Degradation of Ba(DPM)₂ during Storage in a Desiccator for Extended Periods

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Abstract—We have investigated the degradation mechanism of $Ba(DPM)_2$, which has been stored in a desiccator for extended periods using thermogravimetry, FTIR and mass spectroscopy. TG analysis shows that the aged sample loses the initial weight significantly at relatively low temperatures, the rate of weight loss decreases above 380 °C, and large amounts of residue remain at 550 °C. FTIR and mass spectroscopy show that $Ba(DPM)_2$ is easily attacked by CO_2 and H_2O in air, which results in the dissociation of chemical bonds between the Ba ion and the ligand at low temperatures. This eventually enhances the oligomerization of $Ba(DPM)_2$ and the formation of carbonates that exhibit low volatility and unstable thermal properties.

Key words: Degradation, $Ba(DPM)_2$, Hydration, Carbonates, CVD

INTRODUCTION

β-diketonates of Ba are used as precursors of multi-component oxide films containing BaO, e.g., $YBa_2Cu_3O_{7-\delta}$ and (Ba, Sr)TiO₃, in metal organic chemical vapor deposition (MO-CVD) processes. So far, $Ba(DPM)_2$ (DPM: 2,2,6,6,-tetramethyl-3,5-heptadionate, $C_{11}H_{38}O_2$) has been used as the most popular precursor although it shows poor thermal stability and undergoes a substantial degradation during storage [Panson et al., 1988; Yoshida et al., 1995].

Thermal instability of $Ba(DPM)_2$ comes from the nature of the precursor in that the Ba ion has a low charge-to-size ratio and therefore the coordination number of the Ba complex is easily saturated by oligomerization [Barron and Rees Jr., 1994; Hanusa, 1993].

Our previous study about the thermal decomposition mechanism of $Ba(DPM)_2$ showed that the chemical bonds of the complex decomposed following the sequence of $C(CH_3)_3$ and Ba-O>C-H>C-C and C-O at elevated temperatures [Ryu et al., 1999]. Although it is well-known that $Ba(DPM)_2$ is significantly degraded during storage, only few studies have been made about structural changes of $Ba(DPM)_2$ after storage for extended periods. Bykov et al. [1997] and Sato et al. [1993] reported that CO_2 and H_2O in air attack and easily combine with the central Ba ion so that $Ba(DPM)_2$ is transformed into carbonates of low volatility during storage.

In this study, we have investigated the properties of Ba (DPM)₂ stored in a desiccator for extended periods using thermogravimetry, FTIR and mass spectroscopy. We have monitored changes in the complex structure after the storage and compared the results with those of a fresh sample.

EXPERIMENTS

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$Ba(DPM)_2$ was purchased from Strem Chemicals and used without further purification. The thermogravimetric behavior of the sample was observed in N₂ with the Perkin Elmer TGA7. The heating rate was 10 °C/min. The sample was either fresh or aged after storage in a desiccator for 3 or 6 months. For dehydrating materials in the desiccator, we used a mixture of anhydrous CaCl₂ manufactured by Yakuri Pure Chemicals Co. (Japan) and silica. The impurity levels of gases other than nitrogen and oxygen in the desiccator were too low to be detected quantitatively.

The FTIR spectra of the sample were monitored at elevated temperatures in an in-situ IR cell which can be evacuated down to 10^{-5} Torr and heated up to 550 °C [Moon et al., 1981]. The sample was mixed with KBr powder, pressed into a self-supporting disk, and then placed at the center of the IR cell for the experiments. IR spectra were obtained while the sample was linearly heated in vacuum. We monitored the intensity of a few IR peaks representing the specific chemical bonds and compared the results between fresh and aged samples.

Changes in the mass signal intensity of the sample were observed with a mass spectrometer (JEOL, JMS-AX505WA) while the sample was heated at the rate of 30 °C/min. The sample was ionized by the electron impact (EI) method. We used mass spectroscopy instead of FTIR to monitor H_2O possibly adsorbed on the aged sample because KBr powder used for the sample preparation in the IR measurement also adsorbed H_2O when exposed to air.

RESULTS AND DISCUSSION

Fig. 1 shows the weight loss curves of fresh and aged Ba (DPM)₂ when they are heated in N₂ at the rate of 10 °C/min. Fresh $Ba(DPM)_2$ loses the weight relatively slowly up to about 250 °C but is significantly gasified beyond 360 °C to produce 6% of the initial weight as a residue at 550 °C. On the contrary, the aged sample stored for either 3 months or 6 months loses
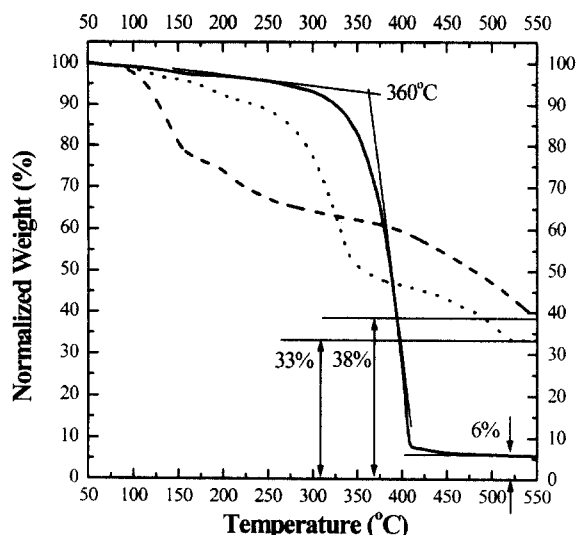
Fig. 1. Thermogravimetric analysis of fresh Ba(DPM)₂ (—), aged Ba(DPM)₂ stored for 3 months (···) or for 6 months (---) in a desiccator.

sample is hydrated even though it has been stored in a desiccator.

Minkina [1993] reported that the thermal instability of Ba (DPM)₂ was mainly due to the hydrolysis of the sample which had already been hydrated during storage. It is worth noting in Fig. 2 that H_2O is liberated at low temperatures, below 90 °C, from aged Ba(DPM)₂, which suggests that water is combined

Fig. 3. Changes in the IR spectrum of Ba(DPM)₂ between 1,800 and 400 cm⁻¹ with the time.
(a) fresh Ba(DPM)₂, (b) stored for 3 months, (c) for 6 months, and (d) IR spectrum of HDPM.

the initial weight significantly from low temperatures showing a complicated TG curve in the whole temperature range.

The sample stored for 3 months undergoes a significant weight loss near 300 °C and produces a residue at 550 °C amounting to about 33% of the initial weight. When the sample is stored for a longer period, e.g., 6 months, the weight loss occurs at lower temperatures, near 100 °C, and the residual amount is higher, about 38% of the initial weight. The results indicate that aged Ba(DPM)₂ contains the volatile species which are liberated at low temperatures and also over a wide temperature range and that the non-volatile species contained in the sample are converted to a large amount of residue at high temperatures.

To check the water content and the dehydration behavior of the samples, we have monitored the ion current of the mass signal at m/z=18, representing ⁺H_2O, at elevated temperatures. Fig. 2 shows that the amount of H_2O from aged Ba(DPM)₂ stored for 6 months is large at low temperatures while the amount from fresh Ba(DPM)₂ is relatively small. Accordingly, the aged
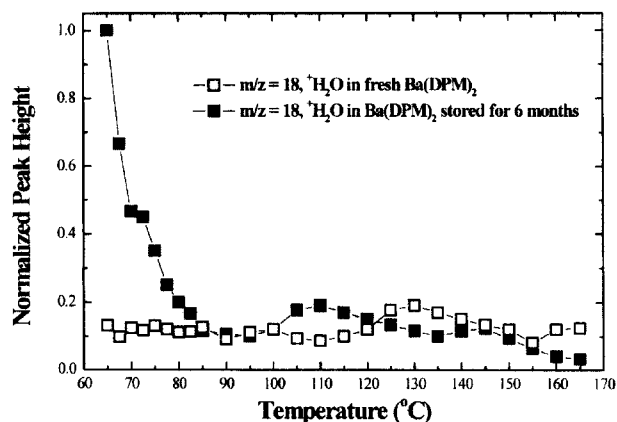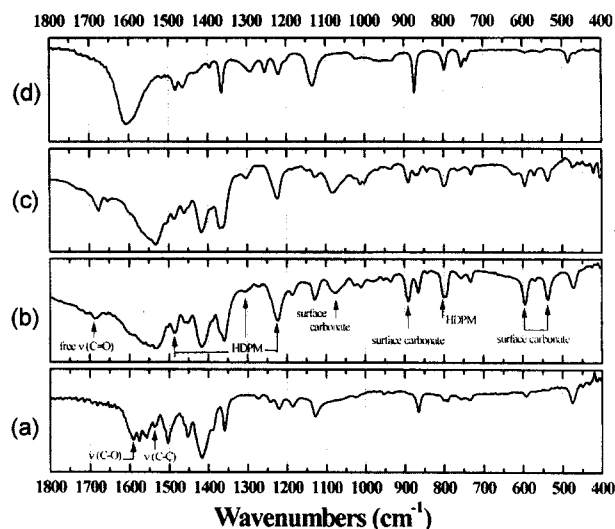
Table 1. Assignments of IR peaks of Ba(DPM)₂

Ba(DPM)₂ (cm⁻¹)	Predominant mode	Ref's
2964, 2904, 2872	v(C-H)	a, b, c
1590, 1576	v(C-O)	d, e
1560 w/.sh.	v(C-O)+v(C-C)	d, e
1533	v(C-C)+v(C-O)	d, e
1504 w/.sh.	v(C-O)+v(C-C)+δ(C-H)	d, e
1452 w/.sh.	v(C-C)+δ(C-H)	a, b, c
1419	δₐ(CH₃)	a, b, c
1389	v(Ba-O)+v(C-O)	a, b, c
1359	δₛ(CH₃)	a, b
1273, 1242, 1221, 1187	v(C-(CH₃)₃)+δ(C-C)	a, b
1129	v(C-C(CH₃)₃)+δ(C-H)	a, b
1025, 953, 933	ρᵣ(CH₃)	a, b
865	v(C-C(CH₃)₃)+v(C-O)	a, b
799, 790	π(C-H)	a, b
758, 735	v(C-C(CH₃)₃)+v(C-C-O)+v(Ba-O)	a, b, c
592	Ring deformation+v(Ba-O)	a
472	v(Ba-O)	b

a) Harima, H., et al., *Jap. J. Appl. Phys.*, **29**, 1932 (1990).
b) Nakamoto, K. and Martell, A. E., *J. Chem. Phys.*, **32**, 588 (1960).
c) Mikami, M., et al., *Spectrochimica Acta*, **23A**, 1037 (1967).
d) Pinchas, S., et al., *J. Chem. Phys.*, **46**, 1506 (1967).
e) Zheng, B., et al., *J. Electrochem. Soc.*, **142**, 3896 (1995).

Fig. 2. Changes in the mass signal of Ba(DPM)₂ at m/z=18 at elevated temperatures.

relatively weakly with the sample. The major role of water seems to be the triggering of the $Ba(DPM)_2$ transformation at elevated temperatures to yield the complicated TG patterns of Fig. 1.

Fig. 3 shows the IR spectrum of fresh $Ba(DPM)_2$ and Table 1 lists assignments of a few important IR peaks with references [Nakamoto and Martell, 1960; Mikami et al., 1967; Pinchas et al., 1967; Harima et al., 1991; Zheng et al., 1995]. Fig. 3 also shows that the IR spectrum changes when the sample is stored in a desiccator for extended periods.

Complex IR bands between $1,590\ cm^{-1}$ and $1,452\ cm^{-1}$ observed with the fresh sample, which represent the vibration modes of the chelate ring, become simpler and broader as the storage periods are extended. Among the bands in the region, however, one at $1,533\ cm^{-1}$ representing $v(C\text{-}C)$ in the ligand becomes relatively stronger than the other peaks with the storage period. This is because the C-C bond in the ligand ring is the most stable in $Ba(DPM)_2$, as previously reported [Ryu et al., 1999].

The $1,590\ cm^{-1}$ peak due to $v(C\text{-}O)$ in the fresh sample disappears and a new peak at $1,680\ cm^{-1}$ corresponding to free $v(C=O)$ appears after the storage. The result indicates that the bond between the Ba ion and the ligand ring, e.g., Ba-O-C, is partially dissociated during the storage. The reason for the partial dissociation is that the Ba ion with a relatively large ionic radius is easily attacked by CO_2 and H_2O in air. When CO_2 and H_2O combine with the Ba ion, the Ba-O bond with only the ionic σ-bonding character weakens and is partially dissociated. Accordingly, aged $Ba(DPM)_2$ contains relatively large amounts of free ligands that are almost completely detached from the central Ba ion at elevated temperatures.

It is noteworthy that the peaks at 1,487, 1,300, 1,220 and 800 cm^{-1}, which show no or insignificant intensity with fresh Ba

$(DPM)_2$ but exhibit significant intensity with the aged samples, correspond to the vibrational modes of HDPM. The result again suggests that the free HDPM ligand is accumulated in the sample after extended storage.

Aged $Ba(DPM)_2$ also shows new IR peaks at 1,080, 890, 594 and 540 cm^{-1}. These peaks represent the formation of surface carbonate in the sample, which is due to the reaction of CO_2 with the central Ba ion as reported by Hair [1967].

To study the thermal decomposition behavior of the aged sample, we have monitored the intensity of a few IR peaks representing the specific chemical bonds while the sample is heated in the IR cell. Fig. 4 shows the results. Peaks at 1,220 cm^{-1} and 1,680 cm^{-1} begin to lose their intensity significantly at temperatures as low as 50 °C, indicating easy liberation of the HDPM ligand and the free C=O species from the sample. This agrees well with the TGA results of Fig. 1. Harima et al. [1990] also reported that IR peaks corresponding to HDPM were observed when $Ba(DPM)_2$ was spontaneously decomposed after unpacking. Accordingly, the significant weight loss of the aged sample at low temperatures is due to the liberation of HDPM and the free C=O species produced during the storage.

The 865 cm^{-1} and 476 cm^{-1} peaks also begin to lose their intensity at low temperatures, indicating that the tert-butyl group and the Ba-O bond are dissociated relatively easily. This result is not surprising because the above two bonds are the weakest in $Ba(DPM)_2$ [Ryu et al., 1999]. The tert-butyl group forms a stable radical after dissociation from the ligand and the Ba-O bond is weak due to its ionic σ-bonding character.

The peak at 1,080 cm^{-1} due to the surface carbonates in aged $Ba(DPM)_2$ maintains the initial intensity up to 100 °C, then slowly decreases as the sample is heated to 400 °C. The peak intensity at 400 °C is as high as 48% of the initial one because the surface carbonates are gradually converted to non-volatile $BaCO_3$ at elevated temperatures. The 1,533 cm^{-1} peak representing the C-C bond maintains the initial intensity up to about
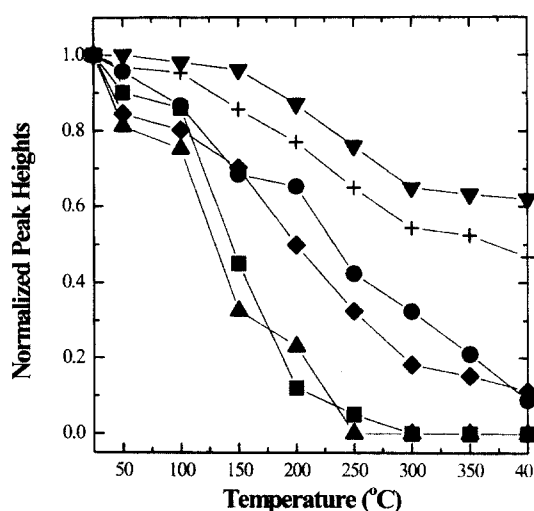

Fig. 4. Changes in the normalized heights of IR peaks at elevated temperatures for aged $Ba(DPM)_2$ stored in a desiccator for 6 months.

(▼); $v(C\text{-}C)$ at 1,533 cm^{-1}, (+); surface carbonate at 1,080 cm^{-1}, (●); $v(Ba\text{-}O)$ at 476 cm^{-1}, (◆); $v(C\text{-}C(CH_3)_3)+$ $v(C\text{-}O)$ at 865 cm^{-1}, (▲); HDPM ligand at 1,220 cm^{-1}, and (■); v(free C=O) at 1,680 cm^{-1}.

Fig. 5. Changes in the intensity of IR peaks representing v $(Ba\text{-}O)$ at 476 cm^{-1} and $v(C\text{-}C(CH_3)_3)+v(C\text{-}O)$ at 865 cm^{-1} in either fresh or aged $Ba(DPM)_2$ when the sample is heated up to 200 °C.

150 °C, then slowly loses intensity at higher temperatures. The residual intensity at 400 °C is about 62% of the initial one, which indicates that the C-C bond in the ligand ring is the most stable.

Fig. 5 compares changes in the intensity of IR peaks representing $v(Ba-O)$ and $v[C-(CH_3)_3]+v(C-O)$ in either aged or fresh Ba(DPM)₂. It is apparent that both peaks decrease more rapidly with the temperature in aged Ba(DPM)₂ than in fresh Ba(DPM)₂. Again, this is because the aged sample has been attacked by CO_2 and H_2O in air during the storage. Removal of the electrophilic tert-butyl group from the ligand is accompanied with the dissociation of the Ba-O bond, which results in the opening of the ligand ring. With the ligand ring open and the bulky tert-butyl group removed from the ligand, the central Ba ion is exposed to neighboring reactants and the Ba complex is easily oligomerized. The complex oligomer is eventually transformed into the non-volatile carbonate species at elevated temperatures.

CONCLUSION

Ba(DPM)₂ is degraded during storage in a desiccator for extended periods and the aged sample exhibits the following properties as verified by TGA, MS and FTIR observations.

1. Aged Ba(DPM)₂ loses the initial weight significantly at relatively low temperatures but produces a larger amount of residue at high temperatures than for fresh Ba(DPM)₂.

2. Aged Ba(DPM)₂ undergoes the dissociation of the bond between the Ba ion and the ligand ring at low temperatures, which eventually leads to the oligomerization of the sample and the formation of the carbonate species. CO_2 and H_2O are the major reasons for the complex transformation, which combine with the central Ba ion to trigger the dissociation of Ba (DPM)₂ producing volatile as well as non-volatile species.

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