Analysis of polymers, minerals and pharmaceuticals by TG-DTA-MS

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1. Introduction

Hyphenated methodology combined with thermal analysis and other analysis methods has been widely applied to the investigation of complex phenomena. Thermo Mass Photo (Fig. 1) is a thermogravimetry-differential thermal analysis-mass spectrometry (TG-DTA-MS) instrument, which is one of the most widespread hyphenated systems, and a main product in the lineup of Rigaku's evolved gas analytical systems. It consists of thermogravimetry-differential thermal analysis (TG-DTA) and photoionization mass spectrometry (PIMS) equipped with a unique skimmer-type interface[(1),(2)]. The simultaneous analysis of weight changes, endothermic or exothermic phenomena, and evolved gases can be applied to fundamental research, quality control, and development of new materials, etc. In this article, we have introduced several applications of the thermal decompositions of the polymers, minerals, and pharmaceuticals by Thermo Mass Photo.

2. Applications

2.1. Thermal decomposition of polyvinylchloride (PVC)

Polymer resins have been produced for various uses, and eventually become a waste. We must take care of their incineration, especially those harmful gases such as HCl and organic halogen compounds are often evolved from PVC. Here, we have investigated the thermal decomposition of PVC by Thermo Mass Photo with electron ionization mass spectrometry (EIMS) and PIMS.

Figure 2 shows the TG profile and mass spectra of PVC measured by a heating rate at 20°C/min under He atmosphere. PVC exhibits the two-step weight loss during the heating. On the 1st weight loss in the temperature range from 250 to 400°C, HCl and the aromatic compounds such as benzene and naphthalene are identified. The molecular and fragment ions of HCl (m/z 35, 36, 37, 38) are detected by EIMS. Electron ionization (EI) is a conventional ionization method, and can be applied to the sensitive detection of molecular and fragment ions. Photoionization (PI) is one of the soft ionization methods, which can be applied to specific detection of molecular ions. The molecular ions of benzene (m/z 78) and naphthalene (m/z 128) are remarkably detected by PIMS. Other aromatic compounds such as toluene (m/z 92) and xylene (m/z 106) are evolved on the 2nd weight loss in the temperature range from 400 to 550°C.

The MS ion thermograms in Fig. 3 demonstrate the profile of each evolved gas as a function of the temperature. These graphs reveal that HCl and benzene are evolved simultaneously on the 1st weight loss while toluene and xylene on the 2nd weight loss. As shown in the schematic diagram in Fig. 2, the thermal decomposition of PVC induces the desorption of HCl followed by the formation of the polyene structure. Then the various aromatic compounds are produced by the cyclization of the polyene.

Fig. 1. Photograph of Thermo Mass Photo.

2.2. Thermal decomposition of asbestos

As it is well-known, asbestos give rise to serious health hazards. The fusion treatment is necessary for the disposal of asbestos waste. Therefore, it is indispensable to obtain information about the thermal behaviors of asbestos. Thermo Mass Photo has been applied to the investigation of the thermal decomposition of chrysotile, which is the main silicate mineral in asbestos.

Figure 4 shows the TG-DTA curve and EIMS ion thermograms of chrysotile measured by a heating rate at 20°C/min under He atmosphere. The weight loss, endothermic peak and evolution of H_2O from 600 to 700°C are caused by the dehydration of chrysotile, as described in the following reaction.

$$2Mg_3Si_2O_5(OH)_4 \rightarrow 3Mg_2SiO_4 + SiO_2 + 4H_2O$$

The evolution of H_2O from 300 to 400°C is due to the dehydration of brucite.

$$Mg(OH)_2 \rightarrow MgO + H_2O$$

In addition, we can see clearly the evolution of CO_2 and

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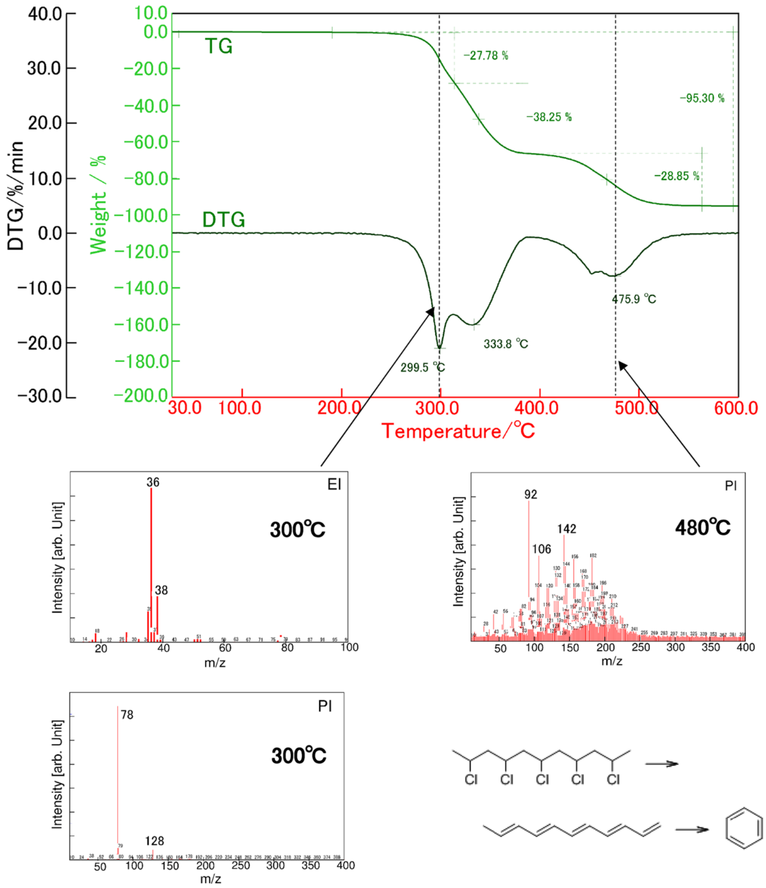

Fig. 2. TG-DTA profile and mass spectra of PVC.

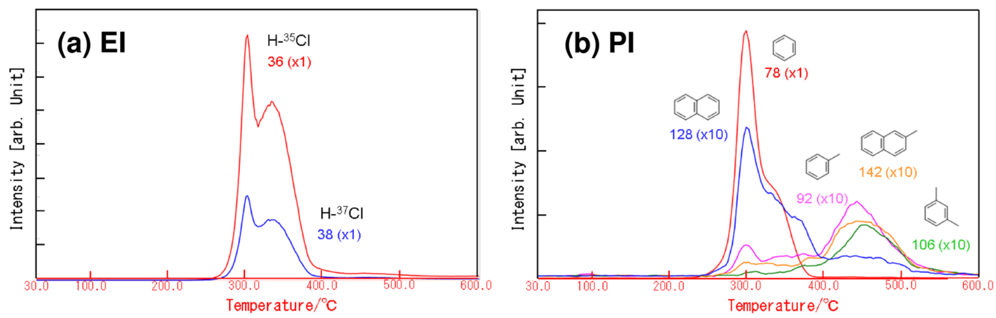

Fig. 3. MS ion thermograms of PVC for (a) EI and (b) PI.

SO_2. The evolution of CO_2 around 400°C is attributed to the decarboxylation of magnesite.

$$MgCO_3 \rightarrow MgO + CO_2$$

The DTA curve indicates the remarkable exothermic peak at 839°C, which is caused by the formation of enstatite as reported by Kishi[(3)].

2.3. Thermal Decomposition of Coal

The study of thermal decomposition of coal is important since it is the initial step in most conversion processes of coal, and Thermo Mass Photo with EIMS and PIMS provides useful information. Figure 5 shows the TG and total ion current (TIC) curves, corresponding to the total amount of evolved gases. The large amount of weight loss and the remarkable peak of the TIC are observed around 460°C, while the small peaks of the TIC are observed around 110 and 790°C, respectively. Figures 5(a), (b), and (c) show the mass spectra at these temperatures. H_2O is observed at 110°C; several hydrocarbons as well as phenol derivatives at 460°C; H_2O, CO, and CO_2 at 790°C.

Quasi-quantification in a Thermo Mass Photo measurement can be performed with respect to 10 kinds of inorganic gases: H_2, He, CH_4, NH_3, H_2O, CO, N_2, O_2, Ar, and CO_2. H_2, CH_4, H_2O, CO, and CO_2 are mainly evolved on the thermal decomposition of coal in He atmosphere. Figure 6 shows the MS ion thermogram with the conversion from the signal intensity (A) to the amounts of evolved gases per second (ppm/s).

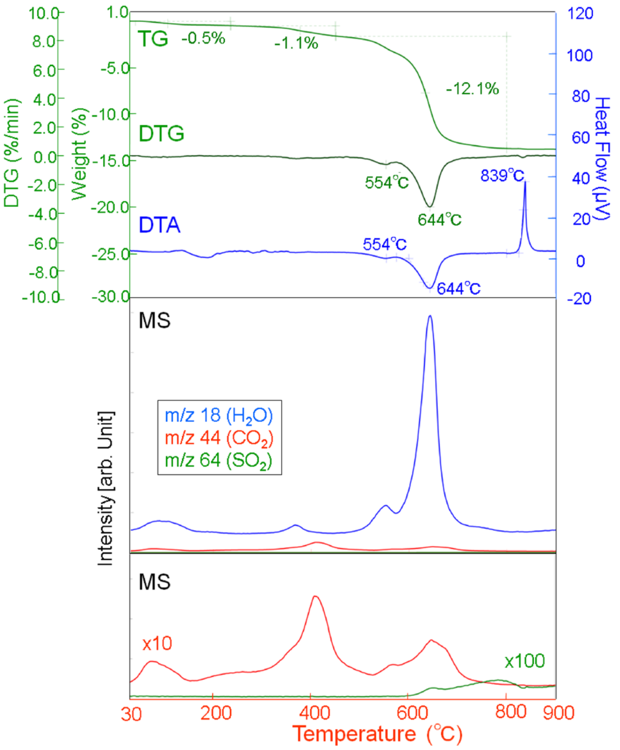

Fig. 4. TG-DTA profile and MS ion of thermogram of chrysotile.

2.4. Evolved gas and kinetic analysis of acetylsalicylic acid

Acetylsalicylic acid is used to relieve pain, fever, and inflammation in various conditions such as lower back pain, flu, and common cold. In this investigation, we have detected the evolved gases from acetylsalicylic acid upon heating by Thermo Mass Photo. Furthermore, we have estimated the activation energy and the reaction time.

Upon heating acetylsalicylic acid under He atmosphere, two-step weight losses are observed in Fig. 7. On the first weight loss (120–250°C), the two endothermic peaks appear at 144 and 188°C in the DTA curve. In addition, we detect the characteristic ions for salicylic acid, acetylsalicylic acid, and acetic acid in MS. The endothermic peak at 144°C is attributed to the fusion of acetylsalicylic acid. The peak at 188°C is considered due to the sublimation or evaporation of acetylsalicylic acid and the thermal decomposition which generates salicylic acid and acetic acid. The evolution of these gases was confirmed by other method[4]. On the second weight loss (250–400°C), we observe the endothermic peak at 357°C in DTA and the phenol ion in MS, which is generated by the thermal decomposition.

The dependence of the curve-shape on the heating conditions reflects the kinetics of the reaction in thermal analysis. This information has been widely utilized for estimation of reactivity and stability of materials, such as lifetime. Generally, TG curves have been applied to the kinetic analysis. However, TG curves are not applicable to the kinetic analysis if multiple reactions

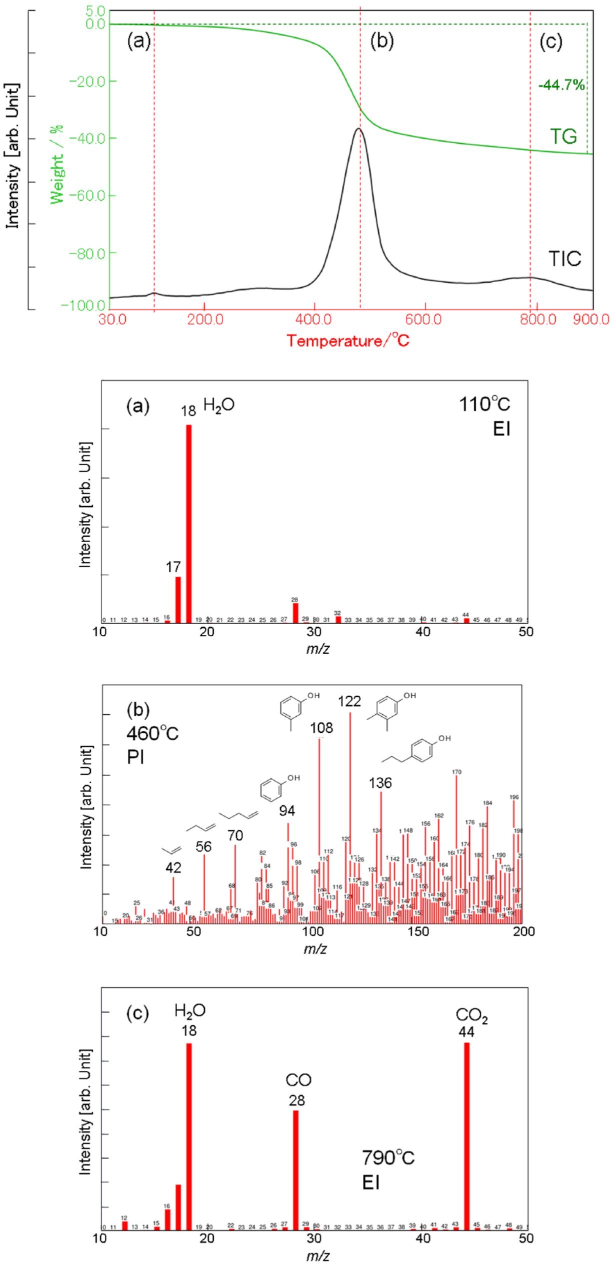

Fig. 5. TG and TIC profiles of coal and the mass spectra at (a) 110, (b) 460, and (c) 790°C.

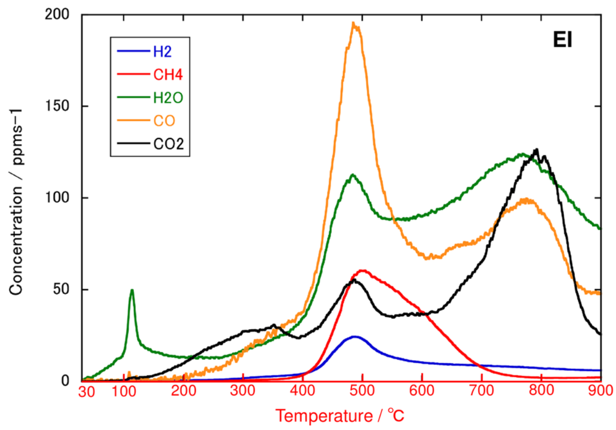

Fig. 6. Quasi-quantitative MS ion thermogram of coal.

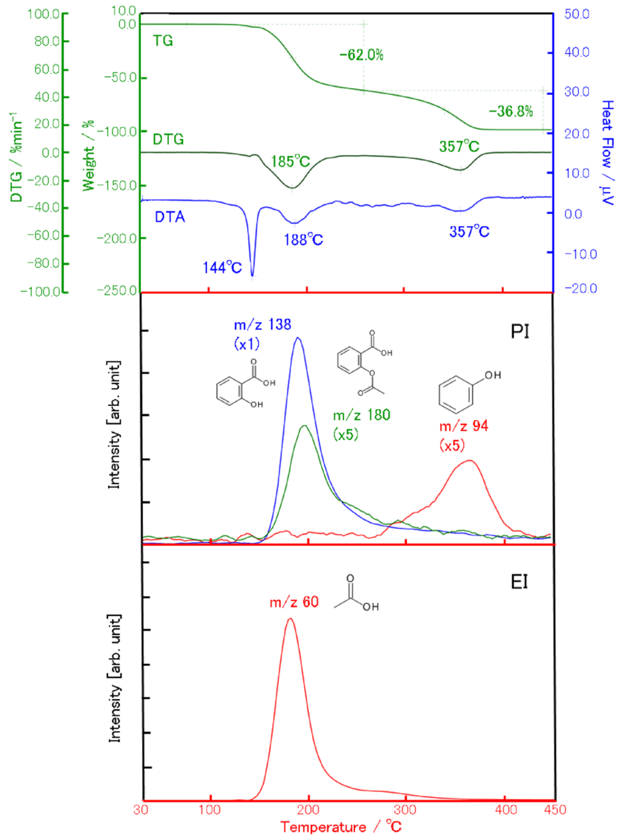

Fig. 7. TG-DTA profile and MS ion thermogram of acetylsalicylic acid.

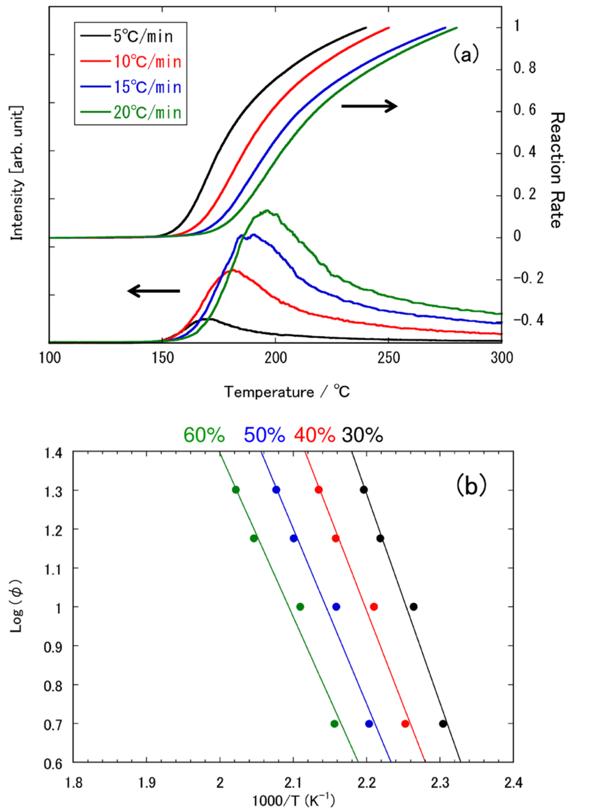

Fig. 8. (a) MS ion thermogram of m/z 138 (PI) and its conversion profile.
(b) Flynn-Wall-Ozawa plots for generation of salicylic acid.

occur in the same temperature range such as the first weight loss in this measurement. We propose that the thermal profiles of evolved gases are applied to the kinetic analysis of the multiple reactions. This analysis provides the specified information on the reaction products.

The activation energy of the reaction for the evolution of salicylic acid was calculated from the MS ion thermogram of m/z 138 in PI, corresponding to the molecular ion of salicylic acid. Figure 8(a) shows the MS ion thermogram of m/z 138 with various heating rates and the reaction rate derived from their integration as well. The reaction rate allows us to form the Flynn-Wall-Ozawa plots as shown in Fig. 8(b). The activation energy is calculated at 89 $kJmol^{-1}$ on the reaction rate of 40% where the generation of salicylic acid becomes maximum. Finally, we can estimate the reaction time of 6849 hours (285 days) required for this reaction rate at 25°C.

3. Summary

Thermo Mass Photo plays an important role in the detailed analysis of the thermal decomposition of polymers, minerals, and pharmaceuticals as introduced here. Furthermore, it can be also applied to analysis of hydrogen absorbing alloys, catalytic reaction, and quantification of dehydration.

References

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