

STUDY OF THERMAL DECOMPOSITION OF SILVER ACETATE

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Thermal decomposition of silver acetate was studied (TG, DSC, mass-spectrometry, X-ray analysis, electron microscopy). Non-isothermal thermogravimetric data (obtained at two different rates of linear heating) were used for kinetic studies. Kinetic parameters were calculated only for the chosen decomposition step.

Keywords: 'model free' kinetics, silver acetate, silver nanoparticles, silver salts, thermal decomposition

Introduction

Thermal decomposition of metal carboxylates is now widely used for the preparation of highly dispersed metals and metals oxides; synthesized metals and metal oxides can be used as catalysts [1–3]. Nanoparticles of metal can be obtained in such processes because of rather low temperature of this intramolecular reduction of metals.

Experimental

The salt CH_3COOAg was synthesized by the reaction of silver carbonate with glacial acetic acid at 45–60°C; the precipitate was filtered after cooling [4].

The study of thermal decomposition was performed by means of Derivatograph Q-1500-D (MOM, Hungary). Thermogravimetric curves were obtained for kinetic studies (plate-like sample holder, sample mass about 100 mg, heating rate 2.5 and 10°C min⁻¹; helium flow 60 cm³ min⁻¹). DSC curves were obtained on Mettler DSC-822e/700 ($m=13.5$ mg, argon flow 25 cm³ min⁻¹). For the study of the structural and morphological change in the silver acetate crystals, the sample ($m=1$ g) was heated consecutively at 180±1°C, 210±1°C and 350±1°C (during 15, 25 and 25 min, accordingly).

SEM and TEM studies of intermediate products and residue were made by means of a JEM-2000 FX II microscope (the resolution 200 Å), equipped by ASID-20 gear, with the accelerating voltage 200 kV. The dimensions of product decomposition were evaluated by the examination of approximately 300 particles on TEM images, formed

by Sigma Scan Pro (version 3.0, Jandel Scientific Software, 1966).

Mass-spectrum were recorded by a mass-spectrometer with high resolution ($R=2000$) Funnigan MAT 8200; ionizing electrons energy 70 eV, accelerating voltage 3000 V. Gaseous products (from the special heating system) were injected into the ionic source through the leak (with molecular leaking regime), with ionic source temperature from 10 till 340°C.

The non-isothermal thermogravimetric data were processed using the computer program 'NETZSCH Thermokinetics' (version 2001.9d). Since the thermal decompositions were multi-step, the convenient variant of calculation was selected. Special program module, 'Model free' allows processing several thermogravimetric curves, obtained with different heating rates, without the information about the kinetic topochemical equations. Programs 'Ozawa–Flynn–Wall Analysis' and 'Friedman Analysis' [5] allow calculating both the activation energies for the every experimental point of fractional conversion (in the interval $0.02 < \alpha < 0.98$, conjointly from two curves). The same set of experimental data was used further for searching the topochemical equation [selecting from 16 equations (chemical reaction on the interface, nucleation, and diffusion)]. This calculation is made by the improved differential method of Borchardt–Daniels with linear regression [6]. F-test is used for the search of the best kinetic description [7]. If the calculations result in two or three kinetics equations with near values of correlation coefficients (or F-test), but with noticeably different values of kinetics parameters, it is rationally to choose the equation with parameters values near to data of 'Model free' module programs.

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Results and discussion

The decomposition of the salt (under the conditions of linear heating) proceeds at 170–280°C, the mass loss (30%) corresponds to the formation of metallic silver (Fig. 1).

The mass-spectrum of gaseous products points to the evolving of CO, CO₂, H₂O, CH₃COOH and fragments with mass numbers 107, 216, 275.

DSC curve (Fig. 2) confirms that the decomposition process itself is complex: the heat-evolution at 260–286°C itself is multistep, the long flat exothermic peak at 286–331°C is not connected with any mass loss and can be referred to the fine particles enlargement (recrystallization).

The initial crystals of silver acetate are long needles: length is 70–100 μm, and thickness is 5–10 μm (Fig. 3). The fine silver particles appearance is observed at the decomposition beginning (X-ray analysis detects the metal silver after 15 min heating at 180°); the initial size of Ag-particles is 40–50 nm (Fig. 4); they intergrow and form the porous structure at higher temperatures (Fig. 5). It is worth to note, that all consecutive temperatures of the long-term isothermal treatment of samples (for the study of the

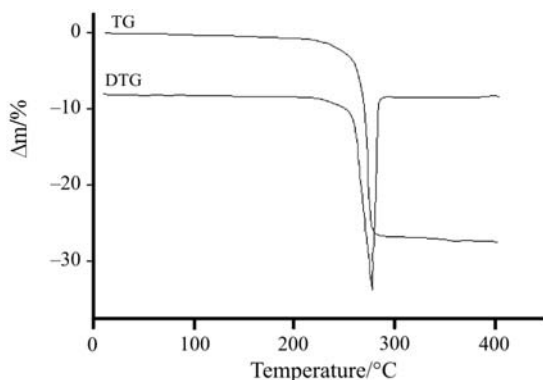


Fig. 1 Thermal decomposition curves of CH₃COOAg; $m=97.3$ mg, plate-like sample holder, helium flow ($60\text{ cm}^3\text{ min}^{-1}$), heating rate $10^\circ\text{C min}^{-1}$

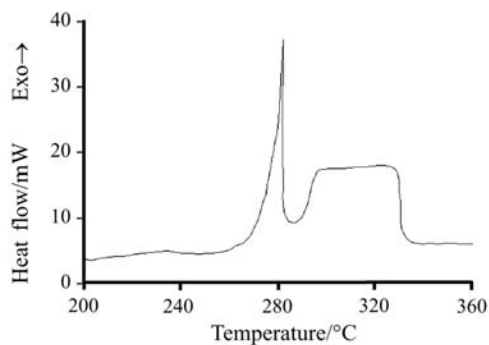


Fig. 2 DSC curve for the decomposition of CH₃COOAg; $m=13.9$ mg, standard aluminum-sample holder (the lid with holes), heating rate 10 K min^{-1} , argon flow ($25\text{ cm}^3\text{ min}^{-1}$)

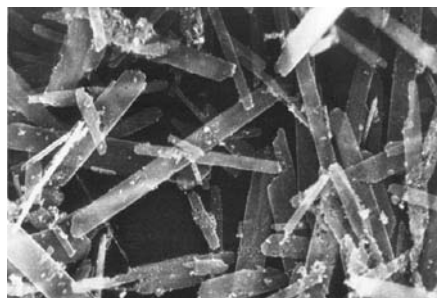


Fig. 3 SEM images of initial crystals of silver acetate ($l=70\text{--}100$, $d=5\text{--}10\text{ }\mu\text{m}$)

structural and morphological changes) are lower than appropriate transformation temperatures under linear heating, which is understandable.

The kinetic analysis by Ozawa–Flynn–Wall and Friedman methods shows the complex course of the decomposition: the relative constancy of the activation energy realizes only at $\alpha=0.45\text{--}0.90$ (Fig. 6), $E_a=330\text{--}376\text{ kJ mol}^{-1}$. The search of the best kinetic equation in this α -region results in two equations: C₁B and Bna with the catalysis by the product (Prout–Tompkins equation and n -th order with autocatalysis, Table 1).

Kinetic parameter ($E_a=330\text{--}376\text{ kJ mol}^{-1}$) is relatively constant only in the region of transformation $\alpha=0.45\text{--}0.90$; the decomposition process is very complex (the mass-spectrum of the evolved gas consist CO, CO₂, H₂O, CH₃COOH and small quantity



Fig. 4 TEM images of Ag-particles (40–50 nm), formed at 210°C (isothermal heating)

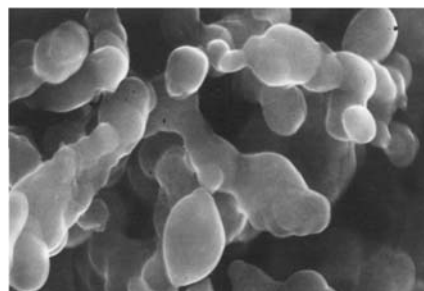
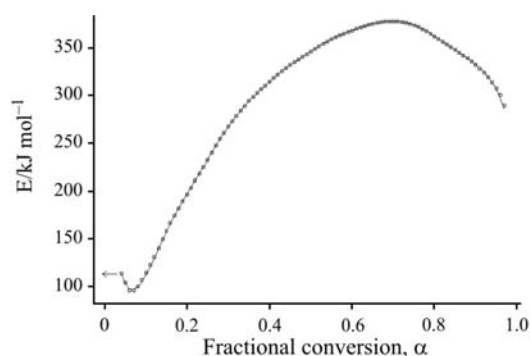


Fig. 5 The porous structure of silver residue composed of accreted particles ($1\text{--}2\text{ }\mu\text{m}$) at 350°C (isothermal heating)

Table 1 Silver acetate AgCH_3COO . Data of F -test on fit-quality (for the search of the best kinetic description, $\alpha=0.45\text{--}0.90$)

No.	Code	Type	F_{act}	F_{exp}	$F_{\text{crit}}(0.95)$	Corr. coeff.
1	S	CnB	5	1.00	5.10	0.998360
2	S	Bna	4	1.29	6.32	0.998359
3	S	D3	6	5.96	4.42	0.988083
4	S	A2	6	132.80	4.42	0.687516

**Fig. 6** The kinetic analysis by Friedman method of TG curves (5 and $10^\circ\text{C min}^{-1}$)

of radicals, included Ag). For the equations CnB or Bna (reactions with autocatalysis) $E_a=358 \text{ kJ mol}^{-1}$, $\log A=33$. Both the high overheating (exothermic reaction) and autocatalysis by the formed metal particles complicates the decomposition still more. So the calculated formal kinetic parameters are evaluative and conditional (which is well seen from the very high pre-exponential factor).

The overall exothermic thermal effect of decomposition process (silver reduction at $270\text{--}286^\circ\text{C}$ with corresponding mass loss 30%) is 13 kJ mol^{-1} . The flat peak ($290\text{--}330^\circ\text{C}$, being not connected with mass loss, can be attributed to the particles enlargement (Figs 4 and 5). The thermal effect of this process is 33 kJ mol^{-1} . These values are evaluative ones (simple average from two measurements), but it is obvious that the formation of the silver nanoparticles (non-equilibrium and metastable) takes place at low temperatures, their enlargement occurs at $290\text{--}330^\circ\text{C}$, and the heat of the enlargement is distinctly more than the heat of reduction reaction.

For checking that the heat of chemical reaction of reduction is really smaller than the particles enlargement (aggregation) we synthesized new sample of CH_3COOAg and repeated the DSC study, the heat ratio is the same.

Conclusions

Thermal decomposition of silver acetate in inert atmosphere is a favorable technique for the prepa-

ration of highly dispersed silver metal. Rather low temperature of this intramolecular reduction of metal (210°C under isothermal heating, $260\text{--}286^\circ\text{C}$ from DSC experiment) results in the formation of non-equilibrium and metastable nanoparticles of silver; this nanoparticle phase is kinetically hindered: the nanoparticles enlargement, occurring with the big exothermic effect (and the constant rate) at $290\text{--}330^\circ\text{C}$, confirms their non-equilibrium state in the moment of formation.

The thermal decomposition of salts and complex compounds of varied metals (lanthanides and transition metals, in general) with carboxylic and other organic ligands is widely studied nowadays [8–13]. Most of decomposition processes were conducted in the air; really the studied process (terminologically) was not the substance ‘thermal decomposition’ (intramolecular reduction of the metal by organic ligand), but the substance ‘thermooxidative degradation’, i.e. oxidation by air oxygen under heating (intermolecular reaction); so the final residues were metal oxy-salts, oxides or sulfides (nanoparticles sometimes [11, 14]). Only the noble metals can be obtained directly during such thermal decomposition in the presence of air [15].

The silver nanoparticles formation (with the reduction of silver ions in aqueous solution by hydroquinone) was studied by the method of titration microcalorimetry. It is interesting to note that there are three consecutive steps leading to the formation of silver nanoparticles: 1) nucleation step (exothermic), 2) growth step (endothermic) and 3) aggregation step (exothermic) [16]. This reduction reaction is intermolecular $\{\text{Ag}^+ + \text{C}_6\text{H}_4(\text{OH})_2\}$.

We think that the intramolecular reaction of silver reduction in solid state, considered above, does not give a chance for clear separation of all these steps in thermoanalytical experiments, especially with linear heating. But the existence of nucleation and aggregation steps is evident.

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