Chinese Journal of Chemistry, **2004**, *22*, 1091—1094 **Article**

Non-Isothermal Kinetics of the Decomposition Reaction of Cluster $[Ag_3WS_3Br](PPh_3)_3$ and $[Cu_3WS_3Br](PPh_3)_3$

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The thermal behaviors of clusters $[Ag_3WS_3Br](PPh_3)_3$ and $[Cu_3WS_3Br](PPh_3)_3$ (PPh_3=triphenyl phosphine) in a nitrogen atmosphere were studied under the non-isothermal conditions by simultaneous TG-DTG-DSC and EDS techniques. The results showed that the evolution of PPh_3 generally proceeded before the release of the other moiety in one or two step-mode. The mechanisms, the kinetic and the thermodynamic parameters for decomposition of PPh_3 of both clusters were determined and calculated by jointly using several methods, which showed that its evolution was controlled by Avrami-Erofeev equation. The results also showed that there was no new stable phase composed of W-Ag(Cu)-S-Br after release of organic moiety PPh_3 and that CVD method was not applicable to their further processing.

Keywords copper, silver, tungsten, metallic cluster, TG-DTG-DSC, thermal analysis kinetics

Introduction

Mo(W)/Cu(Ag)/S clusters are a quite important member of the sulfur-containing metallic cluster family derived from $[MX_4]^{z-}$ (where M=Mo, W, Nb, V, Re, Ta; X=S, Se; z=1—3) and have been of considerable interest due to not only their distinctive molecular structure as heterometallic sulfide cluster, but also their practical importance in various fields,[1-3] such as catalytic hydro-desulfurization in petrochemical industry,[4] and nitrogen fixation in biomimetic chemistry.[5] Meanwhile, they have also shown potential as materials for special purposes, such as superconducting[6] and third-order nonlinear optical materials.[7] So far as we know, however, there has been little information concerning their thermal properties which is actually very important for them to be better processed and thus more extensively used.

In our previous studies,[8,9] we devoted attention to the preparation and the crystal structure of a new sort of clusters, *i.e.*, title compounds $[Ag_3WS_3Br](PPh_3)_3$ and $[Cu_3WS_3Br](PPh_3)_3$ (PPh_3-triphenyl phosphine). In order to further investigate their properties and application, their thermal stability, thermal behavior and decomposition kinetics have been studied using TG-DTG-DSC technique. Besides, we wish to find out a proper temperature at which these clusters may be made into thin film by chemical vacuum deposition (CVD) method so that their optical property could be further determined. We also expect to reveal whether some new phases composed of W-Cu/Ag-S exist after their organic group is expelled and whether new phases, if exist, have special properties such as superconductivity.

Experimental

Sample

The Ag cluster was prepared by a solid reaction of $(NH_4)_2WS_4$, AgBr and PPh_3 under the protection of nitrogen atmosphere, while Cu cluster was synthesized in the same route as Ag cluster with CuBr instead of AgBr under the protection of argon instead of nitrogen. Their compositions were confirmed by elemental analysis and IR, and the quality of the sample for TA study was identified with that of the samples for single crystal XRD study. The detailed procedures of preparing and obtaining both crystals were the same as described in our previous work.[8,9]

Equipment and conditions

Thermal decomposition of the title compounds was carried out on thermoanalyzer (SDT 2960, TA Instruments), which allows simultaneous detection of mass changes and heat effect of the reaction.[10,11] Crucibles were made of alumina. The instrument was previously calibrated against standard substances provided by TA instruments. All experiments were done in nitrogen atmosphere with flow rate 60 $mL \cdot min^{-1}$. The mass of the samples used was 5—10 mg. Non-isothermal measurements were performed at heating rate (β) of 5, 10, 15 and 20 $K \cdot min^{-1}$, respectively. Simultaneous TG-DTG-DSC curves were obtained in the range 35—900 ℃.

Both the intermediates and residues of the decompo-

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sition reaction were analyzed or checked by a Carlo-Erba model 1110 elemental analyzer and an energy-dispersive spectrometer (EDS) of model EDAX PV9900.[10,11]

Kinetic methods

In view of general complexity in the processes involved in solid-state reactions,[12-15] several thermal analysis kinetic (TAK) methods were jointly employed in this paper to process the TG-DTG data to determine the decomposition mechanisms and to calculate the Arrhenius parameters, *i.e.* the activation energy E and the pre-exponential factor A for the clusters studied. These methods are as follows.

Achar-Brindly-Sharp (A-B-S) equation:

$$\ln\left[\frac{1}{f(\alpha)}\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right]=\ln A-\frac{E}{RT} \tag{1}$$

Coats-Redfern (C-R) equation:

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

Kissinger equation:

$$\ln\frac{\beta}{T_p^2}=\ln\frac{AR}{E}-\frac{E}{RT_p} \tag{3}$$

Flynn-Wall-Ozawa (F-W-O) equation:

$$\lg\beta=\lg\frac{AE}{Rg(\alpha)}-2.315-0.4567\frac{E}{RT} \tag{4}$$

Since the above equations and the symbols in them are those in common use, we omit their references and annotation to save space.

As the two multiple scanning methods, *i.e.* Kissinger and Flynn-Wall-Ozawa equations, are model-free isoconversional methods and allow the activation energy to be independently obtained, the E values calculated using them were used to check the constancy and validity of activation energy by the other methods.

After the kinetic parameters E and A were obtained, the thermodynamic parameters of activation can be calculated from the following equation:[16,17]

$$A\exp\frac{-E}{RT}=\nu\exp\frac{-\Delta G^{\neq}}{RT} \tag{5}$$

$$\Delta H^{\neq}=E-RT \tag{6}$$

$$\Delta G^{\neq}=\Delta H^{\neq}-T\Delta S^{\neq} \tag{7}$$

where $\Delta G^{\neq}$, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are free energy, enthalpy and entropy, respectively, ν is the Einstein vibration frequency, $\nu=k_BT/h$ (where k_B and h are Boltzmann and Planck constant respectively).

Results and discussion

Thermal behavior

The TG-DTG and DSC curves at a heating rate of 5 K•min^{-1} for both clusters are given in Figures 1 and 2, respectively. The general information about their thermal behavior in terms of stability range, peak temperature, percentage mass loss and probable composition of expelled groups corresponding to each decomposition stage is presented in Table 1.

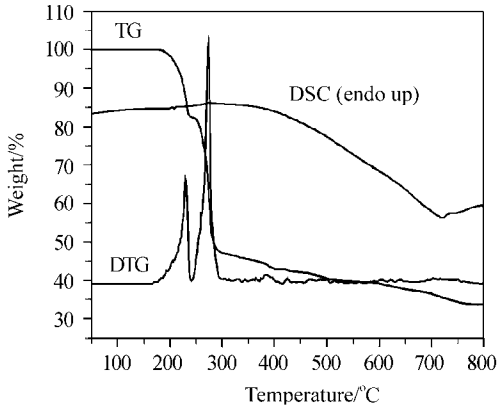

Figure 1 TG-GTG-DSC curve of Ag cluster.

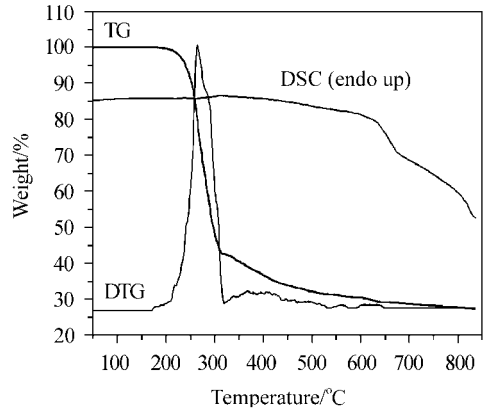

Figure 2 TG-GTG-DSC curve of Cu cluster.

In order to make discussion clearer, it seems helpful to recollect both the main part of molecular and some useful crystal structure data of these clusters, which have been studied by XRD and reported in our previous paper [8,9] and here showed in Figure 3 and Table 2, respectively.

The mass loss percentage indicates that both the clusters release PPh_3 first in two different modes: for Ag cluster is of two-step pattern, that is, the first step corresponds to the evolution of one PPh_3, the second step to

Table 1 Thermal decomposition data for $[Ag_3WS_3Br](PPh_3)_3$ and $[Cu_3WS_3Br](PPh_3)_3$ (PPh_3-triphenyl phosphine) under an atmosphere of dynamic nitrogen (β=5 K•min^{-1})

Compound [a]	Stage	Temp. range/℃	DTG peak temp./℃	Loss of mass/%		Probable composition of expelled groups[b]
				Obs.	Theory	
Ag cluster	I	167—238	229	0.1753	0.1744	1 PPh_3
	II	238—297	275	0.3457	0.3488	2 PPh_3
	III	297—772	—	0.1397	0.1386	4 S, Br
Cu cluster	I	183—315	266	0.5740	0.5743	3 PPh_3
	II	315—811	—	0.3321	0.3475	4 S, Br

[a] $[Ag_3WS_3Br](PPh_3)_3$ and $[Cu_3WS_3Br](PPh_3)_3$; [b] PPh_3=triphenyl phosphine

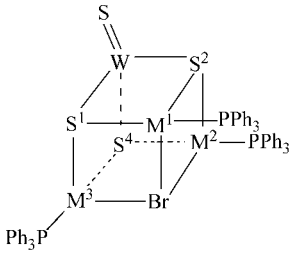

Figure 3 Schematic drawing of title compounds.

Table 2 Some bond length (nm) for title clusters

	Ag cluster	Cu cluster
M(1)—PPh_3	0.2378	0.2209
M(2)—PPh_3	0.2402	0.2211
M(3)—PPh_3	0.2388	0.2222
W—S (average)	0.2216	0.2207
M—Br (average)	0.2924	0.2760

the other two PPh_3; while for Cu cluster is of one step mode, that is, all the three PPh_3 moieties were expelled simultaneously in a single step (see Figures 1 and 2 for comparison). This was confirmed by an analysis of the intermediate products of both clusters isolated immediately after the first step for Cu cluster (while the second step for Ag cluster) using the elemental analyzer and the energy-dispersive spectrometer (EDS). The behavior may be attributed to the fact that the lengths of three coordination bonds, M-PPh_3, for Cu cluster are similar, while for Ag cluster they are different with a bond length (0.2402 nm) longer than the other two (0.2378 and 0.2388 nm) as the bond lengths reflect to a certain extent the bond strength and thus thermal stability. The following decomposition step for both clusters is corresponding to the dissociation of the cubic skeleton composed of M_3WS_3BrS (M=Ag or Cu), which shows a one-step decomposition mode. The mass loss percentage for this step suggests that the four S and a Br atom are simultaneously expelled in such a smooth way even without a clear peak on its corresponding DTG curve. A careful inspection using EDS revealed that this step is actually partly overlapped by the evolutions of Br and S successively (Br first, and then S). Figure 4 shows the result by EDS for the intermediate products of Ag cluster which was isolated at a temperature within this step. This phenomenon may also be explained by comparison of the length values of W-S with Cu(Ag)—Br bond, which also suggests a relatively stable tetrahedral WS_4 structure. The mass loss and the elemental analysis using EDS indicate that the final residue at the end of decomposition was a mixture of metal W and Ag (or Cu).

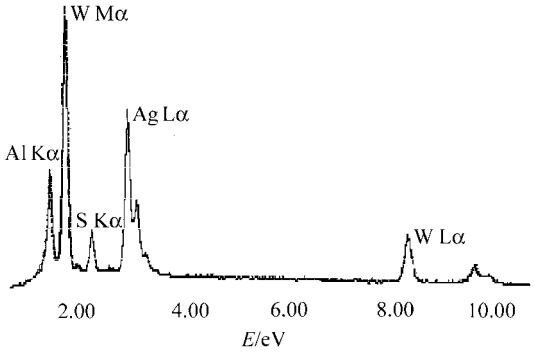

Figure 4 EDS analysis for an intermediate of Ag cluster during its decomposition (element Al is from the sample pan).

The DSC curve of neither Ag nor Cu cluster shows any obvious heat effect.

Thermal decomposition kinetics

The basic data, β and T_p, obtained from TG-DTG curves are summarized in Table 3 which were used to calculate the activation energy E or pre-exponential factor lg A by both Kissinger and Flynn-Wall-Ozawa (FWO) equations. Table 4 gives the complete kinetic parameters, together with their appropriate linear correlation coefficient r and standard deviation, *S.D.* for both clusters studied. The E and lg A values by these two methods were also used to check the reasonableness of those by the other methods, Achar-Brindly-Sharp and

Table 3 Peak temperature T_p of DTG curves at various heating rates β

Compound[a]	Stage	β/(K•min^{-1}) (T_p/℃)			
Ag cluster	I	5 (229.1)	10 (236.6)	15 (241.5)	20 (245.2)
	II	5 (275.2)	10 (283.5)	15 (288.9)	20 (292.3)
Cu cluster	I	5 (265.9)	10 (274.1)	15 (280.0)	20 (282.8)

[a] The same as the note to Table 1.

Table 4 Kinetic parameters of thermal decomposition for both Ag and Cu clusters

Compound[a]	Stage	Method[b]	E/ (kJ•mol^{-1})	lg A	r^c	$S.D.^d$	$\Delta G^{\neq}$/ (kJ•mol^{-1})	$\Delta H^{\neq}$/ (kJ•mol^{-1})	$\Delta S^{\neq}$/ (J•mol^{-1}•K^{-1})
Ag cluster	Ⅰ	Kissinger	178	16.4	0.9995	0.0222	145	174	56.4
		F-W-O	178	—	0.9996	0.00958			
	Ⅱ	Kissinger	198	16.7	0.9998	0.0138	156	193	67.5
		F-W-O	197	—	0.9998	0.00597			
Cu cluster	Ⅰ	Kissinger	191	16.3	0.9985	0.0383			
		F-W-O	190	—	0.9986	0.0166			

[a] The same as the notes to Table 1; [b] F-W-O, Flynn-Wall-Osawa; [c] linear coefficient; [d] standard deviation.

Coats-Redfern methods which employed 43 common kinetic mechanism functions of $f(\alpha)$ and $g(\alpha)$ to obtain "kinetic triplet".[18] The most probable mechanism for decomposition of PPh_3 of both clusters is Avrami- Erofeev equation, *i.e.* random nucleation and nucleus growth mechanism, $f(\alpha)=(3/2)(1-\alpha)[-\ln(1-\alpha)^{1/2}]^{-1}$.

As the second or the third step of Cu or Ag cluster respectively is a partly overlapped step, that is a multiple step, its kinetic parameters are thus considered non-significant and no attempt to kinetically study them has been made.[12]

Conclusions

According to the experimental conditions in the present study, it seems not that there exists a stable new phase composed of W-Ag(Cu)-S-Br after release of organic moiety PPh_3. Besides, the clusters studied show no phase transition, such as melting, before their decomposition, and the CVD method may thus not be applicable to them.

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