APPLICATION**NOTE**

Simultaneous Detection of Organic Functional Groups and Inorganic Molecules in Thiol-Capped ZnO Nanoparticles with Evolved Gas Analysis by FT-IR and MS

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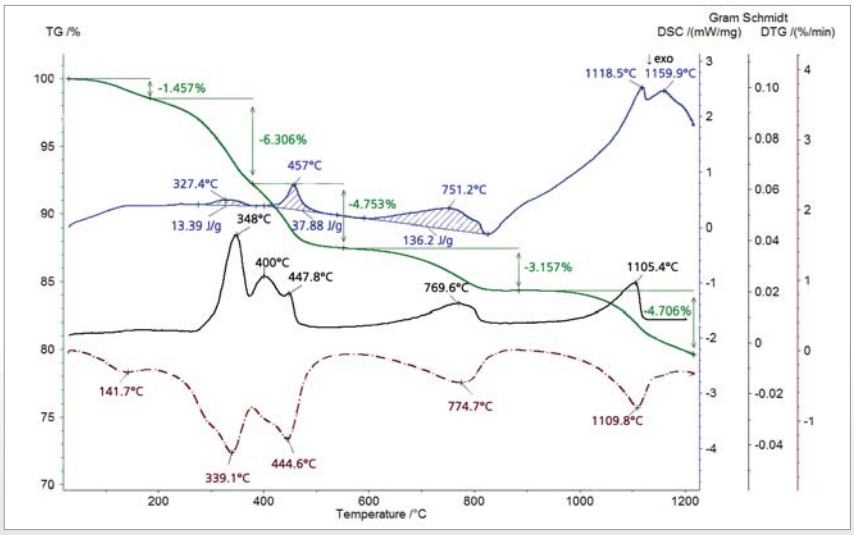
Introduction

Zinc oxide (ZnO) nanoparticles are being investigated for the synthesis of materials with tunable magnetic and electric properties and for possible medical applications in cancer therapy. In this study, a sample of thiol-capped ZnO nanoparticles was studied by simultaneous TGA-DSC (STA) using a NETZSCH STA 449 ***F1*** *Jupiter*® thermal analyzer which was coupled to both a NETZSCH QMS 403 *Aeolos*® mass spectrometer and a BRUKER Optics TENSOR™ FT-IR spectrometer (Figure 1) to perform evolved gas analysis by QMS and FT-IR. The transfer lines, the coupling adapters and the FT-IR gas cell were kept at a constant temperature of 200°C.

1 NETZSCH STA 449 ***F1*** *Jupiter*® coupled to a NETZSCH QMS 403 *Aeolos*® and a BRUKER Optics TENSOR™ FT-IR spectrometer

Measurement Results

The thiol-capped ZnO nanoparticles sample with a mass of 11.18 mg was pressed on the bottom of a Pt-Rh DSC crucible to form a layer of about 1 mm thickness and was heated from 30°C to 1200°C at a heating rate of 20 K/min under 60 ml/min nitrogen purge. The TGA, DTG (mass change rate), DSC and Gram Schmidt (total integral of the IR absorption) curves are plotted in Figure 2. The TGA curve shows five mass-loss steps which have corresponding peaks in the DTG



2 TGA, DTG, DSC and Gram Schmidt curves for the thiol-capped ZnO nanoparticle sample

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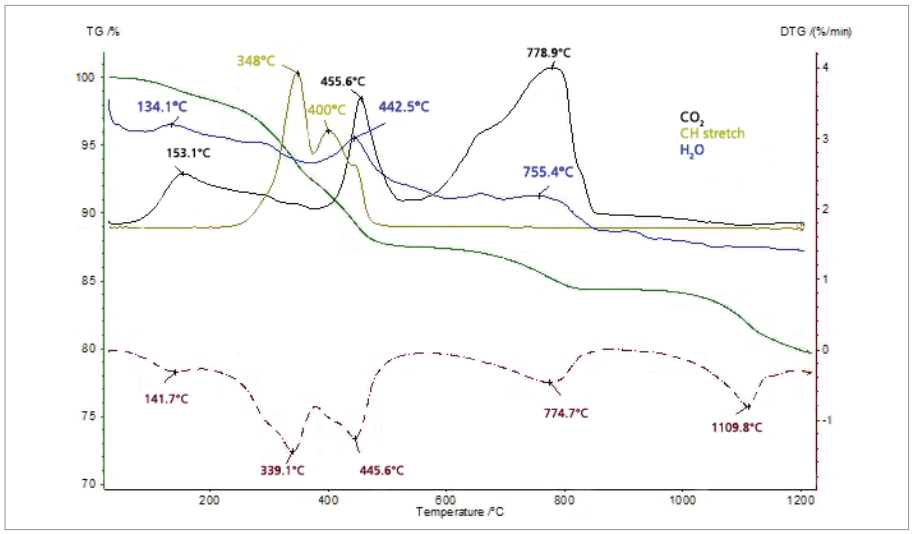
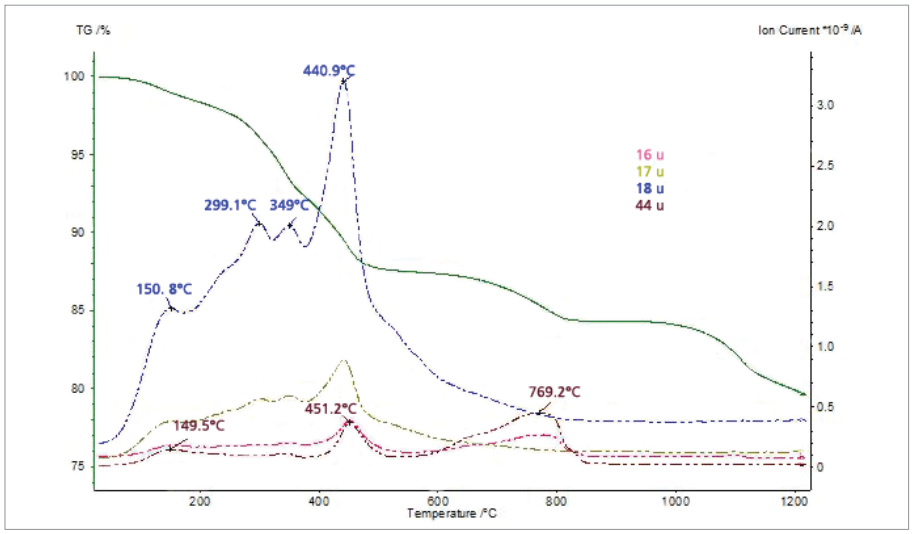
curve and corresponding endothermic features in the DSC curve due to desorption and decomposition processes in the sample. Apart from the very small effect below 200°C, the peak temperatures in the Gram Schmidt plot correspond well with the peak temperatures in the DTG curve. The TGA and DTG curves along with the temperature-dependent integrated band areas (traces) for the O-H stretching of H_2O, the C-H stretching of hydrocarbons and the anti-symmetric C=O stretching of CO_2 are plotted in Figure 3. As can be clearly seen, desorption of H_2O and CO_2 corresponds with the first four mass-loss steps whereas the hydrocarbons evolve in the mid-temperature range in good correspondence with the second and third mass loss steps in the TGA curve. The MS ion-current curves for H_2O (18; 17 and partially 16 u*) and CO_2 (44 and partially 16 u) plotted in Figure 4 together with the TGA curve show more details due to the higher sensitivity of the MS, but the results are in agreement with the FT-IR traces that H_2O and CO_2 evolution corresponds with the first four mass-loss steps in the TGA curve.



3 TGA and DTG curves and the FT-IR traces for CO_2, CH stretch and H_2O for the thiol-capped ZnO nanoparticles sample



4 MS ion-current curves for mass numbers 16, 17, 18 and 44 u and TGA curve for the thiol-capped ZnO nanoparticles sample

*"u" unified atomic mass unit, dated "amu"

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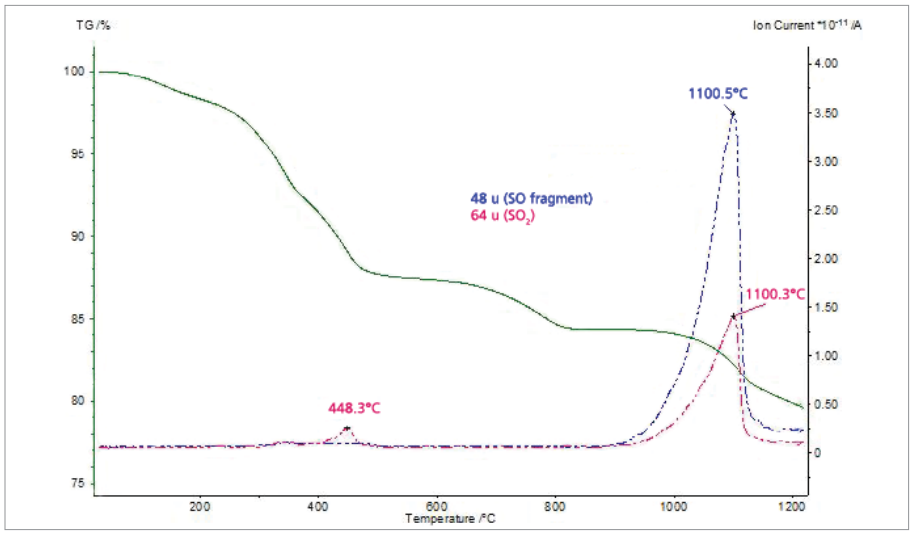
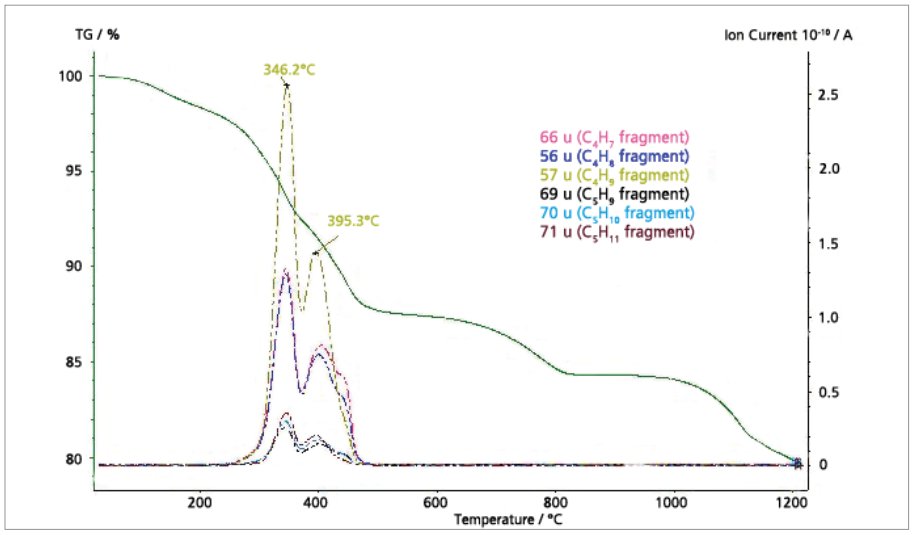
The MS ion-current curves for SO_2 (64; 48 amu) plotted in Figure 5 along with the TGA curve clearly show that small amounts of SO_2 evolve at elevated temperatures in correspondence with the fifth mass loss step in the TGA curve. Finally, the MS ion-current curves for many different organic fragments plotted in Figure 6 show that these species evolve as two peaks in very good agreement with the FT-IR results.

Conclusion

A simultaneous TGA/DSC (STA) instrument coupled to MS and FT-IR spectrometers is a very powerful combination for sample characterization because it supplies data for the mass change (TGA), transformation temperatures and energetics (DSC) and evolved gas analysis (MS, FT-IR) in a single measurement. All the data analysis is carried out with the NETZSCH *Proteus*® software. Simultaneous use of MS and FT-IR for evolved gas analysis is very beneficial because the FT-IR can quickly identify functional groups based on their characteristic bands, but on the other hand, the MS has higher sensitivity and it can also detect homonuclear diatomic molecules (H_2, O_2, N_2) and atomic gases (He, Ne, Ar, etc.) which are not detectable by FT-IR.



5 MS ion-current curves for mass numbers 48 and 64 u and TGA curve for the thiol-capped ZnO nanoparticles sample



6 MS ion-current curves for mass number 55; 56; 57; 69; 70 and 71 u and TGA curve for the thiol-capped ZnO nanoparticles sample

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