Available online at www.sciencedirect.com
ScienceDirect
Thermochimica Acta 456 (2007) 89–93
thermochimica acta
www.elsevier.com/locate/tca

A DSC study on the kinetics of disproportionation reaction of (hfac)Cu^I(COD)

Gene Chen [a], Chiapyng Lee [a,*], Yu-Lin Kuo [a], Yee-Wen Yen [b]

[a] Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei 106, Taiwan, ROC
[b] Graduate School of Materials Science and Technology, National Taiwan University of Science and Technology, Taipei 106, Taiwan, ROC

Received 15 August 2006; received in revised form 30 December 2006; accepted 2 January 2007
Available online 16 January 2007

Abstract

The kinetics of disproportionation reaction of hexafluoroacetylacetonate-copper(I)-cycloocta-1,5-diene [(hfac)Cu^I(COD)] was investigated by the use of differential scanning calorimetry (DSC) with different heating rates in dynamic nitrogen atmosphere. First, the activation energies (E_as) of the disproportionation reaction were estimated with model-free isoconversional methods, respectively. The E_as were found to fall within the range between 17.6 and 18.7 kJ mol^{-1}, with no temperature and heating rate effects observed. Then, when the E_a was ascertained, the model-fitting methods with least square fitting procedure were adopted to determine the kinetic model for the disproportionation reaction. As a result, the disproportionation reaction follows second-order reaction kinetics.

Keywords: Disproportionation reaction; (hfac)Cu(COD); Kinetics; Model-free method; Model-fitting method

1. Introduction

One of the current applications of Cu(I) β-diketonate compounds is their utilization in the metallization of ultralarge-scale integrated circuits (ULSI) [1]. These compounds have been studied extensively as metal–organic chemical vapor deposition (MOCVD) precursors [2–4]. The best known group of all Cu(I) β-diketonate precursors is (hfac)Cu^I–L [5], in which L is a neutral ligand. The CF_3 groups in hfac are strong electron withdrawing groups that decrease the electronic density of Cu(I) and strengthen the Cu–L bond. Among (hfac)Cu^I–L precursors, (hfac)Cu^I(COD) was chosen as the focus of this study because it has an applicable vapor pressure, approximately 0.135 Torr at 62 °C, and it has been proved to produce Cu films of low resistivity over a relatively low temperature range (150–250 °C) [1]. These features make (hfac)Cu^I (COD) a good candidate as a MOCVD precursor for producing Cu films in Cu metallization.

Via thermally induced disproportionation reaction [6–8] of

$$2(\text{hfac})\text{Cu}^{\text{I}}(\text{COD})_{(s)} \rightarrow \text{Cu}^0{}_{(s)} + 2\text{COD}_{(g)}\uparrow + \text{Cu}^{\text{II}}(\text{hfac})_{2(g)}\uparrow \quad (1)$$

high purity copper metal is produced along with $Cu^{II}(hfac)_2$ and COD. This means (hfac)Cu^I(COD) during storage may bring about disproportionation reaction. Therefore, its shelf life would be a crucial factor to be determined before it could be commercialized as a MOCVD precursor for producing quality Cu films. However, the reaction kinetics of solid state disproportionation of (hfac)Cu^I(COD) has never been studied. Thus the present work aims to determine the possible kinetic model of the reaction of (hfac)Cu^I(COD) by the use of DSC.

For the analysis of DSC data, many methods have been reported. Among the reported methods, the isoconversional type has been recommended as a trustworthy way for determining reliable and consistent activation energies (E_as) of solid state reactions [9]. Based on DSC data, the isoconversional methods can determine the actual value of E_a without knowledge of the kinetic model. And with an predetermined activation energy, the kinetic model can be obtained with model-fitting methods. Therefore, this two-step approach to a formal kinetic analysis of processes in solids is adopted in this study.

In the present work, E_as were first calculated with the three model-free isoconversional, (1) Kissinger–Akahira–Sunose (KAS) [10,11], (2) Starink ($\kappa = 1.92$) [12] and (3) Tang [13], methods, respectively. Then, 13 different kinetic functions of the most common models in solid-state reactions were tested with

---

* Corresponding author. Tel.: +886 2 27376623; fax: +886 2 27376644.
E-mail address: cl@ch.ntust.edu.tw (C. Lee).

0040-6031/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2007.01.007

the two model-fitting, (1) differential and (2) integral, methods, respectively.

2. Experimental

The compound (hfac)Cu^{I}(COD) was synthesized from 1,5-COD, hexafluoroacetylacetone(hfacH) and Cu_2O with the procedure reported by G. Doyle et al. [14]. hfacH and 1,5-COD were purchased from Aldrich Chemical Company, and tetrahydrofuran (THF) from ACROS Chemical Company.

The synthesized (hfac)Cu^{I}(COD) was characterized by NMR and TG. The ^{1}H NMR spectrum was obtained from a Jeol EX-400MHz spectrometer. And, TG experiments were conducted on a TGD 7000. For the TG analysis of (hfac)Cu^{I}(COD), samples of approximately of 50 mg each were analyzed under the following experimental conditions: a heating rate of 10 K min^{-1} with a nitrogen flow rate of 20 ml min^{-1}. In a separate experiment, the disproportionation reaction kinetics of (hfac)Cu^{I}(COD) were investigated with the DSC analysis that was conducted on a DSC 2021 TA instrument, with heating rates of 5, 10, 20 and 50 K min^{-1}, under nitrogen flow. A 3.0 mg sample was weighed and then directly placed into an unsealed Al pan for DSC analysis. The reaction residue was analyzed with RIGAKU RTP 300 X-ray diffractometer (XRD).

3. Results and discussion

Fig. 1 shows the molecular structure of (hfac)Cu^{I}(COD). Its NMR Data are: ^{1}H($CDCl_3$, 20 °C) δ (ppm) 2.41 (s.br. 8H, CH_2 in 1,5-COD), 5.55 (s.br. 4H, CH in 1,5-COD), 5.92(s. 1H, CH in hfac). The NMR spectrum is consistent with the one reported by Baum et al. [15].

Fig. 2 shows the TG curve measured by heating (hfac)Cu^{I}(COD) from room temperature to 350 °C at a heating rate of 5 K min^{-1} in nitrogen atmosphere. The TG curve indicates the reaction occurring at 100–220 °C with a mass loss of 87.4%, which is close to the amount of weight loss expected for the formation of Cu metal from (hfac)Cu^{I}(COD) through disproportionation reaction. The slight disagreement observed (∼4%) could be attributed to the evaporation of small amount of (hfac)Cu^{I}(COD) during the heating. For the identification of the final product of disproportionation reaction of (hfac)Cu^{I}(COD) as Cu metal, a large amount of (hfac)Cu^{I}(COD) was heated to bring about the reaction at 130 °C in a 250 m^{3} Schlenk flask in an inert atmosphere. The product after cooling was examined with XRD. Fig. 3 is the XRD spectrum of the reaction product. As can be seen in Fig. 3, the (hfac)Cu^{I}(COD) undergoes disproportionation reaction to form copper metal. The same process was observed by Cohen et al. [6].

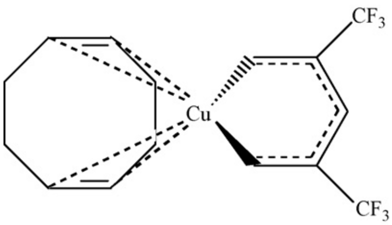

Fig. 1. Molecular structure of (hfac)Cu^{I}(COD).

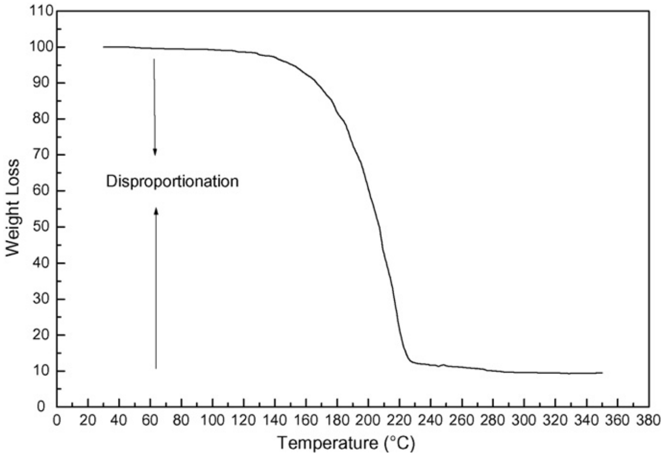

Fig. 2. TG curve of (hfac)Cu^{I}(COD) under flowing nitrogen with a flow rate of 20 ml min^{-1} and a heating rate of 10 K min^{-1}.

The kinetic model of a reaction that occurs under non-isothermal conditions can often be accurately described by Eq. (2) [16,17]:

$$\beta \frac{d\alpha}{dT} = A \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \qquad (2)$$

in which α is the degree of conversion, β the heating rate in K min^{-1}, A the pre-exponential factor in min^{-1}, T the temperature in K, R the gas constant, E_a the activation energy in kJ mol^{-1}, and $f(\alpha)$ is the reaction model. $f(\alpha)$ can take various forms depending on the model under consideration. Thus, E_a, A and $f(\alpha)$ form a “kinetic triplet”.

With other parameters kept constant, various heating rates ($\beta = 5$, 10, 20 and 50 K min^{-1}) were used to obtain the DSC curves of disproportionation reaction of (hfac)Cu^{I}(COD) in nitrogen, as shown in Fig. 4. The Non-isothermal α curves of disproportionation reaction of (hfac)Cu^{I}(COD) were sigmoid shaped. Plots of α curves are illustrated in Fig. 5. In the

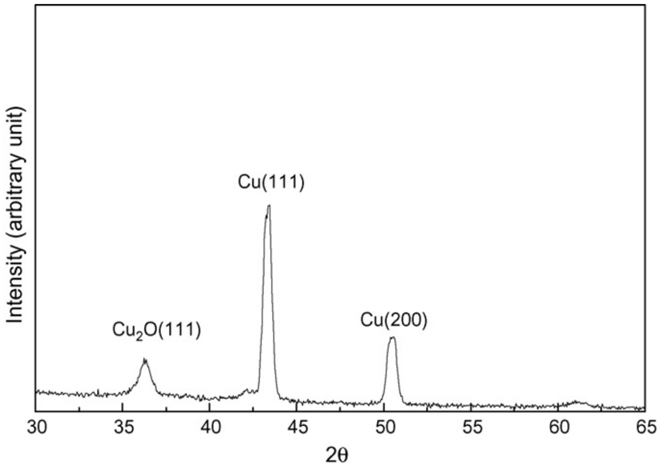

Fig. 3. XRD pattern of the residue after the disproportionation reaction of (hfac)Cu^{I}(COD).

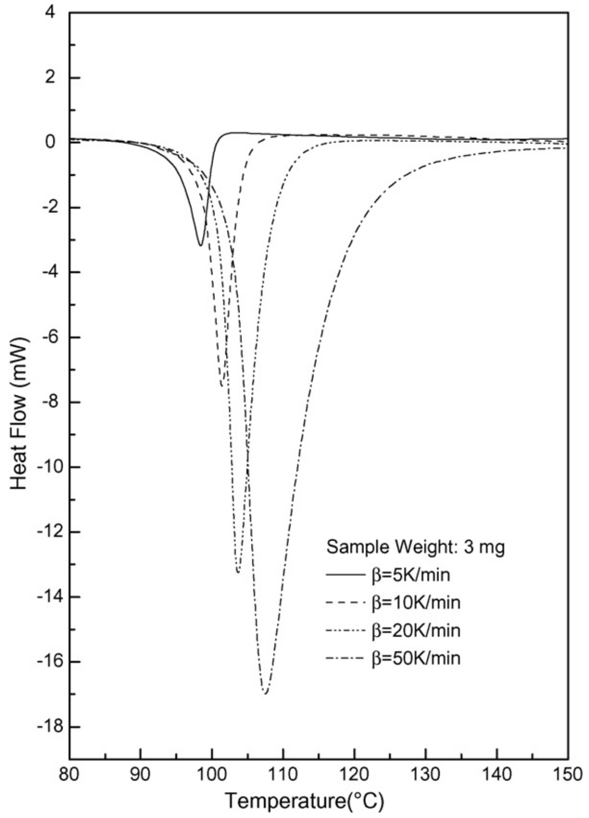

Fig. 4. DSC curves of the disproportionation reaction of (hfac)Cu^I(COD) with different heating rates: 5, 10, 20, and 50 K min^{-1} under flowing nitrogen.

search of the kinetic model of the disproportionation reaction in this study, two steps were taken: First, E_a was calculated with the model-free isoconversional method to avoid complication and confusion that could potentially be caused by the use of explicit kinetic models. Then, when the range of activation energy Ea is ascertained, the model-fitting method with least square fitting procedure was used to search for E_a, A and $f(\alpha)$, the "kinetic triplet". Detailed discussion is presented as follows:

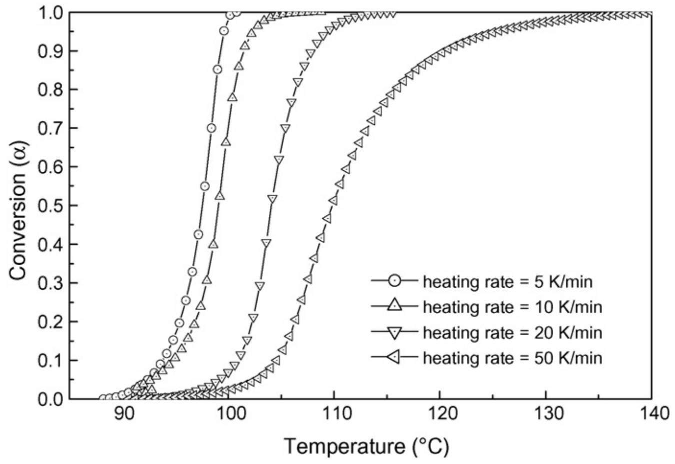

Fig. 5. Plots of the conversion (α) vs. temperature (T) with different heating rates: 5, 10, 20, and 50 K min^{-1}.

3.1. Model-free isoconversional method

The equations used for E_a calculation are: Kissinger–Akahira–Sunose (KAS) equation [10,11]:

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left[\frac{AE_a}{Rg(\alpha)}\right] - \left(\frac{E_a}{RT}\right) \tag{3}$$

Starink ($\kappa = 1.92$) equation [12]:

$$\ln\left(\frac{\beta}{T^{1.92}}\right) = C - 1.0008\left(\frac{E_a}{RT}\right) \tag{4}$$

Tang equation [13]:

$$\ln\left(\frac{\beta}{T^{1.894661}}\right) = \ln\left[\frac{AE_a}{Rg(\alpha)}\right] + 3.635 - 1.894661\ln E_a - 1.00145033\left(\frac{E_a}{RT}\right) \tag{5}$$

According to the above mentioned equations, the plots of (1) $\ln(\beta/T^2)$ versus $1/T$; (2) $\ln(\beta/T^{1.92})$ versus $1/T$; (3) $\ln(\beta/T^{1.894661})$ versus $1/T$, at different αs can be obtained respectively by a linear regress of least square method. The slope of each line yielded an E_a with linear correlation coefficient $-r = 1.0$ and standard deviation S.D. < 0.0001. The values of E_as, calculated from the slopes of the above three plots at various αs, are shown in Table 1. The E_as calculated with Starink ($\kappa = 1.92$) method and those with Tang method are close to each other. Both are lower than the E_as obtained with KAS method. A similar observation of these three methods was reported by Gao et al. [11]. As shown in Table 1, the E_a is: 18.6 ± 0.1 kJ mol^{-1} according to KAS method; 17.9 ± 0.1 kJ mol^{-1}, Starink ($\kappa = 1.92$) method; and 17.6 ± 0.1 kJ mol^{-1}, Tang method. In deciding which method is most reliable, Starink [12] had considered accuracy, robustness/reliability (with respect to possible inaccuracies in measurement of temperature), transparency and convenience of application of each method. He showed that the accuracy of the Starink ($\kappa = 1.92$) method is better than that of the KAS method. Therefore, the E_as obtained from Starink ($\kappa = 1.92$) and Tang methods are more accurate. The results of the isoconversional analysis clearly show that the disproportionation of (hfac)Cu^I(COD) occurs as a single step process. This follows from Table 1, in which no significant variation of Ea with α can be seen.

3.2. Model-fitting method

In the previous section, the Ea of the disproportionation reaction of (hfac)Cu^I(COD), approximately 18 kJ mol^{-1}, was determined. In this section, for the determination of the reaction model, 13 different kinetic functions of the common models in solid-state reactions (listed in Table 2) will be tested respectively with the differential, Eq. (6), and integral, Eq. (7), methods [18,19] listed as follows.

Differential method:

$$\ln\left[\frac{d\alpha/dT}{f(\alpha)[E_a(T-T_0)/RT^2+1]}\right] = -\frac{E_a}{RT} + \ln\left[\frac{A}{\beta}\right] \tag{6}$$

Table 1
Kinetics parameters calculated by the Kissinger–Akahira–Sunose (KAS), Starink ($k = 1.92$) and Tang methods

α	KAS method			Starink method			Tang method		
	E_a (kJ/mol)	$-r$	S.D.	E_a (kJ/mol)	$-r$	S.D.	E_a (kJ/mol)	$-r$	S.D.
0.10	18.7	1.0	<0.0001	17.9	1.0	<0.0001	17.9	1.0	<0.0001
0.20	18.7	1.0	<0.0001	17.8	1.0	<0.0001	17.8	1.0	<0.0001
0.30	18.7	1.0	<0.0001	17.9	1.0	<0.0001	17.9	1.0	<0.0001
0.40	18.6	1.0	<0.0001	17.9	1.0	<0.0001	17.9	1.0	<0.0001
0.50	18.6	1.0	<0.0001	17.9	1.0	<0.0001	17.9	1.0	<0.0001
0.60	18.7	1.0	<0.0001	17.9	1.0	<0.0001	17.9	1.0	<0.0001
0.70	18.7	1.0	<0.0001	17.9	1.0	<0.0001	17.9	1.0	<0.0001
0.80	18.6	1.0	<0.0001	17.9	1.0	<0.0001	17.9	1.0	<0.0001
0.90	18.6	1.0	<0.0001	18.0	1.0	<0.0001	18.0	1.0	<0.0001

in which $f(\alpha)$ is the reaction model. And possible functions of $f(\alpha)$ are listed in Table 2.

Integral equation:

$$\ln\left[\frac{g(\alpha)}{T-T_0}\right] = -\frac{E_a}{RT} + \ln\left[\frac{A}{\beta}\right] \tag{7}$$

in which $g(\alpha) = \int_0^\alpha f(\alpha)^{-1}\,\mathrm{d}\alpha$ is the integral form of the $f(\alpha)$. And possible expressions of $f(\alpha)$ are listed in Table 2.

According to the above mentioned equations, the plots of $\ln[(\mathrm{d}\alpha/\mathrm{d}T)/f(\alpha)\ [E_a(T-T_0)/RT^2+1]]$ versus $1/T$ and $\ln[g(\alpha)/(T-T_0)]$ versus $1/T$ at various βs can be obtained respectively by linear regression. And the kinetic parameters calculated with $-r \geq 0.98$ and S.D. ≤ 0.27 for all possible reaction models are shown in Table 3. It can be further observed in Table 3 that when the differential method is applied at lower heating rates, 5 and 10 K min^{-1}, the kinetics of the disproportionation reaction can be described by one-dimensional diffusion model $D_1(\alpha)$ and three-dimensional diffusion model $D_3(\alpha)$, as well as by first order reaction model $F_1(\alpha)$ and second-order reaction model $F_2(\alpha)$. However, only $D_1(\alpha)$ and $D_3(\alpha)$ are applicable when integral method is used. On the other hand, at higher heating rates, 20 and 50 K min^{-1}, the disproportionation reaction can only be described by the second order reaction model $F_2(\alpha)$ when both differential and integral methods are used. Similar behavior has been observed by Vyazovkin [20] in the investigation of the best kinetic triplets for the decomposition of 1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) with various heating rates. With the increment of heating rate, the reaction model changed from $D_3(\alpha)$ to $R_2(\alpha)$ and the Ea decreased at a certain point.

The E_as of the reaction previously determined by the use of model-free methods are within the range between 17.6 and 18.7 kJ mol^{-1}. These numbers are consistent with the values of the E_as, 17.5 and 18.6 kJ mol^{-1}, estimated respectively with the differential and integral model-fitting methods at 50 K min^{-1} heating rate with the $F_2(\alpha)$ model. Intuitively, bimolecular disproportionation reaction should be second order in kinetics. Therefore, the second order reaction model $F_2(\alpha)$ should fit in with the reaction kinetics.The pre-exponential factor and reaction model have been determined according to the method proposed by Vyazovkin [21] as follows. For experiments carried out at constant heating rate:

$$\beta = \frac{\mathrm{d}T}{\mathrm{d}t} = \text{constant} \tag{8}$$

Eq. (2) can be rearranged and integrated to obtain:

$$g(\alpha) = \int_0^\alpha [f(\alpha')]^{-1}\,\mathrm{d}\alpha' = \left(\frac{A}{\beta}\right)\int_0^T \exp\left(-\frac{E_a}{RT'}\right)\mathrm{d}T' \tag{9}$$

which is the integrated form of the reaction model that is normally used to describe the kinetics of the reactions in solids [22,23]. On the other hand, the values of E_a and

Table 2
Reaction models used to describe solid state reactions[a]

Reaction model	$f(\alpha)$	$g(\alpha)$
P_2: power law	$2\alpha^{1/2}$	$\alpha^{1/2}$
P_3: Power law	$3\alpha^{2/3}$	$\alpha^{1/3}$
P_4: power law	$4\alpha^{3/4}$	$\alpha^{1/4}$
$P_{3/2}$: power law	$2/3\alpha^{-1/2}$	$\alpha^{3/2}$
A_2: Avrami–Erofeev equation	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$
A_3: Avrami–Erofeev equation	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$
A_4: Avrami–Erofeev equation	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	$[-\ln(1-\alpha)]^{1/4}$
R_2: contracting cylinder	$2(1-\alpha)^{1/2}$	$1-(1-\alpha)^{1/2}$
R_3: contracting sphere	$3(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$
D_1: one-dimension diffusion	$1/2\alpha^{-1}$	α^2
D_3: three-dimension diffusion	$(3/2)(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$	$[1-(1-\alpha)^{1/3}]^2$
F_1: first-order	$1-\alpha$	$-\ln(1-\alpha)$
F_2: second-order	$(1-\alpha)^2$	$(1-\alpha)^{-1}-1$

[a] Adapted from Ref. [20].

Table 3
Best kinetic triplets of the disproportionation reaction of (hfac)Cu^I(COD) determined by the use of the differential and the integral methods with different heating rates

The differential method						The differential method					
β (K min^{-1})	Model	E_a (kJ/mol)	A (min^{-1})	$-r$	S.D.	β (K min^{-1})	Model	E_a (kJ/mol)	A (min^{-1})	$-r$	S.D.
5	D_3	84.0	2.4E + 44	0.99	0.21	5	D_1	44.5	1.5E + 23	0.98	0.08
	F_1	53.4	8.7E + 28	0.98	0.21		D_3	60.0	6.3E + 30	0.99	0.18
10	F_2	67.0	1.8E + 36	0.98	0.27	10	D_3	55.6	1.3E + 28	0.99	0.19
20	F_2	56.4	2.4E + 29	0.98	0.24	20	F_2	39.6	2.9E + 20	0.99	0.10
50	F_2	18.6	9.6E + 09	0.98	0.16	50	F_2	17.5	1.3E + 09	1.00	0.03

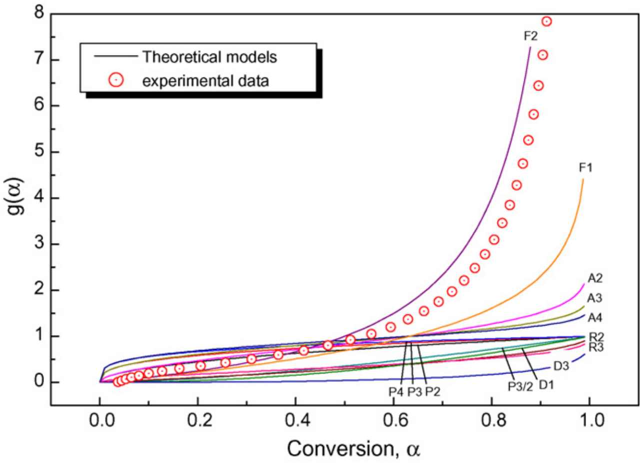

Fig. 6. Dependence $g(\alpha)$ for the models shown in Table 2 (solid curves) and for the experimental data (circles).

$\log A$ of the different reaction models are related linearly because $\log A = cE_a + d$ (compensation effect) where c and d are constants. This relationship may be used to evaluate the pre-exponential factors for the model-fitting analysis. By the use of the values of E_a and $\log A$ obtained from the model-fitting integral method (Table 3) to determine $\log A = cE_a + d$ and by the substitution of isoconversional values of E_a (17.9 kJ mol^{-1}) in $\log A = cE_a + d$ to determine $\log A$, a values of $2.65 \times 10^{+9}$ was obtained for A. With knowledge of E_a and A, the experimental kinetic function, $g(\alpha)$, can be calculated using Eq. (9). The numerically evaluated integral kinetic function, $g(\alpha)$ (circles), is shown in Fig. 6 for the disproportionation reaction of (hfac)Cu^I(COD). The solid lines were calculated according to the models in the Table 2. Because the kinetic function $g(\alpha)$, depends only on the extent of reaction, α, for a given model (Table 2), the construction of these solid lines does not require knowledge of E_a or A. The lines are constructed from knowledge of the individual kinetic function itself. It is clearly observed in Fig. 6 that the disproportionation reaction follows model F_2 (second-order reaction) kinetics.

4. Conclusion

In this study, the kinetics of the disproportionation reaction of (hfac)Cu^I(COD) was investigated with different βs in nitrogen atmosphere by the use of DSC. First, the E_as of the disproportionation reaction of (hfac)Cu^I(COD) were estimated with the three model-free isoconversional methods (KAS, Starink ($\kappa = 1.92$) and Tang). The E_as obtained thereby are 18.6 ± 0.1 kJ mol^{-1} with KAS method, 17.9 ± 0.1 kJ mol^{-1} with Starink ($\kappa = 1.92$) method, and 17.6 ± 0.1 kJ mol^{-1} with Tang method. Then, when the E_a was ascertained, 13 different kinetic functions of the common mechanisms in solid-state reactions were employed to determine the correct form of reaction model by the use of the two model-fitting, differential and integral, methods. As a result, the disproportionation reaction follows model F_2 (second-order reaction) kinetics.

Acknowledgments

The authors would like to thank the National Science Council of the Republic of China for financially supporting this research under Contract No. NSC 91-2214-E-011-017.

References

[1] V.N. Vertoprakhov, S.A. Kropoder, Russ. Chem. Rev. 69 (12) (2000) 1057.
[2] R. Kumar, F.R. Fronczek, A.W. Maverick, W.G. Lai, G.L. Griffin, Chem. Mater. 4 (577) (1992).
[3] T.T. Kodas, M.J. Hampden-Smith, The Chemistry of Metal CVD, VCH, Weinheim, 1994.
[4] S.L. Cohen, M. Liehr, S. Kasi, Appl. Phys. Lett. 60 (1) (1992) 50.
[5] P. Doppelt, Coord. Chem. Rev. 178–180 (1998) 1785.
[6] S.L. Cohen, M. Liehr, S. Kasi, J.Vac. Sci. Technol. A10 (4) (1992) 863.
[7] K.K. Choi, S.W. Rhee, Thin Solid Films 409 (2002) 147.
[8] S.W. Rhee, S.W. Kang, S.H. Han, Electrochem. Solid-State Lett. 3 (3) (2000) 135.
[9] S. Vyazovkin, C.A. Wight, Thermochim. Acta 340/341 (1999) 53.
[10] E.J. Mittemeijer, J. Mater. Sci. 27 (1992) 3977.
[11] Z. Gao, M. Nasahiro, I. Amasaki, Thermochim. Acta 369 (2001) 137.
[12] M.J. Starink, Thermochim. Acta 404 (2003) 163.
[13] T. Wanjun, C. Donghua, Thermochim. Acta 433 (2005) 72.
[14] G. Doyle, K.A. Eriksen, D. Van Engen, Organometallics 4 (1985) 830.
[15] T.H. Baum, C.E. Larson, G. May, J. Organomet. Chem. 425 (1992) 189.
[16] N. Sbirrazzuoli, Y. Girault, L. Elégant, J. Therm. Anal. 38 (1992) 1509.
[17] N. Sbirrazzuoli, Y. Girault, L. Elégant, Thermochim. Acta 293 (1997) 25.
[18] J. Zelić, D. Rušić, R. Krstulović, J. Therm. Anal. Cal. 67 (2002) 613.
[19] M. Shui, L. Yue, Y. Yimiao, Z. Xu, Thermochim. Acta 386 (2002) 43.
[20] S. Vyazovkin, C.A. Wight, Annu. Rev. Phys. Chem. 48 (1997) 125.
[21] S. Vyazovkin, Int. J. Chem. Kinet. 28 (2) (1996) 95.
[22] M.E. Brown, D. Dollimore, A.K. Galwey, Reaction in the Solid State, Comprehensive Chemical Kinetics, vol. 22, Elsevier, Amsterdam, 1980.
[23] J. Sestak, Thermophysical Properties of Solids, Comprehensive Analytical Chemistry, vol. 12D, Elsevier, Amsterdam, 1980.