A TPD-MS Study of Novel Hydrogen Storage Materials

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Abstract

The desire to decrease carbon emissions is placing increased emphasis on the need to find new energy sources. Hydrogen is one such source with considerable potential as it can be easily produced from renewable sources unlike hydrocarbons such as petroleum. It is also non polluting, producing only water as a by-product of combustion. If, however, hydrogen is to be used as a replacement fuel an infrastructure for its safe and cost effective transport, storage and distribution must exist.

Here we present a study of novel hydrogen storage materials. The study used Temperature Programmed Techniques to study the hydrogen desorption profiles from a range of materials. As it was also important to quantify the amount of H_2 desorbing from the sample, results showing how the system was reliably calibrated are also presented.

Background

In order to study the hydrogen storage properties of some new materials a system was required that could be reliably calibrated so that reproducible data could be collected.

It was also important that there was good solid/gas phase interaction to ensure that the samples were properly activated.

The hydrogen storage properties were to be determined using temperature programmed techniques such as temperature programmed desorption (TPD). The system selected to perform these studies on was the Hiden CATLAB integrated microreactor-mass spectrometer system.
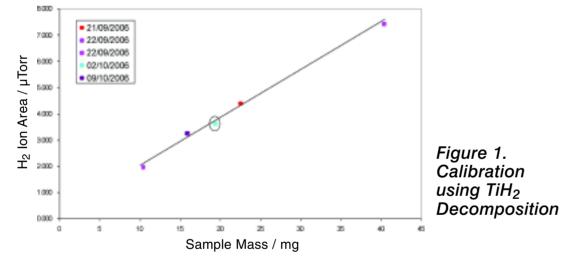
CATLAB Microreactor - Mass Spectrometer

The Hiden CATLAB is a microreactor system specifically for use with a mass spectrometer. The reactor module features a fast response furnace (T_{max} 1000˚C) and can be configured for manual or automatic operation. The MS module (*QIC*-20) includes a 200 amu MS while the *QIC* inlet provides ultra-fast, high response sampling of desorbed or evolved species. The *QIC* – 20 is ideal for H_2 desorption measurements due to the dual rotary pump design of the inlet. Here, the bypass line of the in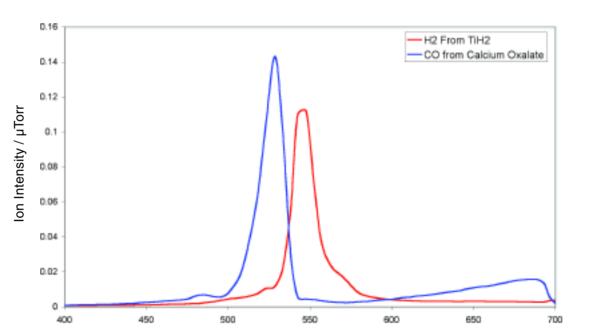let is pumped independently by one rotary pump, therefore this prevents light gases such as H_2 and He permeating through the turbo pump and into the main mass spectrometer chamber affecting results.
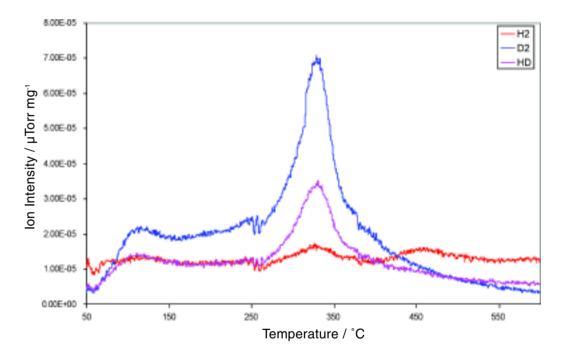
Calibration of CATLAB system

- The TPD-MS system required initial calibration for H_2 to enable quantitative H_2 emission data to be collected.
- This was achieved by the thermal decomposition of TiH_2, which releases 40.04% H_2 by weight on heating.
- Different quantities of TiH_2 were introduced into the Catlab system to give the following calibration curve.
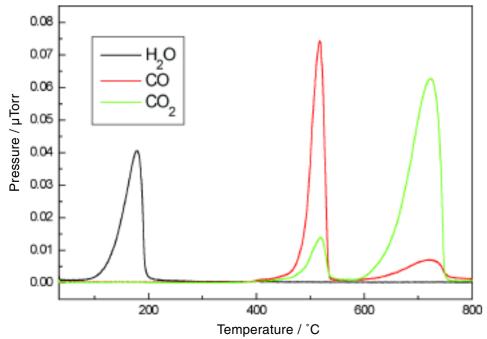

Figure 1. Calibration using TiH_2 Decomposition

Effect of Simultaneous Emission of other ions

- To ensure that the measured H_2 was not influenced by other species being emitted at the same time, TiH_2 was mixed with Calcium oxalate.
- The CO emission from calcium oxalate occurs at a similar temperature to that of H_2 from TiH_2, ca. 520˚C
- No effect on the H_2 signal was found - the data fit is shown on the calibration curve (data point is circled in Figure 1)

Figure 2. Calcium Oxalate Decomposition

Figure 3. Simultaneous CO and H_2 Desorption

H_2 Desorption From Hydrogen Storage Materials

The results from the calibration experiments show the system to be sensitive and reproducible allowing confidence in the H_2 desorption results generated from the hydrogen storage materials developed during this project. Below are two H_2 desorption profiles from typical materials.
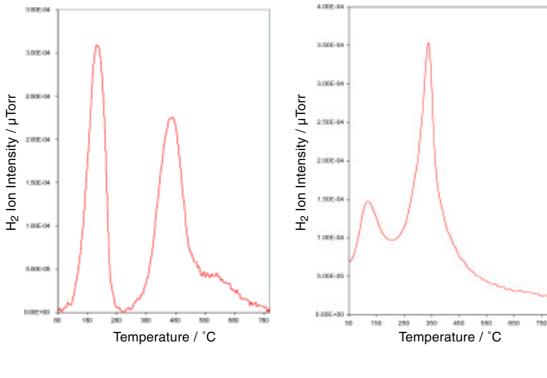

Figure 4. H_2 Desorption Profile From Sample 1

Figure 5. H_2 Desorption Profile From Sample 2

$H_2/D_2/HD$ Desorption

- The effects of D_2 on the samples was also investigated.
- This would also indicate the efficiency of gas-solid mixing in the reactor as D_2/HD are not naturally present in the materials.

Figure 6. H_2 / D_2 and HD Desorpion Profile

Conclusion

These analyses confirm that the Hiden CATLAB TPD-MS system is able to distinguish between low levels of species of 1 amu difference. This results is important as it showed that there was interaction between the D_2 and the samples in the reactor system.

In summary, the Hiden CATLAB microreactor-mass spectrometer system shows excellent reproducibility, sensitivity and linearity in hydrogen desorption measurements and is the ideal choice of system for determining the Hydrogen storage properties of a range of materials.

Acknowledgements

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