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Thermal analysis of organocopper and organotin metal films.
Part 8

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Abstract

The thermal stabilities of copper and tin films containing various organic solvents have been studied by thermogravimetry (TG) between 298 and 823 K under a flow of nitrogen. The thermal stabilities of the Cu films decrease in the order Cu–THF > Cu–DMF > Cu–toluene > Cu–ethanol > Cu–acetone > Cu–2-butanone > Cu–benzene, Cu–2-propanol > Cu–DMSO. On the other hand, the organotin films exhibit a decreasing stability in the following order: Sn–2-propanol > Sn–ethanol > Sn–acetone > Sn–2-butanone, > Sn–benzene > Sn–DMF, Sn–DMSO > Sn–toluene. This suggests that the solvent incorporated into the film has a considerable influence on the stability, in that solvents containing oxygen are very stable and have a comparatively high thermal decomposition temperature (T_D) and low residual weight. The order of the thermal decomposition reaction was found to be zero in most of the cases. The pre-exponential factor and the activation energy of the decomposition of Cu and Sn metal films are also compared.

INTRODUCTION

The thermal stability of thin copper films is commercially important in view of their potential applications for oxidizing alcohols [1], as is that of tin films because of their use in reducing aldehydes and ketones [2]. The thermal properties of these films can be measured from weight loss studies as well as by measurement of their relative decomposition temperature (T_D). Thermogravimetric analysis was used to determine the activation energy, pre-exponential factor and temperature of the decomposition reaction applying a simple decomposition mechanism [3].

The activation energies ΔE_a for the decomposition of the tin films are

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similar to those reported for Pd and In [4]. Organocopper films exhibit lower values, most probably because of the high reactivity of the copper and its ease of oxidation. However, values of this parameter are also comparable to those reported for metal poly(methyl methacrylates) [5] and for the metal polyacrylonitriles [6]. The stability of metal films is important in the synthesis of new materials for solar cells and optical devices [7, 8].

The metal films containing organic solvents were synthesized from colloidal sols [9]. Sols of copper and tin were prepared in solvents such as acetone, 2-butanone, tetrahydrofuran (THF), dimethylformamide (DMF), dimethyl sulfoxide (DMSO), ethanol, 2-propanol, benzene and toluene, and films were produced by evaporation of the solvent.

EXPERIMENTAL

The colloids were prepared by codeposition of the solvents with the metals at 77 K using a metal atom reactor [10]. From the weights of metal evaporated and solvent added, the approximate concentration could be calculated.

The Cu and Sn films were prepared by direct evaporation of the colloids in vacuo by pumping for 24 h at 10^{-3} Torr.

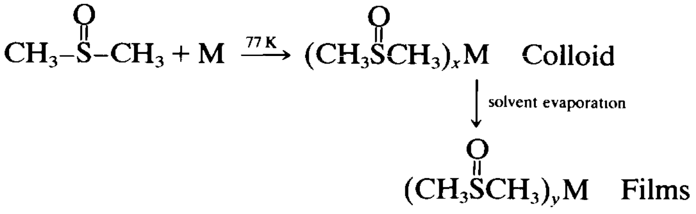
The films were analyzed for metal content and the concentration of solvent was determined from C, H, N and S analyses.

The thermogravimetric analysis was carried out using a Perkin-Elmer TGA-7 thermobalance. Samples (2–5 mg) were placed in aluminum pans and heated under nitrogen flow (50 ml min^{-1}) at 10 K min^{-1} between 298 and 823 K.

RESULTS AND DISCUSSION

The synthesis of thin metal films by evaporation of colloidal sols has been already reported [11, 13]. The Sn films had a higher metal content (>85%) than the Cu films (65%). The films were composed of metal atom clusters with occluded organic solvents, and none of the films exhibited a melting point.

The following scheme summarizes the synthesis.



$$\mathrm{CH_3{-}\overset{\overset{O}{\|}}{S}{-}CH_3} + \mathrm{M} \xrightarrow{77\,\mathrm{K}} (\mathrm{CH_3\overset{\overset{O}{\|}}{S}CH_3})_x\mathrm{M} \quad \text{Colloid}$$

$$\Big\downarrow \text{solvent evaporation}$$

$$(\mathrm{CH_3\overset{\overset{O}{\|}}{S}CH_3})_y\mathrm{M} \quad \text{Films}$$

where M is Cu, Sn, and $y = 2–4$.

The most interesting feature of these films was the incorporation of the

TABLE 1

Percentage weight loss from organocopper films [a]

Temp. (K)	Ethanol (%)	2-Propanol (%)	Acetone (%)	2-Butanone (%)	THF (%)	DMF (%)	DMSO (%)	Toluene (%)	Benzene (%)
393	0.76	3.09	2.56	1.38	0.23	0.84	5.72	0.83	2.15
443	3.47	6.94	10.51	11.80	1.72	2.30	11.63	2.50	5.80
493	5.20	12.50	29.67	20.35	3.28	3.39	16.31	4.02	9.02
543	6.94	13.19	33.22	21.70	4.15	4.17	20.13	5.41	12.50
593	9.02	14.27	34.42	23.26	5.02	5.39	21.87	6.66	13.88
643	9.02	16.66	37.68	25.69	7.34	7.30	24.30	7.36	17.70
693	9.02	17.39	40.62	28.12	9.83	9.38	25.69	8.19	22.15
723	9.02	17.74	42.63	29.51	11.53	10.93	26.04	8.33	26.52
793	9.02	18.05	44.13	30.55	15.18	11.73	27.77	8.61	29.16
823	9.02	18.05	44.13	30.55	15.18	11.73	27.77	8.61	29.16

[a] Heating rate 10 K min^{-1}.

solvent into the metal clusters, most probably by insertion and/or bond formation through the oxygen of the solvent. Mass spectrometry of Sn films showed the presence of 2–4 molecules of solvent per atom of metal. This behavior is similar to that of Ge films [12] and also metal polystyrenes, as already reported [14].

Table 1 shows the percentage weight loss from organocopper films when they are heated from 298 to 823 K, and Table 2 shows the percentage weight loss from the organotin films. The Sn films degrade in one stage at temperatures exceeding 500 K (see Table 3). The Sn films are very stable, especially those with ethanol, 2-propanol, acetone and 2-butanone, which give the lowest weight losses (1–2%); see Table 2. This is in agreement also with the T_D values, which in all cases are high. Alcohols and ketones are the most thermally stable and a bond between the oxygen and Sn can be formed, which could account for the higher stability of these films.

TABLE 2

Percentage weight loss from organotin films [a]

Temp. (K)	Ethanol (%)	2-Propanol (%)	Acetone (%)	2-Butanone (%)	THF (%)	DMF (%)	DMSO (%)	Toluene (%)	Benzene (%)
293	0	0	0	0	0	0	0	0	0
353	0	0	0	0	0	0	0	0	0
393	0	0	0	0	0	0	0	0	0
403	0	0	0.33	0	2.06	0	0	0	0
433	0.74	0	1.15	0.9	2.54	0	2.45	0	0.22
483	1.64	0.96	1.64	1.8	3.17	3.06	7.78	2.12	3.77
513	1.64	1.06	1.64	1.8	3.17	6.13	10.33	10.06	3.85
563	1.64	1.06	1.64	1.8	3.17	11.29	12.24	15.00	3.85
613	1.64	1.06	1.64	1.8	3.17	11.29	12.24	15.00	3.85
663	1.64	1.06	1.64	1.8	3.17	11.29	12.24	15.00	3.85
713	1.64	1.06	1.64	1.8	3.17	11.29	12.24	15.00	3.85
823	1.64	1.06	1.64	1.8	3.17	11.29	12.24	15.00	3.85

[a] Heating rate 10 K min^{-1}.

TABLE 3

Kinetic parameters of organotin films

Film	Reaction order, n	Activation energy (kJ mol^{-1})	Frequency factor A (s^{-1})	T_D (K)
Sn–ethanol	0	85	2.0×10^{-3}	593
Sn–2-propanol	0	38	3.4	553
Sn–acetone	−1	87	2.9×10^{3}	540
Sn–2-butanone	−1	148	5.9	548
Sn–THF	−1	117	5.3	473
Sn–DMF	−1	111	7.4×10^{4}	563
Sn–DMSO	−1	68	2.9×10^{4}	493
Sn–toluene (A)	0	87	1.3×10^{2}	523
Sn–benzene (B)	0	62	2.3×10^{3}	543

The Sn–ethanol film gave the highest activation energy and also the highest residual weight.

The organocopper films lose 10–40% of their weight (see Table 1) and the E values are lower than those for organotin films. Again, Cu films involving ketones, THF and DMF films have higher E values because of a stronger bond formation though the polarized oxygen atoms (see Table 4). The Cu–ethanol and Cu–2-propanol films have very low values because of the increased reactivity of Cu and the tendency for it to oxidize the alcohols to aldehydes. The other difference between these films is that the organocopper films exhibit mainly zero order decomposition kinetics. Most of the ketones exhibit two stage decomposition, and the total E values are listed in Table 4 along with both values of the T_D temperatures. The organocopper films are less stable, most of them with the first decomposition values

TABLE 4

Kinetic parameters of organocopper films

Film	Reaction order, n	Activation energy (kJ mol^{-1})	Frequency factor A (s^{-1})	T_D (K)
Cu–acetone	0	31	4.93	475, 657
Cu–2-butanone	0.25	36	2.9×10^{2}	464, 618
Cu–THF	0	31	92.84	661, 703
Cu–DMF	0	25	6.24	582, 722
Cu–DMSO	0	14	6.3×10^{-1}	432
Cu–ethanol	0	8	6.3×10^{-3}	477
Cu–2-propanol	0	11	8.4×10^{-1}	437
Cu–benzene	0	8	1.2×10^{-2}	463
Cu–toluene	0.5	14	4.0×10^{-1}	490

around 460 K, with the exception of that for Cu–THF which is even higher than the values for the organotin films.

If we consider that the decomposition reaction is irreversible, the rate-dependent parameters such as activation energy and reaction order may be calculated from a non-isothermal thermogravimetric curve [15]. The overall rate constant k can be expressed in the Arrhenius form $k = A\exp(-E_a/RT)$, where A is the frequency factor, E_a the activation energy, R the gas constant and T the absolute temperature.

The thermal decomposition kinetics from the weight loss temperature curves can be described in terms of the general kinetic equation $-d\alpha/dt = k(1-\alpha)^n$, where α is the fraction of the sample weight reacted at time t, n is the reaction order and k is the overall rate constant. The reaction rate $d\alpha/dt$ was calculated using differential thermogravimetry at a heating rate v of 10 K min^{-1} and weight-fraction versus temperature plots [16]. Since $d\alpha/dt = v(d\alpha/dT)$, the following expression can be obtained

$$\beta = \ln\left[\frac{v(d\alpha/dT)}{(1-\alpha)^n}\right] = \ln A - \frac{E}{RT} \qquad (1)$$

A multiple regression program was used to calculate the kinetic parameters E and A assuming a first-order reaction model. Plotting β versus $1/T$ should give a straight line, the slope and intercept of which enable E_a and A to be determined.

For most of the organocopper films, the linear correlation obtained indicated that the reaction order was zero. Only in the case of Cu–2-butanone was $n = 0.25$, probably because of the presence of a multistep decomposition reaction (see Table 4; T_D values were 464 and 618 K, respectively). This film had one of the highest n values, but it is still lower than that for Pd, Ge and In with the same solvent [4]. This is further evidence of the effect of the nature of the metal in determining the stability and activation energy.

The Cu–alcohol films gave very low E_a values owing to their low stability. On the other hand, Cu–ketone films exhibit higher values, ranging from 31 to 36 kJ mol^{-1}. The coefficients of linear correlation vary from 0.959 to 0.997. The kinetic parameters E and A calculated from these plots are summarized in Table 4.

The organotin films exhibit zero reaction order for the alcohols, toluene and benzene. All the other organotin films, those with ketones, THF, DMF and DMSO, show negative reaction orders. This is because of the very low content of carbonaceous species in the films and a multistep decomposition mechanism. The E_a values observed are within the range of those for Pd, Ge and In–2-butanone films reported previously [4]. The E_a values range from 38 to 148 kJ mol^{-1} for Sn–2-propanol and Sn–2-butanone, respectively. The order −1 is probably due to changes in the decomposition mechanism. Furthermore, compounds containing C=O groups show the highest E_a values and are the most stable thermally. The coefficients of linear correlation range between 0.935 and 0.996. The data is summarized in Table 3.

The difference in oxidation potential between the two metals is reflected in the different properties of these films. Also, the colloid stability is related in some cases to their T_D and E_a values.

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REFERENCES

1 R. Oliva C., Licenciado Thesis, University of Concepción, 1992.
2 J. Acuña E., Licenciado Thesis, University of Concepción, 1992.
3 J.R. MacCallum, in G. Allen (Ed.), Comprehensive Polymer Science, Vol. 1, Pergamon, London, 1989, p. 905.
4 G. Cárdenas T. and L.H. Tagle D., Thermochim. Acta, 184 (1991) 131.
5 G. Cárdenas T., C. Retamal C. and L.H. Tagle D., Thermochima. Acta, 176 (1990) 233.
6 G. Cárdenas T., C. Retamal C. and L.H. Tagle D., Thermochim. Acta, 188 (1991) 221.
7 I. Chambouleyron, F.C. Marques, J.P. de Souza and J.R. Baumvol, J. Appl. Phys., 63 (1988), 5596.
8 M.S. Holt, W.L. Wilson and J.H. Nelson, Chem. Rev., 89 (1989) 11.
9 G. Cárdenas T. and R. Oliva C., XX Congreso Latinoamericano de Química, Sto. Domingo, Dominican Republic, 1992.
10 G. Cárdenas-Triviño and P.B. Shevlin, Bol. Soc. Chil. Quím., 32 (1987) 111.
11 G. Cárdenas T., K.J. Klabunde and E.B. Dalt, Langmuir, 3 (1987) 986.
12 G. Cárdenas T., M. Alvial J. and K.J. Klabunde, Bol. Soc. Chil. Quím., 35 (1990) 277.
13 G. Cárdenas T., M. Alvial J., K.J. Klabunde and Li Yong Xi, Bol. Soc. Chil. Quím., 37 (1992) 19.
14 G. Cárdenas-Triviño and K.J. Klabunde, J. Appl. Polym. Sci., Appl. Polym. Symp., 49 (1991) 15.
15 E.S. Freeman and B. Carroll, J. Phys. Chem., 621 (1950) 394.
16 W.Y. Wen and J.W. Lin, J. Appl. Polym. Sci., 22 (1978) 2285.