOT) were prepared for the reduction experiments. The desired, weighed portions of both components were thoroughly mixed in an agate mortar.

The reduction experiments were carried out with a thermoanalyzer (a Derivatograph C, MOM, Budapest). Simultaneous TG-DTG-DTA curves under non-isothermal conditions in flowing (~15 dm^3 h^{-1}) argon of 99.9999% purity and argon with some oxygen admixture (O_2~30 ppm) were registered at the heating rate β=5 K min^{-1} between 298–1373 K. The sample mass was as follows: the studied mixtures and pure COD, CFD and HACOT 100 mg but pure activated carbon 15 mg. Commonly, open alumina crucibles were used both for the specimen and for the reference (α-Al_2O_3) material. Some experiments were done in covered alumina crucibles.

X-ray diffraction patterns (XRD) of the substrates, intermediate and final products were obtained by a Philips 1680 X Pert diffractometer using CuK_α radiation. XRD measurements were obtained at room temperature after cooling the solid products in the experimental atmosphere.

Cobalt content in the solid products of decomposition was determined by ICP–AES (Inductively Coupled Plasma Atomic Emission Spectrometry) with a Jobin–Yvon 38 S apparatus. The black solid residue was digested with a hot concentrated HNO_3+HCl (1:3) mixture. A part of the black residue was insoluble. Filtered cobalt solution was diluted and cobalt content was determined.

Results and discussion

Thermodynamics

On the basis of the calculated values (Table 1) of the Gibbs energy of reaction, $\Delta_r G$, (using the literature data of the Gibbs energy of formation [33, 34]) the thermodynamic probability of the potential primary and secondary reactions that could occur, was estimated. The calculated values of the Gibbs energy of reaction at the lowest temperatures where $\Delta_r G<0$ as well as at T=600 K (the temperature lying in the decomposition range of the examined pure salts and mixtures in inert atmosphere) are gathered in Table 1. The $\Delta_r G$ values for reactions no. (1)–(4) are doubtful because for CoC_2O_4 only a $\Delta_f G°$ value at 298.15 K 772 kJ mol^{-1} (=–184.7 kcal mol^{-1}) was available in the literature [34]. Moreover, for CFD and HACOT the Gibbs energies of formation are not available in the literature. The thermodynamic data, submitted in Table 1, of possible primary and secondary reactions indicate that some of these reactions, under equilibrium conditions, can take place within the temperature range of COD, CFD and HACOT decomposition (~600 K). However, some of these reactions can be hindered for kinetic reasons. Therefore, theoretical prediction of their occurrence has to be confirmed experimentally.

Table 1 Gibbs energy values calculated for some thermodynamically probable (Δ_rG<0) reactions that can occur during heating of the examined mixtures

No.	Reaction	Temperature/K	Δ_rG/kJ mol^{-1}
1	CoC_2O_4+2C=Co+4CO	1000	–27.9^{a,b}
2	$3CoC_2O_4$+4C=Co+2CoO+10CO	1000	–10.2^{a,b}
3	$2CoC_2O_4$+C=Co+CoO+$2CO_2$+3CO	1000	–9.6^{a,b}
4	CoC_2O_4+C=Co+CO_2+2CO	900	–5.3^{a,b}
		1000	–23.2^{a,b}
5	2CoO+C=2Co+CO_2	600	–11.9^{a}
6	CoO+C=Co+CO	800	–5.0^{a}
7	CoO+CO=Co+CO_2	300	–43.0^{a}
		600	–39.0^{a}
8	CoO+H_2=Co+H_2O	300	–14.5
		600	–22.5^{a}
9	2CO=CO_2+C	300	–119.7^{a}
		600	–66.1^{a}
10	H_2O+C=CO+H_2	1000	–7.5^{a}
11	$2H_2O$+C=$2H_2$+CO_2	1000	–10.4^{a}
12	CO+H_2O=CO_2+H_2	300	–28.5^{a}
		600	–16.6^{a}
13	CO_2+$4H_2$=CH_4+$2H_2O$	300	–113.3^{a}
		600	–55.9^{a}
14	Co+1/$2O_2$=CoO	300	–214.0^{a}
		600	–191.6^{a}
15	Co+2/$3O_2$=1/$3Co_3O_4$	300	–264.7^{a}
		600	–226.1^{a}
16	3CoO+1/$2O_2$=Co_3O_4	300	–152.0^{a}
		600	–103.5^{a}
17	C+O_2=CO_2	300	–394.4^{a}
		600	–395.1^{a}
18	2C+O_2=2CO	300	–274.6^{a}
		600	–329.0^{a}
19	CO+1/$2O_2$=CO_2	300	–257.0^{a}
		600	–230.6^{a}
20	Co+CO=CoO+C	300	–76.7^{a}
		600	–27.1^{a}
21	2Co+CO_2=2CoO+C	300	–33.7^{a}
		600	+11.9^{a}

^{a,b} the values of the Gibbs energy of the reaction were calculated using the Δ_fG values taken from the references: ^{a}[29] and ^{b}[30]

The data listed in Table 1 suggest that after dehydration the probable decomposition of CoC_2O_4 to Co_{met}+CoO proceeds (T~600 K) followed by CoO reduction with carbon and/or CO and H_2 (secondary gas product). Some of the assumed reactions i.e. no. (7)–(9) and (12)–(17) were experimentally confirmed in the temperature range of COD decomposition with TA-MS-PTA simultaneous technique. It is worth noting that freshly formed Co_{met} acts as a very active catalyst in the secondary reactions (no. (9), (12) and (13)) [13]. The above mentioned reactions can proceed during heating all the examined mixtures because of the presence of Co_{met} and CoO (solid phase) and H_2O, H_2, CO, CO_2 and CH_4 (gas phase), as revealed earlier [12, 28, 35, 36] in the products of the decomposition of CFD and HACOT.

Thermal analysis (TA)

TA results of the active carbon sample in argon and argon with an oxygen admixture are shown in Table 2. In argon, in the temperature range of 298–1373 K mass loss ca 38 mass% was registered. Up to 716 K the loss of adsorbed water occurs (Δm=3.7 mass%) followed by the carbon degasification (Δm=33.1%) up to 1373 K (a large endotherm ~1317 K is observed). In Ar+O_2 atmosphere after the loss of moisture (Δm=3.6 mass%) the exotherm at 795 K corresponds to oxidation of the released volatile matter and preceeds the larger exotherms at 890–990 K due to carbon combustion.

The profiles of TG-DTG-DTA curves obtained for the thermal decomposition of the studied mixtures in Ar and Ar+O_2 atmospheres are shown in Figs 1 and 2. The TG-DTG-DTA curves recorded during dissociation of the pure salts can be found elsewhere [12, 13, 28]. The representative thermoanalytical data of the examined mixtures and pure salts decomposition obtained at the heating rate β=5 K min^{-1} are listed in Table 2. The thermal decomposition of the pure cobalt salts (COD, CFD) in argon runs in two stages as it was observed previously [12] and in this work. In Ar+O_2 atmosphere, similarly as in air [12], the observed third stage is oxidation of CoO to Co_3O_4. The dissociation of HACOT is more complicated and in argon proceeds in three stages which was up to ~700 K [28]. It was observed that the decomposition process of the studied mixtures in argon consisted of three (COD-C and CFD-C) or four (HACOT-C) stages (Figs 1 and 2, Table 2). This additional stage in respect to the pure salt decomposition runs in the temperature range above that registered as the final temperature, T_f, for the pure salt dissociation. The temperature range of the last stages of the mixtures decomposition falls into the temperature range characteristic of the main mass loss of active carbon. The mass losses recorded for the mixtures (in particular stages of decomposition) were corrected as follows:

$$\Delta m_{corr.}\ (mass\%)=[(\Delta m_{obs.mix.}-\Delta m_{obs.C})/m_{p.s.}]\cdot 100\% \qquad (1)$$

where $\Delta m_{corr.}$ is the corrected mass loss of the mixture, $\Delta m_{obs.mix.}$ (mg) the observed mass loss of the mixture, $\Delta m_{obs.C}$ (mg) the observed mass loss of the active carbon and $m_{p.s.}$ (mg) the mass of pure salt in the sample.

The temperature ranges, DTA_{peak} temperatures, as well as the corrected mass losses for the stages I and II (COD, COD-C, CFD, CFD-C) and stages I–III (HACOT, HACOT-C) were close to each other for each pure salt and the respective mixture. This suggests that in these stages the decomposition of the mixture components (pure salt and carbon) occurs independently. Some slight thermal effects observed in the last stage of the mixtures decomposition in argon (Figs 1 and 2, DTA curves) result probably from

Table 2 Thermoanalytical results (TG-DTG-DTA) on the examined mixtures and pure components, β=5 K min^{-1}

Compound	Stage	T_{range}/K	DTA_{peak}/K	Mass loss/%			Composition of residue	Atmosphere
				observ.	corr.[a]	theor.		
Carbon	I	347–716	–	3.7			C (without moisture)	Ar
	II	716–1373	1317_{endo}	33.1			R[b]	
	I	340–870	–	6.9			C (without moisture)	$Ar+O_2$ covered crucible
	II	870–1373	1284_{endo}	8.3			R[b]	
	I	331–387	337_{endo}	3.6			C	$Ar+O_2$
	II	387–711	–	1.8			R[b]	
	III	711–1010	795_{exo}	82.0			A[c]	
			892_{exo}					
			989_{exo}					
COD	I	439–555	488_{endo}	17.8		19.7	CoC_2O_4	Ar
	II	555–694	643_{endo}	47.0		45.9	Co+CoO (25 mol%)	
COD + C	I	416–562	486_{endo}	16.5	19.2	19.7	CoC_2O_4+C	Ar
	II	562–699	648_{endo}	40.4	46.6	45.9	Co+CoO (25 mol%)+C	
	III	699–1373	810_{endo}	6.0	1.5	2.2	Co+R[b]	
			1028_{endo}					
			1089_{exo}					
			1155_{endo}					
COD	I	412–546	488_{endo}	19.0		19.7	CoC_2O_4	$Ar+O_2$
	II	546–666	623_{exo}	38.4		37.9	CoO+Co_3O_4 (50 mol%)	
	III	666–802	677_{exo}	+1.3		+1.5	Co_3O_4	
COD+C	I	399–551	486_{endo}	16.6	18.8	19.7	CoC_2O_4+C	$Ar+O_2$
	II	551–679	615_{exo}	34.6	40.1	39.4	CoO+R[b]	
	III	679–942	681_{exo}	9.5	+2.2	+3.0	Co_3O_4+A[c]	
			780_{exo}					
	I	406–579	501_{endo}	16.6	18.2	19.7	CoC_2O_4+C	$Ar+O_2$ covered crucible
	II	579–724	657_{endo}	40.9	47.7	46.9	Co+CoO (13 mol%)+R[b]	
	III	741–1373	858_{endo}	2.6	1.6	1.2	Co+R[b]	
			1323_{endo}					

Table 2 Continued

Compound	Stage	T_{range}/K	DTA_{peak}/K	Mass loss/%			Composition of residue	Atmosphere
				observ.	corr.[a]	theor.		
CFD	I	389–503	460_{endo}	19.2		19.5	$Co(HCOO)_2$	Ar
	II	503–604	542_{endo}	41.8		42.2	Co+CoO (75 mol%)	
CFD+C	I	378–501	454_{endo}	17.1	19.5	19.5	$Co(HCOO)_2$+C	Ar
	II	501–595	538_{endo}	35.5	40.7	40.8	Co+CoO (90 mol%)+C	
	III	595–1373	840_{endo}	11.6	8.0	7.8	Co+R[b]	
			1063_{exo}					
			1311_{endo}					
CFD+C	I	394–506	465_{endo}	17.2	18.9	19.5	$Co(HCOO)_2$+C	Ar+O_2 covered crucible
	II	506–640	539_{endo}	36.3	42.4	42.2	Co+CoO (75 mol%)+R[b]	
	III	640–1373	855_{endo}	8.4	8.4	6.9	Co+R[b]	
			1311_{endo}					
HACOT	I	401–476	455_{endo}	11.0		10.9	$[Co(NH_3)_6]_2(C_2O_4)_3$	Ar
	IIa	476–545	497_{endo}	39.8		39.2	$CoC_2O_4{\cdot}NH_3$	
	IIb	545–582	567_{endo}	2.6		2.7	$CoC_2O_4{\cdot}0.5NH_3$	
	IIIa	582–634	606_{endo}	7.3		8.0	CoC_2O_4+CoO (25 mol%)	
	IIIb	634–684	650_{endo}	19.3		18.8	Co+CoO (50 mol%)	
HACOT+C	I	399–465	458_{endo}	10.5	11.3	10.9	$[Co(NH_3)_6]_2(C_2O_4)_3$+C	Ar
	IIa	465–542	495_{endo}	36.2	39.3	39.2	$CoC_2O_4{\cdot}NH_3$+C	
	IIb	542–582	570_{endo}	3.0	3.3	2.7	$CoC_2O_4{\cdot}0.5NH_3$+C	
	IIIa	582–617	604_{endo}	6.4	7.0	8.0	CoC_2O_4+CoO (25 mol%)+R[b]	
	IIIb	617–684	647_{endo}	17.0	18.5	18.8	Co+CoO (50 mol%)+R[b]	
	IV	740–1373	1070_{exo}	6.1	3.6	2.5	Co+R[b]	
			1320_{endo}					

[a] Eq. (1) in the text

[b] Residual, amorphous carbon

[c] Ash

overlapping of the large endotherm connected with the carbon degasification and thermal effects accompanied by possible reduction reactions of CoO with:

i) carbon (Table 1, no. (5), Δ_rH=73.0 kJ mol^{-1} at 800 K)
ii) CO (Table 1, no. (7), Δ_rH=–49.6 kJ mol^{-1} at 800 K)
iii) H_2 (Table 1, no. (8), Δ_rH=–12.8 kJ mol^{-1} at 800 K)

and/or Boudouard reaction (Table 1, no. (9), Δ_rH= –172.3 kJ mol^{-1} at 800 K) and/or, in a lower extent, secondary reactions of the gas products (Table 1).

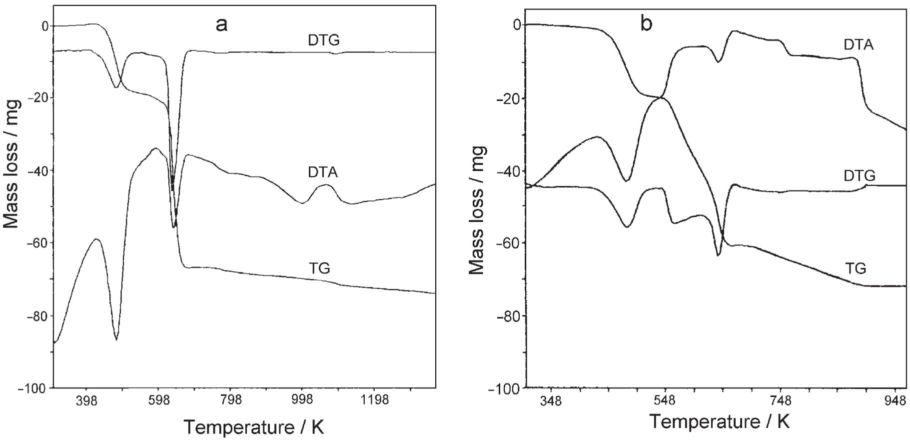

Fig. 1 TG-DTG-DTA curves for the decomposition of COD–C mixture; β=5 K min^{-1}, m=100 mg: a – in argon, b – in argon with an oxygen admixture

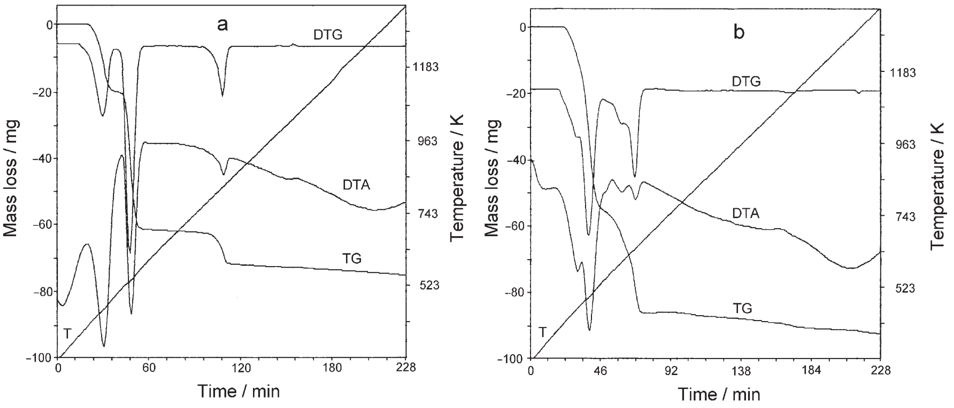

Fig. 2 TG-DTG-DTA curves for the decomposition of the mixtures in argon (β=5 K min^{-1}, m=100 mg): a – CFD–C, b – HACOT–C.

The large complex exotherm recorded on the DTA curve of COD-C decomposition in Ar+O_2 atmosphere (open crucible) is connected with oxidation of carbon and secondary oxidation of the primary products of salt decomposition (Table 1, no. (14)–(16)). This effect is not observed when the decomposition runs in a covered crucible. Some slight endotherms are observed instead (Table 2).

XRD analysis

The intermediate and final products of the studied mixtures decomposition identified by XRD analysis are listed in Table 3. JCPDS database was used to analyse the diffractograms [37]. It is worth noting that XRD does not show the CoO content below 4–5 mass% in a sample as it was previously observed [13].

Table 3 Intermediate and final products of the thermal decomposition of the examined mixtures and cobalt salts identified by XRD

Mixture/compound	Atmosphere	T_f/K	Residue
COD	Ar	687	α-Co, β-Co, CoO[a]
COD+C		1373	β-Co[a]
COD+C		696	α-Co, β-Co, CoO, $Co_3O_{4\,\mathrm{traces}}^{x,a}$
COD+C		1373	β-Co, CoO[b]
COD	Ar+O_2	692	$Co_3O_4^{c}$
COD+C		969	$Co_3O_4^{c}$
COD+C		680	$Co_3O_4^{x,c}$
COD+C	Ar+O_2, covered crucible	1373	β-Co
CFD	Ar	604	α-Co, β-Co, CoO[a]
CFD+C		1373	β-Co, $Co_3O_{4\,\mathrm{traces}}^{a}$
CFD+C	Ar+O_2, covered crucible	1373	β-Co
HACOT	Ar	676	β-Co, CoO[a]
HACOT+C		1373	β-Co, CoO[a]

[x] intermediate products
[a] the residue cooled in argon
[b] the residue cooled in ambient atmosphere
[c] the residue cooled in argon with an oxygen admixture

It was revealed that an amorphous matter was formed during heating the active carbon. It was impossible to follow the presence of carbon in the intermediate and final products of the decomposition of the studied mixtures by XRD. The final product of the thermal decomposition of COD-C and CFD-C mixtures in pure argon was the high-temperature β-Co (Fig. 3) whereas there was a mixture of Co_{met} (α and β phases) and CoO for COD and CFD decomposition as it was stated elsewhere [12] and also in this work. So, even ca 14 mass% of activated carbon in the above mentioned mixtures was enough to reduce the CoO contained in the final products of the salts decomposed in argon. Instead the addition of carbon ca 8.3 mass% to HACOT was too small to reduce all the CoO contained, apart from α and β-Co, in the final product [28]. The observed content of CoO and traces of Co_3O_4 in the intermediate of COD-C mixture decomposi-

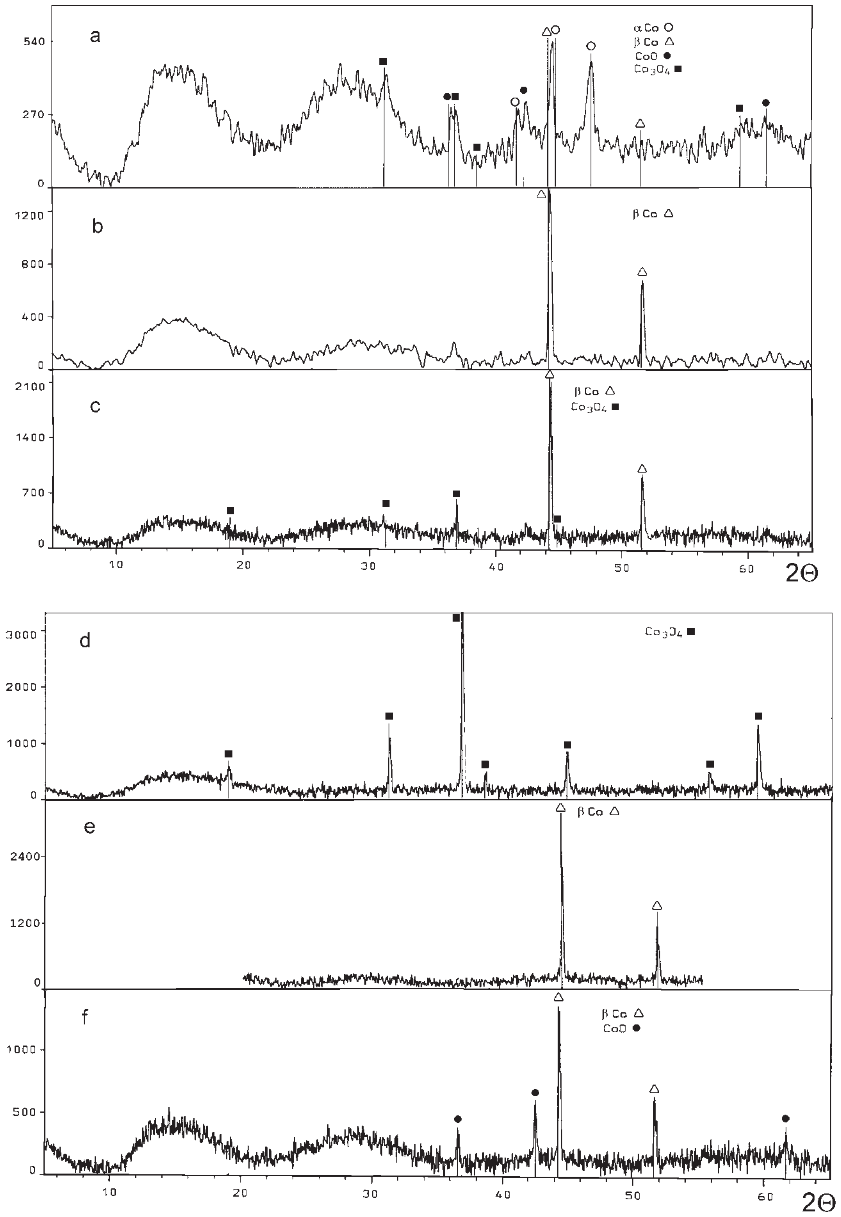

Fig. 3 XRD powder diffractograms of the intermediate and final products of decomposition: a – COD–C mixture in argon (intermediate), b – COD–C mixture in argon (final product), c – CFD–C mixture in argon (final product), d – COD–C mixture in argon with an oxygen admixture, e – COD–C mixture in argon with an oxygen admixture (covered crucible), f – HACOT–C mixture in argon (final product)

tion (Table 3, Fig. 3a) suggests that the reduction of CoO – the component of the residue of pure salts decomposition - occurs only in the third stage of decomposition. This is in agreement with the presented results of the thermal analysis (Table 2).The presence of CoO in the residue cooled in ambient atmosphere (Table 3) is the result of secondary oxidation of the freshly formed Co_{met} powder, what is in agreement with the data presented in [13].

Cobalt content in the solid products

Results of the total cobalt content (mass% Co in residue) in solid residues obtained by chemical analysis are presented in Table 4. The results show that cobalt content is within the range 71–92 mass% of the final products. Calculated (based on the values from Table 4) CoO contents are 37.5 and 81.6 mass% in the residue of COD (in Ar) and CFD (in Ar) decomposition respectively. In the intermediate of COD-C decomposition (T=688 K) cobalt content is approx. 10 mass% lower than in the final product because of CoO presence apart from Co_{met} (Table 3). It is noticed that content of carbon (mass%) in the residue (calculated under assumption that carbon does not react with salt and/or intermediates of its decomposition) is higher than the rest of residue (% of the rest by difference – Table 4, samples no. 4, 6, 7, 9). It suggests that some part of carbon is consumed during reaction(s) with primary decomposition products of above mentioned samples. The rest of carbon, present in the final product as amorphous residual carbon, was not detectable by XRD but was noticed visually as a black acid-insoluble deposit after filtration of cobalt solution.

Table 4 Cobalt content in the solid residue after decomposition of the examined mixtures and pure salts

No.	Compound	Mass of residue/ mg	Mass% Co in residue	Mass% of the rest (by difference)	Mass% C in residue (calculated)[a]	Atmosphere
1	COD	35.2	92.0	8.0	–	Ar
2	COD + C	43.1[b]	64.0	36.0	31.9	Ar
3	COD + C	37.1	75.2	24.8	24.4	Ar
4	COD + C	39.9	70.7	29.3	30.3	Ar+O_2 covered crucible
5	CFD	39.0	82.6	17.4	–	Ar
6	CFD + C	35.8	77.9	22.1	25.2	Ar
7	CFD + C	38.1	73.8	26.2	31.8	Ar+O_2 covered crucible
8	HACOT	20.0	90.5	9.5	–	Ar
9	HACOT+C	20.8	79.8	20.2	25.3	Ar

[a] mass% of carbon in residue calculated under assumption that C does not react with salt and/or intermediates of its decomposition

[b] intermediate (T=688 K)

Conclusions

- The results show that the thermal decomposition of the studied cobalt salt – activated carbon mixtures in argon proceeds in the same manner. It begins with the salt decomposition (with the same temperature range, the number of stages and the mass loss as for the pure compound) and during the following additional stage (T>680 K) the simultaneous reduction of CoO to Co_{met} as well as carbon degasification takes place.
- The final product of the thermal decomposition of COD-C and CFD-C mixtures in argon and in argon with an oxygen admixture (covered crucible) is β-Co and there is also amorphous residual carbon. Even ca 14 mass% of activated carbon in the mixtures is enough to reduce the CoO contained in the final products of the salts decomposed in argon.
- In argon with an oxygen admixture in all the studied mixtures the end product was Co_3O_4 with some content of ash. However when decomposition was run in a covered crucible, the β-Co was identified as the main component of residue. It can suggest a significant influence of some secondary reactions on the final product composition, among others an increased participation of CO as the reducing agent.
- To explain the reduction mechanism in the examined systems and point out the reducing agent(s), a continuation of these studies is necessary i.e. identification of gas products of the thermal decomposition and the determination of the secondary solid–gas or gas–gas reactions will be done.

References

1 D. V. Goia and E. Matijević, New. J. Chem., 22 (1998) 1203.
2 B. Ernst, S. Libs, P. Chaumette and A. Kiennemann, Appl. Catal., A 186 (1999) 145.
3 E. Bekyarova, M. Khristova and D. Mehandijiev, J. Colloid Interface Sci., 213 (1999) 400.
4 B. Djonev, B. Tsyntsarski, D. Klissurski and K. Hadjiivanov, J. Chem. Soc., Faraday Trans., 93 (1997) 4055.
5 R. Molina and G. Poncelet, J. Catal., 173 (1998) 257.
6 A. Barbier, Hanif Ahmad, J. A. Dalmon and G. A. Martin, Appl. Catal., 168 (1998) 333.
7 Pat. Jpn. Kokai Tokkyo Koho JP 1161, 208, Chem. Abstr., Vol. 130: 190825w.
8 Pat. Ger. DE 19,544,107; Chem. Abstr. Vol.127: 7876q.
9 A. K. Galwey and M. A. Mohamed, Reactivity of Solids, Proc. 10th Int. Symp. on the Reactivity of Solids, Dijon, August 27–31, 1984, Part B, p. 699.
10 L. M. Gandia and M. Montes, J. Catal., 145 (1994) 276.
11 A. Gil, L. M. Gandia and M. Montes, J. Phys. Chem. Solids, 58 (1997) 1079.
12 E. Ingier-Stocka and A. Grabowska, J. Therm. Anal. Cal., 54 (1998) 115.
13 M. Maciejewski, E. Ingier-Stocka, W.-D. Emmerich and A. Baiker, J. Therm. Anal. Cal., 60 (2000) 735.
14 V. Rosenband, Ch. Sokolinsky, D. Lekhtman and N. Efremenko, Sci. Isr. – Technol. Advantages, 1 (1999) 35; Chem. Abstr., Vol. 131: 217318t.

15 M. Bouchemoua, M. Che, D. Olivier, D. Delafosse and M. Kermarec, Reactivity of solids, Proc. 10th. Int. Symp., Dijon, August 27–31, 1984, Part B, p. 1083.

16 S. G. Oh and R. T. K. Baker, J. Catal., 128 (1991) 137.

17 D. S. Cameron, S. J. Cooper, I. L. Dogson, B. Harrison and J. W. Jenkins, Catal. Today, 7 (1990) 113.

18 R. D. Oades, S. R. Morris and R. B. Moyes, Catal. Today, 7 (1990) 199.

19 H. Yang and P. G. McCormick, Metall. Mater. Trans. B, 29 B (1998) 449.

20 F. Jasim and I. Jamed, Thermochim. Acta, 147 (1989) 199.

21 S. K. Sharma, F. J. Vastola and P. L. Walker, Jr, Carbon, 34 (1996) 1407.

22 A. Berman and M. Epstein, J. Phys. IV (1999), 9 (Pr 3, Proc. of the 9th Solar PACES International Symp. on Solar Thermal Concentrating Technologies, 1998, Pr 3/319).

23 L. Lin, Y. Song-Liu, D. Yuan-Da and C. Kun, Chin. Phys. Lett., 16 (1999) 591; Chem. Abstr., Vol. 131: 339766h.

24 H. Y. Sohn and J. Szekely, Chemical Engineering Science, 28 (1973) 1789.

25 R. T. K. Baker, M. A. Barber, P.S. Harris, F. S. Feates and R. J. Waite, J. Catal., 26 (1972) 51.

26 S. B. Jagtap, B. B. Kale and A. N. Gokarn, Metall. Trans. B, 23 B (1992) 93.

27 C. J. Lin, Metall. Trans. B, 19 B (1988) 685.

28 E. Ingier-Stocka and M. Maciejewski, Thermochim. Acta, 354 (2000) 45.

29 M. E. Brown, D. Dollimore and A. K. Galwey, Comprehensive Chemical Kinetics, Vol. 22, Reactions in the solid state, Eds. C. H. Bamford and C. F. H. Tipper, Elsevier, Amsterdam 1980, p. 218.

30 D. Dollimore, Thermochim. Acta, 117 (1987) 331.

31 D. Dollimore, Thermochim. Acta, 177 (1991) 59.

32 A. Coetzee, D. J. Eve and M. E. Brown, J. Thermal Anal., 39 (1993) 947.

33 I. Barin, Thermochemical Data of Pure Substances, VCH, 1989.

34 V. P. Glushko and V. A. Medvedeva (Eds), Termicheskie Konstanty Veshestv (Thermal Constants of Substances), Vol. 6, Part 1, AN SSSR and VINITI; Moscow, 1972, p. 254.

35 S. Shishido and Y. Masuda, Nippon Kagaku Kaishi, 1 (1973) 185.

36 M. Maciejewski and E. Ingier-Stocka (in preparation).

37 JCPDS Mineral Powder Diffraction Data Files, International Centre for Diffraction Data, Park Lane, PA, USA.