Available online at www.sciencedirect.com

SCIENCE DIRECT®

Thermochimica Acta 431 (2005) 53–57

thermochimica acta

www.elsevier.com/locate/tca

Released gas analyses from ternary graphite intercalation compounds at high temperatures

R. Matsumoto [a, *], T. Arii [b], Y. Oishi [b], Y. Takahashi [c, 1]

[a] Faculty of Engineering, Tokyo Polytechnic University, 1583 Iiyama, Atsugi-shi, Kanagawa 243-0297, Japan
[b] RIGAKU Corporation, 3-9-12, Matsubara-cho, Akishima-shi, Tokyo 196-8666, Japan
[c] Department of Applied Chemistry, Chuo University, Tokyo, Japan

Received 14 October 2004; received in revised form 5 January 2005; accepted 20 January 2005
Available online 16 February 2005

Abstract

Ethylene molecules are considered to oligomerize in the interlayer nano-space of ternary graphite intercalation compounds (GICs), $CsC_{24}(C_2H_4)_x$; however, the mechanism and the degree of oligomerization have not yet been clarified. In the present study, the released gases from $CsC_{24}(C_2H_4)_{1.4}$ at high temperatures were investigated by TG/GC–MS under helium atmosphere. The detection of alkanes (C3–C20) by TG/GC–MS analysis in both the trap and direct modes supported the existence of the oligomers in the nano-space. Other gases such as water vapor, methane, etc., were also detected.
© 2005 Elsevier B.V. All rights reserved.

Keywords: Graphite intercalation compound; Ethylene; Oligomerization; TG/GC–MS

1. Introduction

Graphite intercalation compounds (GICs) are compounds in which chemical species such as atoms and molecules intercalate into the graphite layers [1]. Due to their high electric conductivity, GICs is considered as a promising candidate of light-weight high-conductivity materials. Since most GICs are unstable in air, their practical applications have not been realized. The objective of our research is “the synthesis of a high-conductivity GIC stable in air”. In our previous studies, we found that Cs–C_2H_4–GIC is highly stable in air [2–5]. Cs–C_2H_4–GIC is a ternary compound composed of $CsC_{24}(C_2H_4)_x$ formed from the binary compound Cs–GIC (CsC_{24}). As this binary compound has rather large nano-space between Cs atoms placed in every other graphite interlayer, it absorbs ethylene molecules as the third species (Fig. 1). The resulting ternary compound, Cs–C_2H_4–GIC, is considered to be highly stable in air because the ethylene molecules oligomerize in the nano-space, and these oligomers form oligomer-networks to trap Cs atoms in the graphite interlayer. However, since suitable methods to directly observe the ethylene oligomers formed in the nano-space are not available, it is difficult to examine the oligomerization mechanism, the degree of oligomerization, etc., in detail.

The existence of ethylene oligomers between the graphite layers in Cs–C_2H_4–GIC has been hitherto verified by analyzing extracts with liquid toluene from $CsC_{24}(C_2H_4)_{1.1}$ by GC–MS and FD–MS (gas chromatography mass spectroscopy and field desorption mass spectrometry) [6,7]. As a result of these analyses, $C_{12}H_{24}$–$C_{14}H_{28}$ and $C_{12}H_{26}$–$C_{14}H_{30}$ were also detected by GC–MS, and $C_{20}H_{40}$–$C_{40}H_{80}$ were detected by FD–MS.

These data seem to be sufficient to clarify the existence of the ethylene oligomers; however, an adequate understanding of the generation mechanisms of the ethylene oligomers, such as the origin of the H atoms of alkanes, has not been achieved. Moreover, the oligomerization mechanism and the degree of oligomerization have not been clarified.

---

[*] Corresponding author. Tel.: +81 46 242 9575; fax: +81 46 242 9575.
E-mail address: mrika@gen.t-kougei.ac.jp (R. Matsumoto).
[1] Present address: 4-5-25, Minamiaoyama, Minato-ku, Tokyo 107-0062, Japan.

0040-6031/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2005.01.036

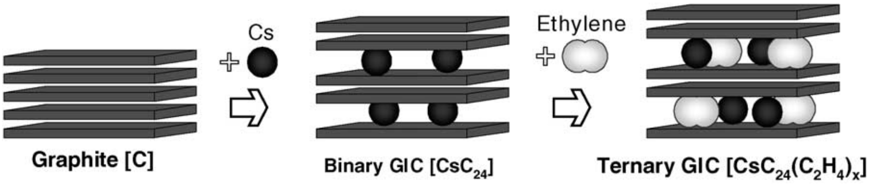


Fig. 1. Schematic outline of formation process of Cs–C_2H_4–GIC.

In this paper, we present the results on the detection of ethylene oligomers by TG/GC–MS analysis of the released gas from Cs–C_2H_4–GIC. In recent years this analysis has been used very effectively for some materials [8–10].

2. Experimental

2.1. Samples

PGS graphite sheets (Matsushita Electric Industrial Co.), 2 mm × 40 mm × 0.1 mm, were used as the host graphite material. First, the binary compound CsC_{24} was synthesized by the two-bulb method. Subsequently, CsC_{24} was allowed to absorb ethylene gas by a gas-contacting method, resulting in the ternary compounds $CsC_{24}(C_2H_4)_x$ ($x = 1.0$, 1.4). These samples were synthesized in vacuum glass ampoules, and were maintained in the vacuum ampoule until loading in the following measuring system.

2.2. Measurements

Measurements of $CsC_{24}(C_2H_4)_{1.4}$ and $CsC_{24}(C_2H_4)_{1.0}$ were performed by the use of a TG–DTA/GC–MS system in the trap mode [11,12]. The TG–DTA/GC–MS system used was manufactured by RIGAKU using a GC–MS made by SHIMADZU, QP-5050A. The mass of the measured sample was approximately 2 mg, the released gas collection temperature ranged from 400 to 1000 °C, and the MS detection mass (*m*/*z*) ranged from 10 to 350. The measurements were performed under a flowing helium gas atmosphere at a rate of 300 ml/min. Measurements of $CsC_{24}(C_2H_4)_{1.0}$ were also made in the direct mode under the following conditions: a heating rate of 20 °C/min, temperatures ranging from room temperature to 1000 °C, and sample with a mass of approximately 3.6 mg.

3. Results and discussion

3.1. Trap mode (TG/GC–MS)

The trap mode measurements were made on $CsC_{24}(C_2H_4)_{1.4}$ and $CsC_{24}(C_2H_4)_{1.0}$. Fig. 2 shows the TG curve of $CsC_{24}(C_2H_4)_{1.4}$ from room temperature to 1000 °C. The results for $CsC_{24}(C_2H_4)_{1.4}$ and $CsC_{24}(C_2H_4)_{1.0}$ were almost similar. A significant weight loss was observed above 400 °C. The weight loss of $CsC_{24}(C_2H_4)_{1.4}$ reached 23% at 1000 °C. This value far exceeds the 8.5 wt.% of C_2H_4 in $CsC_{24}(C_2H_4)_{1.4}$. Hence, it is evident that the observed weight loss is due to not only the ethylene components released but also on the Cs atoms released. It is known that the binary CsC_{24} decomposes slowly above 750 °C in vacuum.

In the trap mode, the results of the GC–MS measurements of released gases at 400–1000 °C are shown in Figs. 3 and 4, which indicate total ion chromatograms (TICs) for $CsC_{24}(C_2H_4)_{1.4}$ and $CsC_{24}(C_2H_4)_{1.0}$, respectively. *N*-alkanes, C3–C20, were detected in both samples. In the case of $CsC_{24}(C_2H_4)_{1.0}$, in addition to *n*-alkanes, traces of certain cyclic compounds (labeled a–f) such as cyclopentadiene and benzene were also detected, as shown in Table 1. These results suggest that oligomerization of ethylene occurs in the interlayer nano-space. Furthermore, certain *n*-alkanes with odd carbon numbers, C3 and C5, etc., were detected. The above facts suggests that of the primary C chain of the ethylene oligomers randomly decompose and *n*-alkanes are formed. Similar effects is observed during the thermal decomposition of polyethylene. Takahashi et al. [6,7] have also detected such alkanes and alkenes with odd carbon numbers in their GC–MS and FD–MS measurements in previous studies. This implies that the carbon chains of the ethylene oligomers are dissociated on the inner or the outer side of the nano-space by thermal decomposition. By these methods, therefore, it may be difficult to determine the exact degree of oligomerization of ethylene molecules in the interlayer nano-space.

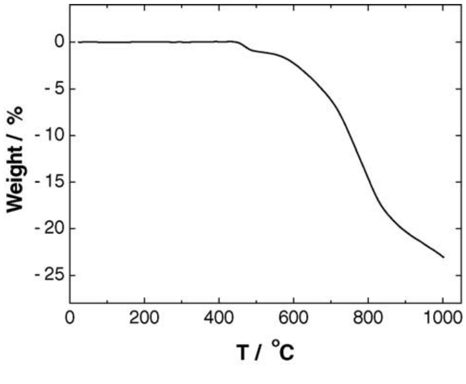


Fig. 2. TG curve of $CsC_{24}(C_2H_4)_{1.4}$.

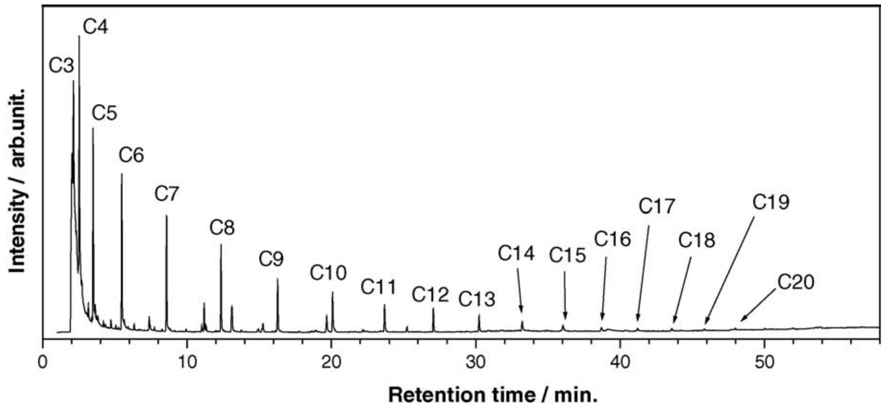


Fig. 3. TIC of released gas from $CsC_{24}(C_2H_4)_{1.4}$ (trap mode).

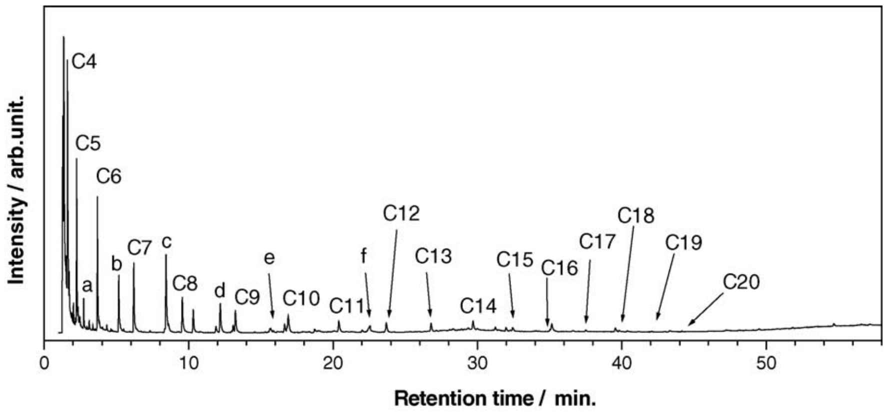


Fig. 4. TIC of released gas from $CsC_{24}(C_2H_4)_{1.0}$ (trap mode).

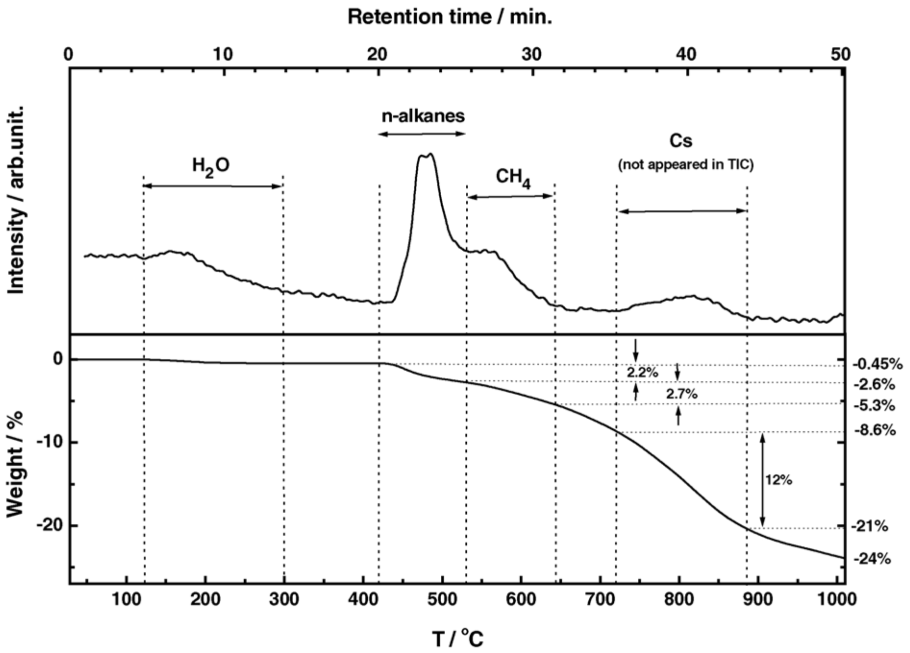
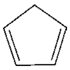
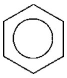
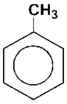
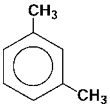
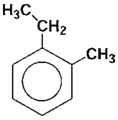
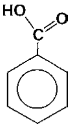


Fig. 5. TIC of released gas and TG curve for $CsC_{24}(C_2H_4)_{1.0}$ (direct mode).

Table 1
Cyclic compounds detected in released gas from $CsC_{24}(C_2H_4)_{1.0}$ (trap mode)

Peak index (Fig. 4)	Retention time (min)	Compound	
a	2.733	Cyclopentadiene	
b	5.173	Benzene	
c	8.440	Toluene	
d	12.187	Dimethyl-benzene	
e	15.640	1-Ethyle-2-methyl benzene	
f	22.560	Benzoic acid	

3.2. Direct mode (TG–MS)

In order to investigate the relationship between the released gas and the temperature, TG–MS measurements of $CsC_{24}(C_2H_4)_{1.0}$ were carried out in the direct mode. The TG curve and the TIC are shown in Fig. 5. The TG curve of $CsC_{24}(C_2H_4)_{1.0}$ was similar to that of $CsC_{24}(C_2H_4)_{1.4}$ (Fig. 2).

Released gases were observed in the following four regions. The first region ranges between 120 and 300 °C. The main peaks of the mass spectrum of the released gases were detected at $m/z = 17$ and 18, at 160 °C. From the peaks, we could identify that the released gas in this region is mainly H_2O. The weight loss in this region was 0.45%; this moisture is considered to be adsorbed on the sample during a short period of loading in the measuring system.

The second region lies between 420 and 530 °C, and the peaks were detected at $m/z = 16$, 28, 43, 57, 71, 91, etc. at 480 °C. The peaks at $m/z = 43$, 57, 71, etc., indicate that certain types of *n*-alkanes are released in this region. Although *n*-alkanes up to $m/z = 141$, equivalent to C12, were detected in the ion-chromatogram, C20, which was found in the trap mode, was not detected in this mode. This may be because the detection sensitivity in the trap mode is higher than that of the direct mode, since, in the trap mode, the released gases are condensed just before being introduced into the GC–MS system. The weight loss in this region was 2.2%.

The third region lies between 530 and 640 °C. Since the peaks were detected at $m/z = 15$, 16, etc., at 550 °C, the main released gas in this region was identified as CH_4. The weight loss in this region was 2.7%. It is considered that the *n*-alkenes in the second region and CH_4 in the third region originated from the C_2H_4 component of $CsC_{24}(C_2H_4)_{1.0}$. The sum of the weight losses in these two regions is 4.9%. Since the wt.% of C_2H_4 of $CsC_{24}(C_2H_4)_{1.0}$ is 6.2%, it implies that approximately 80% of the ethylene component was released up to 640 °C.

The fourth region lies between 720 and 890 °C. The main peaks of the mass spectrum of the released gas were detected at $m/z = 18$, 27, 28 and 44, at 810 °C. The weight loss in this region was 12%. The substantial part of the weight loss in this region may be caused by the release of decomposed Cs. Because of low volatility of metallic Cs ($m/z = 133$), it seems reasonable that no peak was observed at this mass number in the mass spectrum. The gases detected might be small amount of impurities such as H_2O, N_2, CO, CO_2, etc.

4. Conclusions

The released gases from $CsC_{24}(C_2H_4)_x$ at high temperatures were analyzed by TG/GC–MS. The measurements in the trap mode revealed that *n*-alkanes, C3–C20, and a small number of cyclic compounds were detected. The analysis strongly suggested the formation of ethylene oligomers in the interlayer nano-space of CsC_{24}. However, since the carbon chains of the ethylene oligomers were cut by thermal decomposition, the exact degree of oligomerization in the nano-space could not be determined. It will be necessary to conduct measurements under more severe conditions in order to provide a further detailed investigation on ethylene oligomers in the nano-space.

Acknowledgements

The authors thank Dr. A. Taomoto (Matsushita Electric Industrial Co.) for providing samples of PGS graphite sheets. Useful suggestion of Prof. Y. Sawada, Tokyo Polytechnic University, is also gratefully appreciated.

References

[1] M.S. Dresselhaus, G. Dresselhaus, Adv. Phys. 30 (1981) 139.
[2] Y. Takahashi, K. Oi, T. Terai, N. Akuzawa, Carbon 29 (1991) 283.
[3] H. Pilliere, Y. Takahashi, T. Yoneoka, T. Otosaka, N. Akuzawa, Synth. Met. 59 (1993) 191.
[4] R. Matsumoto, Y. Takahashi, N. Akuzawa, Mol. Cryst. Liq. Cryst. 340 (2000) 43.
[5] R. Matsumoto, Y. Takahashi, K. Watanabe, N. Akuzawa, Synth. Met. 125 (2002) 142.

[6] Y. Takahashi, N. Akuzawa, T. Terai, Y. Hanzawa, Y. Takeshita, K. Tanaka, JSPS Report 117-219-A-2, 1992 (in Japanese).
[7] Y. Takahashi, Tanso 160 (1993) 301 (in Japanese).
[8] T. Arii, S. Ichihara, H. Nakagawa, N. Fujii, Thermochim. Acta 319 (1998) 129.
[9] T. Ozawa, T. Arii, A. Kishi, Thermochim. Acta 352–353 (2000) 177.
[10] T. Arii, Y. Masuda, Thermochim. Acta 342 (1999) 139.
[11] T. Arii, K. Terayama, N. Fujii, J. Therm. Anal. 47 (1996) 1649–1661.
[12] T. Arii, T. Senda, N. Fujii, Thermochim. Acta 267 (1995) 209.