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Thermal decomposition process of silver behenate

Xianhao Liu [a,b], Shuxia Lu [c], Jingchang Zhang [a,*], Weiliang Cao [a]

[a] *Institute of Modern Catalysis, The Key Laboratory of Science and Technology of Controllable Chemical Reactions of Ministry of Education, Beijing University of Chemical Technology, Beijing 100029, China*
[b] *Institute of Research and Development, China Lucky Film Corp., Hebei Baoding 071054, China*
[c] *College of Mathematics and Computer Science, Hebei University, Hebei Baoding 071002, China*

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Abstract

The thermal decomposition processes of silver behenate have been studied by infrared spectroscopy (IR), X-ray diffraction (XRD), combined thermogravimetry–differential thermal analysis–mass spectrometry (TG-DTA-MS), transmission electron microscopy (TEM) and UV–vis spectroscopy. The TG-DTA and the higher temperature IR and XRD measurements indicated that complicated structural changes took place while heating silver behenate, but there were two distinct thermal transitions. During the first transition at 138 °C, the alkyl chains of silver behenate were transformed from an ordered into a disordered state. During the second transition at about 231 °C, a structural change took place for silver behenate, which was the decomposition of silver behenate. The major products of the thermal decomposition of silver behenate were metallic silver and behenic acid. Upon heating up to 500 °C, the final product of the thermal decomposition was metallic silver. The combined TG-MS analysis showed that the gas products of the thermal decomposition of silver behenate were carbon dioxide, water, hydrogen, acetylene and some small molecule alkenes. TEM and UV–vis spectroscopy were used to investigate the process of the formation and growth of metallic silver nanoparticles.

Keywords: Silver behenate; Combined TG-MS analysis; Thermal analysis; Thermal decomposition process

1. Introduction

Silver alkane carboxylate can be considered as inorganic–organic hybrid materials due to the structure of inorganic layers (the carboxylate groups and the silver ions) alternating with an organic layer (the double layers of alkyl chains) [1]. In the last few years, increasing attention has been paid to the structure and thermal behavior of silver carboxylates [1–4]. Silver salts of the long-chain fatty acids are used as the silver source in thermographic and photothermographic materials [5–8]. The most often used silver fatty acids in thermographic and photothermographic materials are silver behenate, silver stearate, or a mixture thereof [5–8].

Silver alkane carboxylate was reported to have a layered structure [9,10]. The knowledge of the thermal behavior of the silver carboxylates is of importance for an understanding of the thermographic process. Silver carboxylate does not simply melt in one step upon heating, but it undergoes a series of phase transitions before it melts with thermal decomposition [11,12]. As early as in 1886, Iwig and Hecht reported that silver butanoate is thermally decomposed into butanoic acid, carbon dioxide, carbon and metallic silver: $8C_3H_7COOAg \rightarrow 8Ag^0 + 7C_3H_7COOH + CO_2 + 3C$ [13]. Griffin et al. reported the thermal decomposition reaction mechanism of silver acetate [14]. The decomposition reaction they proposed is $2CH_3COOAg \rightarrow 2Ag^0 + CH_3COOH + CO_2 + H_2 + C$. Binnemans et al. [4] had proposed the decomposition of silver behenate is $2CH_3(CH_2)_{20}COOAg \rightarrow 2Ag + CO_2 + CH_3(CH_2)_{20}COOH + CH_3(CH_2)_{18}CH{=}CH_2$. The above authors found that the main decomposition products of the silver alkanoates were metallic silver and corresponding alkanoic acid, but they were not able to detect gas products during the thermal decomposition process. Although the presence of silver metal and alkanoic acid can be confirmed by XRD measurement and IR spectroscopy [15,16], respectively, the reported actual gas products at high temperatures are only a matter of conjecture.

To develop technologically relevant inorganic–organic hybrid materials, the whole thermal decomposition process must

* Corresponding author. Tel.: +86 10 64434904; fax: +86 10 64434898.
E-mail address: zhangjc1@mail.buct.edu.cn (J. Zhang).

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be known for their applications. In this paper, the detailed thermal behavior and decomposition process of silver behenate have been investigated by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR) and thermal analysis (TG-DTA). In order to confirm the species transported in the gas phase at different temperatures, the thermal decomposition intermediate gas products of silver behenate will be discussed by the combined TG-MS. Moreover, the thermal formation and growth of metallic silver nanoparticles will be characterized using TEM and UV–vis spectroscopy.

2. Experimental

2.1. Synthesis

All chemicals were purchased from commercial sources and used as received. The sodium behenate solution was prepared by firstly dissolving behenic acid in water-tert butyl alcohol mixing solvent at 80 °C, and then 0.25 mol L^{-1} sodium hydroxide solution was added with stirring at 1500 rpm. The molar ratio of behenic acid and sodium hydroxide was 1:1. Subsequently, the mixture was left being stirred for 1 h at 80 °C to obtain a solution of sodium behenate. Water-tert butyl alcohol mixed solvent, 5% (w/w) dodecylbenzene sulfonic acid sodium solution, tributyl phosphate and 3.0 mol L^{-1} silver nitrate solution were added with stirring into a reaction vessel. To enhance monodispersibility of grains and eliminate the formation of bubbles, dodecylbenzene sulfonic acid sodium and tributyl phosphate were added into the preparation process, respectively. The whole amount of the aforementioned sodium behenate solution and the equivalent mole amount of 3.0 mol L^{-1} aqueous silver nitrate solution were added at constant flow rates into the reaction vessel with fast stirring at 30 °C. After additions, the solution was stirred for 40 min at the same temperature and stirring rate. Subsequently, the white precipitate was filtered, and thoroughly washed with alcohol and distilled water until electric conductivity of the filtrate became less than 100 μS cm^{-1}. Finally, the white silver behenate was dried for 24 h in vacuum. The purity of the silver behenate was checked by C, H elemental analysis (% calc./found: C 59.05/59.04, H 9.69/9.67).

2.2. Characterization

The XRD patterns of powder sample were recorded on a Rigaku D/Max 2500 X-ray diffractometer using Cu $K\alpha_1$ (1.5406 Å) radiation operated at 40 kV and 200 mA for a 2θ angular range from 3° (2θ) to 50° (2θ) with a stepsize of 0.02° (2θ).

Infrared spectra were measured using a Bruker Vector 22 spectrometer. Pure KBr was used as the background. The proportion of KBr and sample was 1:0.015.

TG-DTA was performed on Pyris Diamond (Perkin-Elmer). The analyse was conducted in nitrogen atmosphere (100 mL min^{-1}) between 25 and 600 °C. Sample of 10 mg was put in a Pt cell and heated at a constant rate of 10 °C min^{-1}. MS spectra were measured on ThermostarTM (InProcess Instruments). The analysis was carried out in helium atmosphere (100 mL min^{-1}) between 25 and 600 °C.

Transmission electron microscopic (TEM) photographs of metallic silver nanoparticles were taken on a JEM-1200 EX-II (JEOL) microscope.

The UV–vis spectra of thermally decomposed samples at different temperatures were taken in toluene solvent with a Hitachi U-3000 spectrophotometer.

3. Results and discussion

3.1. The thermal behavior and decomposition processes of silver behenate

Fig. 1 shows a series of X-ray diffraction patterns of as-prepared silver behenate at various temperatures, ranging from 25 to 220 °C. In the small angle region a set of well-defined diffraction peaks is observed at 25 °C. These diffraction peaks belong to the (0 0 l) reflections. Such a diffraction pattern is consistent with a layer structure [4]. Each layer is separated from the other by twice the length of the alkyl chain [1]. It is noticeable from Fig. 1 that a well-produced progression of intense reflections is invariably seen below 140 °C. The presence of progressional reflections up to 120 °C indicates that the bilayer structural motif is sustained [16]. However, heating to 140–160 °C leads to substantial decreases of the layer reflections d(0 0 l) intensities, and the reflections are broadened. It can also be noticed from Fig. 1 that the XRD peak indexed as (0 0 l) abruptly decreases at 160 °C and cannot be identified at all at 190 °C. Instead, two new peaks are identified at 38.6° (2θ) and 44.3° (2θ) when the sample is heated above 190 °C. These peaks can be assigned to (1 1 1) and (2 0 0) reflections of metallic silver, showing that the major decomposition product of silver behenate is metallic silver.

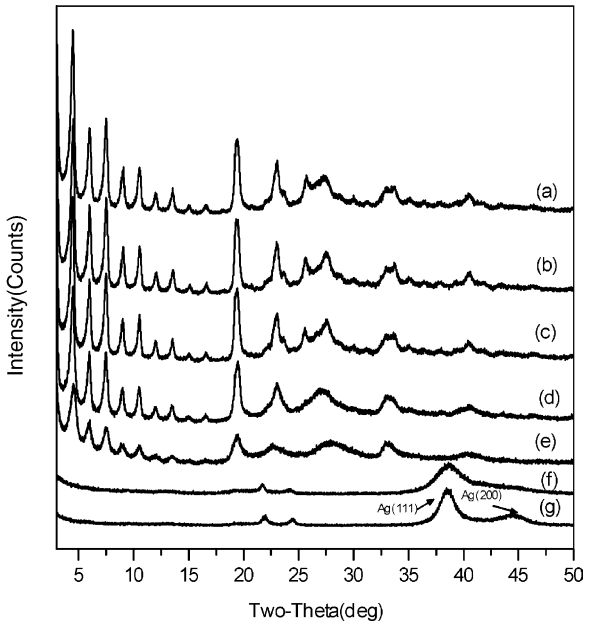

Fig. 1. XRD patterns of silver behenate at different temperatures: (a) 25 °C; (b) 100 °C; (c) 120 °C; (d) 140 °C; (e) 160 °C; (f) 190 °C; (g) 220 °C.