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Coupling of thermogravimetric analysis and thermo-Raman spectroscopy for in situ dynamic thermal analysis

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Abstract

Thermogravimetric (TG) analysis provides information related to weight change but is not conclusive enough for direct identification of the composition of the sample in the dynamic thermal process. Raman spectroscopy has the advantage of detecting the composition and phase of the sample. Thermo-Raman spectroscopy (TRS) on the other hand, measures Raman spectra continuously at regular temperature interval for the identification of composition and phase of the species that appear in a dynamic thermal process. Therefore, the composition changes and phase transformations can be studied in the whole dynamic thermal process. Unfortunately, the results obtained from separate thermogravimetric analyzer (TGA) and TRS experiments may not be entirely consistent due to different sampling and experimental conditions. This problem has been overcome by direct coupling of the TGA and TRS instruments in this work so that it is ensured that the experimental and sampling condition do not hamper the results. In this work, coupling of a TGA to a thermo-Raman spectrometer (TRS) for in situ investigation of composition with weight loss have been illustrated using $CaC_2O_4{\cdot}H_2O$ which is widely used as a calibration standard for TGA. The thermo-Raman intensity (TRI) and differential thermo-Raman intensity (DTRI) thermograms were consistent with those of TG and differential thermogravimetry (DTG) thermograms, respectively.

Keywords: Thermo-Raman spectroscopy; Thermogravimetric analyzer; Coupling; $CaC_2O_4{\cdot}H_2O$

1. Introduction

Thermogravimetric analyzers (TGA), differential temperature analyzers (DTA) and differential scanning calorimeters (DSC) are important instruments for thermal analysis of solids [1]. The weight changes observed in TG thermogram serves as an indirect evidence to detect the compositional changes but have its own limitation. Techniques like gas chromatography and mass spectrometry can be coupled to TGA and can be used to detect volatile or gaseous compounds evolved during the thermal process. Coupling of IR to TGA for identification of reaction products have also been reported [2,3]. But requirements of special sample preparation and possibility of ion exchange between sample and alkali metal halides are disadvantages of IR. The temperature differences from DTA and enthalpy changes from DSC can provide the information on chemical reactions and phase transformations. However, no direct information on the composition and phase of the sample could be obtained in situ.

Raman spectroscopy provides information about the vibrational bands, which are excellent for identification

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of composition and phase [4]. Raman spectra measured continuously in a dynamic thermal process gives the systematic variation in the spectra [5]. Furthermore, the intensity of the characteristic bands can be plotted against temperature for determination of the relative amount of each species just as in TG analysis. The derivative of the intensity indicates the variation in amount and resembles the DTG thermogram. The band positions and band widths also show the changes in sample. In this way, the ability of Raman spectroscopy is fully utilized for thermal analysis. This method is referred to as thermo-Raman spectroscopy (TRS) and was tested using $CaC_2O_4{\cdot}H_2O$ [6]. The spectral variation in TRS was in that work [6] compared with the weight change observed in TG thermograms. The results were consistent but did not match perfectly as separate experiments for TG and TRS were carried out which may lead to temperature variation and different sample and experimental conditions. It is known that sampling and experimental conditions affect the results in thermal analysis [1], which were observed in our earlier work. Earlier work includes, dehydration processes of $CuSO_4{\cdot}5H_2O$ [7], $CaSO_4{\cdot}2H_2O$ and $CaSO_4{\cdot}0.5H_2O$ [8], the sintering processes of TiO_2 [9,10], the thermal hysteresis of KNO_3 [11,12] and the polymorphism of Na_2SO_4 [13] which were explored with TRS method and compared with TGA. The decomposition process of hydrated MoO_3 [14] and $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ [15] were also not conclusive using either TGA or TRS. These drawbacks were overcome by coupling TGA with TRS as the thermograms could be measured simultaneously on the same sample with the same experimental conditions. This enabled correct measurement of temperatures and thermo-Raman spectra and simultaneously the weight changes during the thermal process.

In this work, the coupling of TGA to TRS was successful and the thermograms were found comparable. The changes in the weight and the Raman spectra could be measured simultaneously on the same sample under the same experimental conditions in a dynamic thermal process. $CaC_2O_4{\cdot}H_2O$ being a standard for calibration in TGA was used as its Raman spectra was also known. The plots of intensity of the characteristic Raman bands and their derivatives are referred to as thermo-Raman intensity (TRI) thermogram and differential thermo-Raman intensity (DTRI) thermogram, respectively. Further, it was found that the final temperatures in both thermograms matched perfectly which indicates that the end of the composition change or the chemical reaction. However, differences in initial and peak temperatures were found. This is apparently due to the different character of the two methods. In TGA, the total weight that is a property of the whole sample was under consideration, whereas the TRS monitors the surface layer of the sample. Finally, the coupling of these two instruments is not difficult and can be applied for wide range of applications in material research laboratories or analytical laboratories for routine analysis work.

2. Experimental

The optical arrangement required in coupling of TGA to thermo-Raman spectrometer (TRS) is as shown in Fig. 1. The sample was placed in alumina crucible in TGA (Perkin Elmer, model TGA6). The crucible was seated on the crucible holder attached to the balance. A glass window for transmission of the incident laser beam and for collecting scattered light was used instead of the metal cover of the TGA oven. An argon ion laser (Spectra Physics, model 162) was used as the light source (50 mW) operating at the wavelength of 514.5 nm. The laser beam was aligned and focused to pass through a small hole in the first surface mirror, onto the sample in the crucible. The scattered light was collected through the glass window, reflected by the first surface mirror and measured by Raman spectrometer (Spex, 0.5 m focal length) with CCD camera (Princeton Instruments, 1024 × 1024 pixels). The light path in the optical system is shown in Fig. 1. In this way, both TGA and TRS could be measured on the same sample with the same experimental conditions.

The thermal process was set from 30 to 850°C with a heating rate of $5^{\circ}C\,min^{-1}$ in oxygen flow of $20\,ml\,min^{-1}$. Raman spectra were taken with an exposure time of 12 s successively, such that each spectrum covered 1°C. The positions of the spectral bands were calibrated by argon spectral lines. The resolution was about $2\,cm^{-1}$.

The $CaC_2O_4{\cdot}H_2O$ sample, the calibration standard for the TGA was obtained from Seiko, Japan. The amount of sample required for the experiment depends

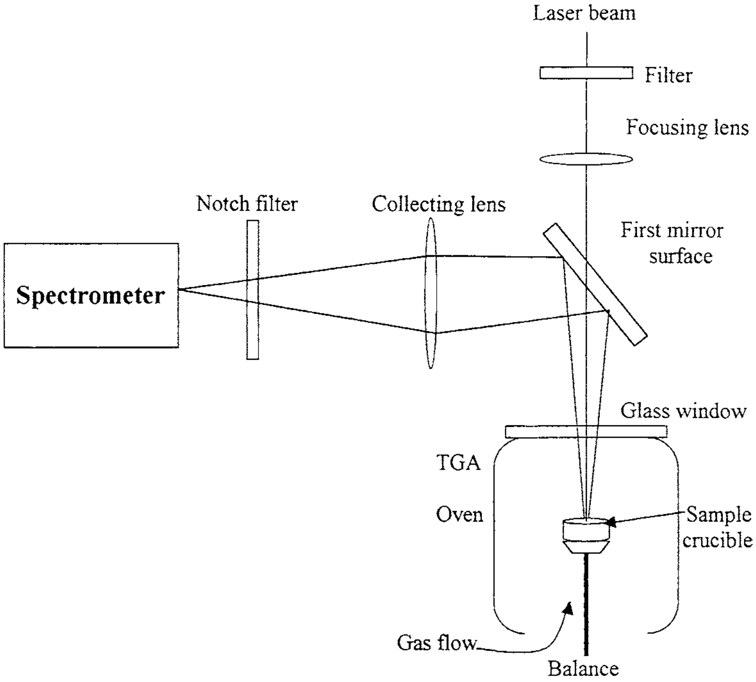

Fig. 1. The experimental setup for coupling a thermogravimetric analyzer to a thermo-Raman spectrometer.

upon the shape and size of the crucible used. About 20 mg was found to be sufficient for measuring good Raman spectra.

3. Results and discussion

The weight loss took place in three stages corresponding to dehydration, oxidation and decomposition during heating $CaC_2O_4{\cdot}H_2O$ up to 850°C. The intermediates thus obtained are CaC_2O_4, $CaCO_3$ and CaO. The characteristic Raman spectra of these species are reported in our previous work [6]. The thermo-Raman spectra could identify the composition and phase of the intermediates and reveals the amount of each species from the surface layer.

The characteristic Raman bands of $C_2O_4{}^{2-}$ and $CO_3{}^{2-}$ were observed around 1465 and 1070 cm^{-1}, respectively. The intensity (area) represents the amount of each species, therefore the intensities of these two bands were calculated and are shown in Fig. 2. The TRI-A and TRI-B thermograms represented the band intensities at around 1465 and 1070 cm^{-1}, respectively, corresponding to the amounts of $C_2O_4{}^{2-}$ and $CO_3{}^{2-}$. In TRI-A thermogram, intensity decreased during the dehydration from 126 to 202°C and during oxidation to $CaCO_3$ from 401 to 526°C. For dehydration the doublet at 1465 cm^{-1} became singlet. During oxidation, the band at 1465 cm^{-1} was replaced by the band at 1070 cm^{-1} for $CaCO_3$ as described in our earlier work [6]. In TRI-B thermogram, intensity increased during the formation of $CaCO_3$ from 401 to 526°C and subsequently decreased dramatically to vanish during its decomposition to CaO from 740 to 774°C. The third curve is the TG thermogram, which was measured simultaneously. It indicated three reaction stages with weight losses of 13, 18 and 27%, corresponding to the losses of H_2O, CO and CO_2, respectively. The TG and TRI-A thermograms were consistent in the temperature range from 126 to 202°C for the dehydration stage. For the oxidation of CaC_2O_4 in the temperature range from 401 to 526°C, the TG and the TRI-A thermograms were consistent but a little delay in TRI-A thermogram was observed. TRI-B thermogram showed delayed increase in intensity and a sharp decrease in intensity

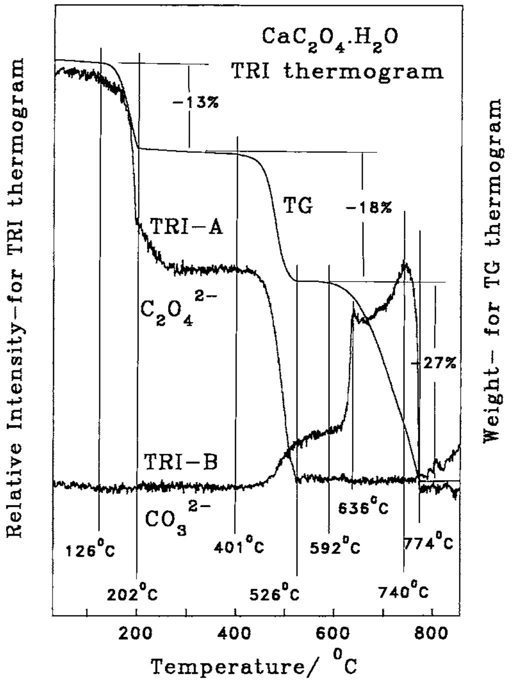

Fig. 2. The weight from TGA (TG thermogram), the intensity of the band at 1465 cm^{-1} for $C_2O_4^{2-}$ (TRI-A thermogram) and the intensity of the band at 1070 cm^{-1} for CO_3^{2-} (TRI-B thermogram).

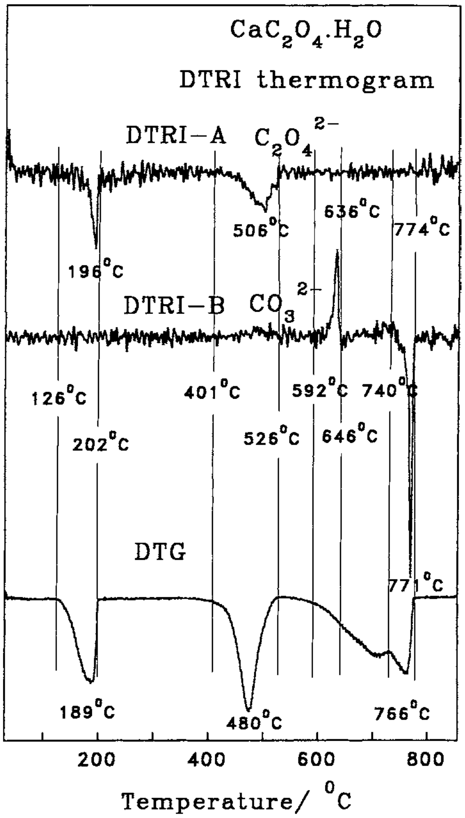

Fig. 3. The derivative of the thermogram from TGA (DTG thermogram), the derivative intensity of the band at 1465 cm^{-1} for $C_2O_4^{2-}$ (DTRI-A thermogram) and the derivative intensity of the band at 1070 cm^{-1} for CO_3^{2-} (DTRI-B thermogram).

in the temperature ranges from 740 to 774°C but the decrease in TG thermogram started at 592°C, much lower temperature with slow rate. However, they showed the same final temperature at 774°C. The TRI-A and TRI-B thermograms showed two extra variations around 250 and 636°C corresponded to the phase transformations of CaC_2O_4 from phase α to phase β and of $CaCO_3$ from aragonite to calcite, respectively [6].

The derivatives of these TRI thermograms showed distinct varaitions and are referred to as DTRI thermograms. They show pits and humps with dips and peaks for the maximum rate for the changes, respectively, as shown in Fig. 3. The DTRI-A and the DTRI-B thermograms correspond to the TRI-A and TRI-B thermograms referring to changes in the amounts of $C_2O_4^{2-}$ and CO_3^{2-}, respectively. DTRI-A thermogram showed two pits with dips at 196 and 506°C for dehydration and oxidation, respectively. In DTRI-B thermogram two humps and one pit were observed. The hump around 506°C indicated the formation of $CaCO_3$ which was weak, whereas the one at 636°C for phase transformation was sharp. The pit for the decomposition was at 771°C which was very sharp and distinct. The DTG thermogram corresponding to the TG thermogram representing the weight changes during each step is also shown in Fig. 3. For dehydration and oxidation, the dip temperatures of both the DTG and the DTRI-A thermograms were within 20°C, however the final temperatures were the same, 202 and 526°C. For the DTRI-B thermogram, the corresponding dip for oxidation was weak. For the decomposition of $CaCO_3$, the DTG thermogram showed a very broad pit in the temperature range from 592 to 774°C with a dip at 766°C indicating maximum rate of transformation. Interestingly, the corresponding dip in DTRI-B thermogram was very strong and sharp, from 740 to 774°C with a dip at 771°C. It was clear from this that the initial and peak temperatures for these three reactions in DTG thermogram were lower than those in DTRI thermograms. However, the final temperatures were found to be the same as shown by the vertical lines in Fig. 3 for all the three reactions.

The experimental results may not be entirely consistent when separate experiments on two separate samples were made by TGA and TRS. It is particularly important for solid samples, where the sample conditions may affect the results. Coupling the two instruments enables us to use TGA and TRS simultaneously for measurement on the same sample and under the same experimental conditions and hence the results will be more reliable.

The discrepancies in the initial and peak temperatures of the three reactions of $CaC_2O_4{\cdot}H_2O$ can be predicted as follows. Dehydration is initiated around 126°C in the layer close to the crucible where the temperature is highest. Hence, a small initial weight loss is observed. The evolved water vapor diffuses out and keeps the sample in the surface layer in equilibrium with the surroundings. In other words, dehydration at surface layer occurs later so the Raman bands of the anhydrous species also appear later. As the temperature rises, the water vapor above the surface is reduced and more anhydrous species are formed. Thus, the initial and the peak temperatures of the dehydration process were observed at higher temperature in TRS than in TGA. On completion of the dehydration, both the surface layer and the bulk are anhydrous. As a result, the final temperatures of dehydration process shown in TG and TRI-A thermograms are the same. In the case of decomposition of $CaCO_3$, the equilibrium might be more favorable to the surface layer of $CaCO_3$. The CO_2 gas evolved from the bulk of the sample may diffuse out keeping the surface layer in the form of $CaCO_3$. Hence, $CaCO_3$ on the surface did not decompose until almost all CO_2 gas from the bulk was driven out. This delayed the beginning of the decrease in Raman intensity of the band of $CaCO_3$ from 592 to 740°C. The decomposition of $CaCO_3$ in the surface layer was rapid. The gas was driven off fast as evident from the drastic decrease in intensity of the ${CO_3}^{2-}$ band. The diffusion of CO_2 and the shape of this dip apparently depend upon the packing condition of the sample. In the previous work, the sample was loosely packed and thus a broad dip was observed. The peak temperature was lower, 709°C [6]. The behavior observed was different for the oxidation of CaC_2O_4, an irreversible process. The starting temperature for oxidation appeared nearly the same in DTG and DTRI thermograms. However, the oxidation in the bulk might be promoted by local heating in the bulk from the enthalpy of reaction. Apparently, the peak temperatures in DTRI and DTG for oxidation differed but the final temperatures were the same.

In TRS, Raman spectra showed the composition and phase of each species appearing in the sample during the dynamic thermal process providing qualitative information. On the other hand, the TRI and DTRI thermograms revealed the relative amount and variation in amount of each individual species providing quantitative information. Furthermore, the band positions and band widths of characteristic bands also indicate the composition change, phase transformation and the physical properties of the species. However, the shifts in band positions and change in band width may not be distinct in low resolution spectra.

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