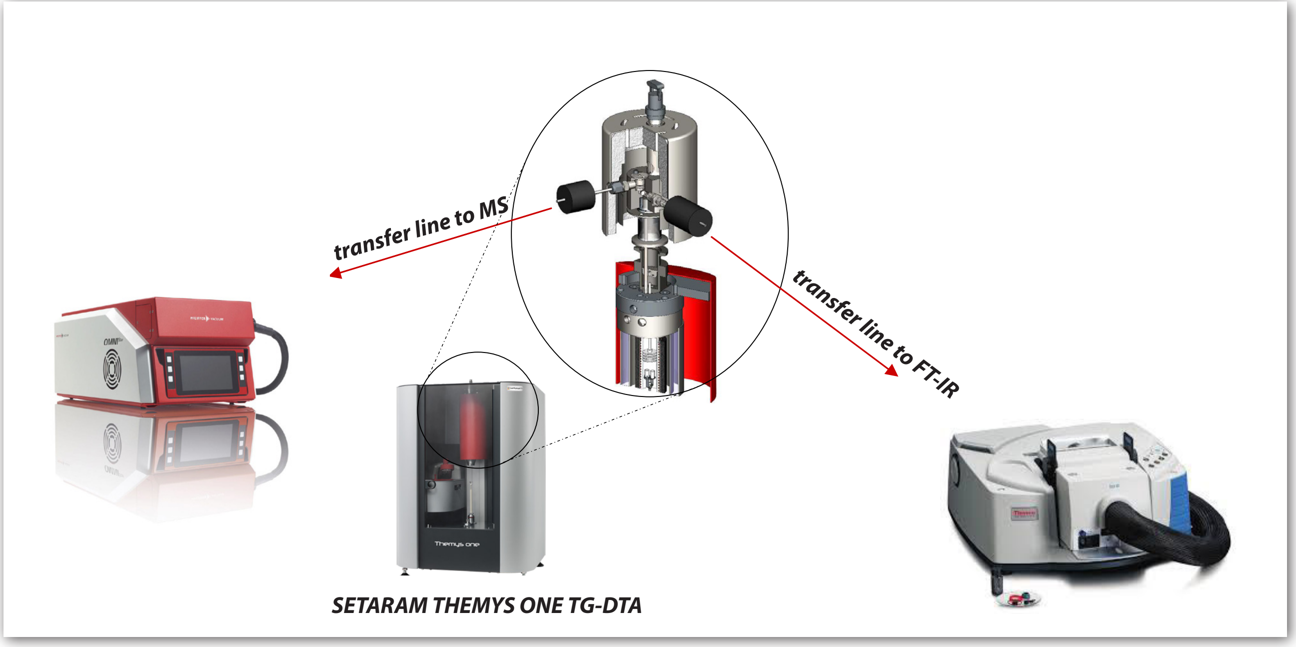
Desorption of a zeolite studied by simultaneous thermal analysis techniques

INTRODUCTION

In recent years, hyphenated thermogravimetry and gas analysis techniques have experienced a wide development. In such experimental set-ups, the gases evolved during decomposition can be transferred on-line or off-line to a gas analyzer. Usual gas analyzers are Fourrier transformed infra red spectrometers (FT-IR), gas chromatographs (GC), and mass spectrometers (MS) - probably the most employed.
Two major problems arise when interpreting TG-MS data: firstly, multiple fragmentation peaks can lead to a complex spectrum, especially when a lot of organic species are emitted by the decomposing substances at the same time. Secondly, species of different nature and / or conformation but same molecular weight can lead to similar peaks and thus confuse the data interpretation.
This can be addressed by multiple simultaneous coupling as described in the present application note.



EXPERIMENT

A SETARAM Instrumentation THEMYS ONE TG-DTA system was coupled to both Pfeiffer Omnistar mass and Thermo FT-IR spectromers. The gas transfer system as shown on figure 1 allows for simultaneous signal acquisition of the three techniques. It is heated up to 300°C, with no cold part (avoids gas condensations), and allows all the gases to be transferred in the gas analyzers.

The analyzed sample is a proprietary formulated zeolite, whose carbon dioxide production during heat treatment needs to be carefully followed up.

The sample was heated between ambient and 1000°C at 5°C/min under a flow of nitrogen at 40mL/min. The MS was used in the multiple ion detection mode, with the following targeted masses & molecules :
- Carbon dioxide : CO_2+, CO+, C+, O+: amu 44, 28, 16 and 12
- Nitrogen (Purge gas) : N_2+, N+: amu 28 and 14
- Water : H_2O+, OH+, O+: amu 18, 17 and 16
- Ammonia : NH_3+, NH_2+, NH+, N+, H+: amu 17, 16, (15) and 14
- Nitrogen dioxide : NO_2+, NO+, N+, O+: amu 46, 30, 16 and 14
- Nitrous oxide :N_2O+, NO+, N_2+, N+, O+: amu 44, 30, 28, 16 and 14

RESULTS AND CONCLUSION

Figure 2 exhibits a three (TG) to four (DTG) steps mass loss of the zeolithe due to gas desorption. Peak Separation as proposed by Calisto thermal data analysis software allows to separate actually five thermal events at 159°C, 306°C, 306°C, 462°C, 648°C and 159°C (see Figure 3).

As mentionned on figure 4 and figure 5, mass spectrometry signals, combined with both full FT-IR spectra and intensity variation follow-up of characteristic wavelengths, allowed to associate the second and third events respectively to nitrous oxide and ammonia evolution.

The presented work allowed show how multiple coupling techniques could help to understand the mechanism of desorption of a zeolite, and more particularly how FTIR data could show that, what was firstly supposed to be CO_2 production, turned out to be nitrous
oxide production.

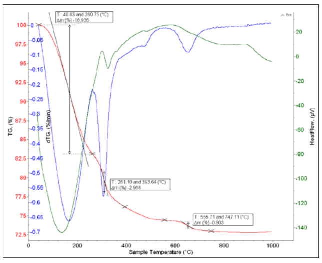


***Fig 2 –** Weight loss (TG), weight loss rate (DTG), and DTA signals for the zeolithe desorption*

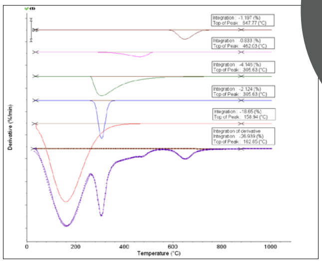


***Fig 3 –** Asymmetric Gaussian deconvolution of the weight loss rate (DTG) signal*

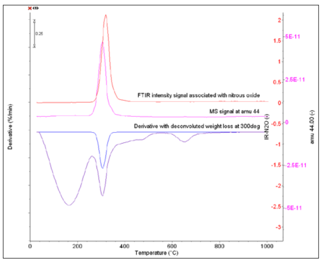


***Fig 4 – Evolution of N_2O –** The intensity variation of the absorption wavelength (2200cm-1) linked with nitrous oxide vibration confirms that the uma 44 detected by MS is not linked with CO_2 evolution.*

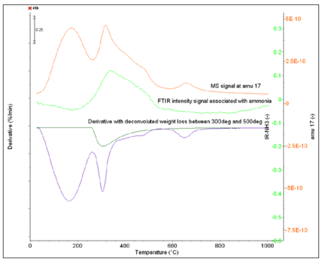
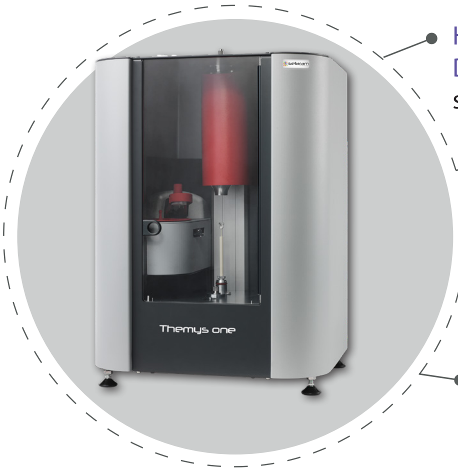


***Fig 5 – Evolution of NH_3 –** The intensity variation of the absorption wavelength linked with ammonia vibration indicates that the uma 17 detected by MS is firstly linked with water evolution, then to ammonia evolution (starts around 200°C).*

INSTRUMENT

THEMYS ONE



- HIGH SENSITIVITY BALANCE FOR THE DETECTION OF SMALL MASS VARIATIONS specifically designed for TGA analysis.
- CONVENIENCE OF ONE FURNACE to reach temperatures as high as ***1150°C or 1600°C***.
- PLUG AND PLAY INTERCHANGEABLE RODS to perform TGA only, TG-DSC, TG-DTA, and 3D high sensitivity/Cp measurements.
- EXTERNAL COUPLING CAPABILITY including evolved gas analysers