

SUPERSONIC MOLECULAR BEAMS -TPD-MS- A NOVEL HIGH SENSITIVE DEVICE FOR SURFACE CHARACTERIZATION

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Introduction

Temperature-programmed desorption mass spectrometry (TPD-MS) at atmospheric pressure is a sensitive tool for studying high surface area adsorbents [1].

In a typical TPD-MS apparatus the essential problem is the coupling between the atmospheric pressure TPD to the high vacuum required for the MS. Several interface constructions have been reported, including capillary, double orifice and jet separator. TPD-MS systems have a very poor time response and they cannot handle, with substantial accuracy, desorption products that may condense, such as water [2].

A supersonic molecular beam (SMB) is formed by expanding an inert carrier gas at above atmospheric pressure to vacuum through a nozzle with an orifice of about 80-120 μ m in diameter. This gas expansion creates a supersonic jet in which the molecular random thermal energy is converted into directional mass flow. The central portion of the free jet is sampled with a skimmer. SMB is characterized with the highest possible molecular flow in vacuum by a unidirectional motion, intramolecular cooling and heavy species focusing. An inherent feature of SMB is atmospheric pressure introduction [3].

In this paper we describe a new TPD-MS approach which contains a SMB that bridge between the atmospheric pressure sample chamber and the quadrupole mass spectrometer (QMS).

Experimental

The experimental setup is shown in fig.1. It is based on differentially pumped two vacuum chambers. The inert carrier gas is introduced via a needle valve at a flow rate of about 20-50 ml/min at a pressure of \approx 800 torr. The sample holder is composed of 1/4" o.d. quartz or silicosteel tubes (1). The tube is sealed by graphite ferrules through a 1/8" silicosteel tee (14) to a megabore capillary column. The sample can be heated up to 1100°C. Liquids and gasses can be injected, for calibration, through a septum on a 1/8" silicosteel tee (14). The nozzle (3) and the capillary

column (2) can be separately heated and temperature controlled (12). The supersonic beam nozzle is a ceramic nozzle which has an aperture of 80 μ m diameter. The carrier gas with the desorbed sample molecules expand through the nozzle (3) into the first chamber.

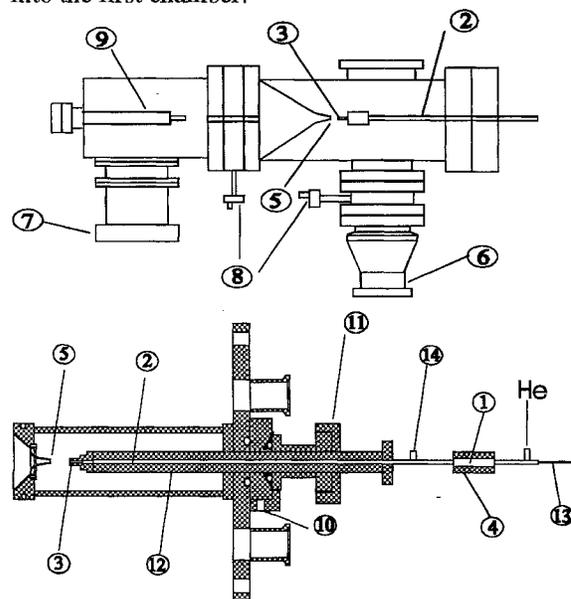


Fig.1 The TPD-MS-SMB apparatus. (1) the sample holder, (2) capillary column, (3) supersonic nozzle, (4) sample heating oven, (5) skimmer, (6), (7) vacuum pumps, (8) gate valve, (9) QMS (10,11) nozzle alignment screws, (12) heating cables (13) thermocouple (14) injection port.

The emerging supersonic free jet is skimmed with a 1.1 mm in diameter hole skimmer and enters to the second vacuum chamber. The supersonic beam enters axially to the QMS (9) ion source fly through without collisions with the walls.

Results and discussion

The system performance was checked with the decomposition of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. Fig. 2 shows

typical TPD spectrum of water molecules from 510 μg $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

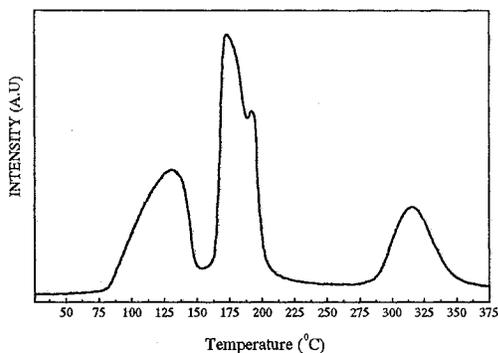
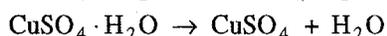
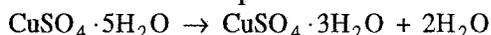


Fig. 2 TPD-MS spectrum of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. Heating rate $60^\circ/\text{min}$. Sample weight $510\mu\text{g}$. $M/e = 18$

The three reaction steps:



are fully resolved even with the high heating rate. The obtained areas under the three peaks in fig. 2 are 2:2:1 as expected.

The signal to two noise ratio in this spectrum is about 500. The second peak width, which correspond to $74\mu\text{g}$ H_2O is about 30 seconds. Thus, the calculated detection limit for water is 5 ng/sec. The noise of the water signal in the quadrupole mass spectrometer is due to high water background from the carrier gas and long transfer line. Using purer gas or appropriate water filters can reduce the water background and further improve the detection limit for water.

By tuning the mass spectrometer to $m/e=20$, the natural abundance of H_2O^{18} in the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ can be measured. A similar spectrum as in fig 2 but with 500 times lower signal due to 0.2% O^{18} natural abundance is obtained. The calculated detection limit for H_2O^{18} from this spectrum is about 400 pg/sec.

Fig 3 shows the desorption of water from CMSF sample. It can be seen that up to 350°C there are 3 water sites on the CMFS. The first site in which the water molecules are loosely bound contain most of the water. The amount of water desorbed from the other two sites are two orders of magnitude lower. A TPD spectra of a new as received sample, which was evacuated in the system at room temperature for 16 hours to less than 10^{-1} Torr, shows (Fig.5b) that most of the water content in the large first site were

removed while the other 2 sites remains as is.

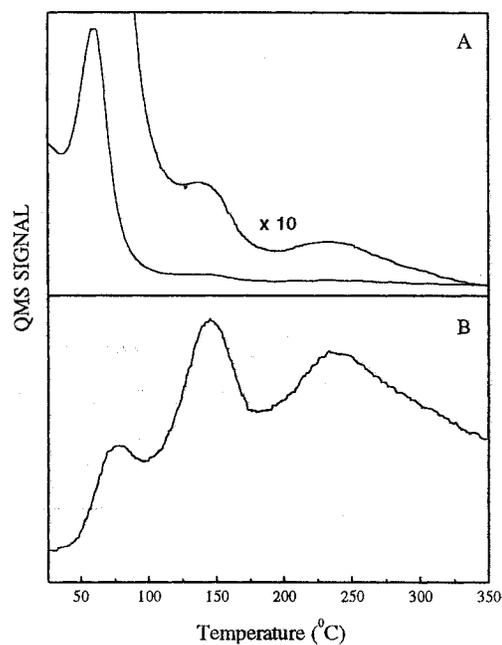


Fig. 3 TPD desorption of H_2O from CMSF . A- as receive, B- after evacuation for 16 hours at $p < 0.1$ Torr. Heating rate was $30^\circ/\text{min}$.

In other words evacuation at ambient temperature is not sufficient to overcome the activation energy for the desorption of water from all sites.

Conclusions

The TPD-MS- SMB inlet port have few advantages:

- High adsorption sensitivity of 5 ng/sec for H_2O^{16} and 400 pg/sec for H_2O^{18} .
- Monitoring simultaneous adsorption of different molecules and adsorption of the same molecule on different sites of an adsorbent.
- Fast quantitative adsorption measurements
- Very short time constant that enable to distinguish between neighboring sites.

These advantages turn the novel TPD-MS-SMB system to be very unique for quantitative measurements of both equilibrium and sorption kinetics of minute amount adsorbed.

References

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