APPLICATIONS OF HIGH PRESSURE THERMOGRAVIMETRY IN CARBON RESEARCH

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Introduction

Thermogravimetric (TG) instruments measure and record mass change as a function of temperature and/or time. These instruments provide a variety of information including thermal and oxidative stability of materials, compositional analysis, and kinetics of degradation. They typically consist of a wire-wound or infrared furnace capable of reaching temperatures of 1000°C or more, mated to a highly sensitive thermobalance from which the sample to be studied is suspended. High pressure thermogravimetric instruments are specially designed to incorporate the furnace inside a pressure vessel. These instruments are ideal for studying sorption processes and general gas/solid or vapor/solid reactions that occur under conditions of high pressure or vacuum, and high temperature. A great variety of work has been done in the field of carbon sorption research using these instruments. This paper will review application examples on the storage of hydrogen, the sequestration of carbon dioxide, and the gasification of carbon-rich materials.

Experimental

The high pressure TGAs used in the experiments described in this paper were all manufactured by TA Instruments. The TGA-HP 150 and 150s are both constructed around Rubotherm magnetic balances that are isolated from the reaction chamber, making them ideal to work at high pressures (up to 150 bar) and with corrosive gases. The 150s also has an integrated steam generator. Sample pans were either quartz or alumina.

Results and Discussion

Gasification is a process whereby carbon is reacted with steam at high temperatures and pressures to produce a combination of carbon monoxide (CO) and hydrogen (H_2)[1]. This product is referred to as Syngas. There is wide interest in gasification because it produces lower quantities of air pollutants and the syngas burns cleaner than the original material[2]. Figure 1 shows the results obtained by running a sample of BPL® carbon in a TA Instruments HP150s high pressure TGA. The HP150s, with its integrated steam generator, is specifically designed for gasification investigations. In this experiment the sample temperature was raised to 800° C under a constant pressure of 15 bars. A purge gas combination of 80% nitrogen and 20% steam was the pressurizing gas. The data indicate that the mass is reasonably stable for about 120 minutes and then there is a sharp decrease. Figure 2 overlays the results from mass spectrometry (MS) data collected simultaneously with the TGA data. The MS results show that at the 120 minute mark, there is a noticeable increase in hydrogen production, thus confirming that the weight loss observed is due to the gasification process. It is also noted that there is an increase in carbon dioxide production. This is due to a second reaction between the CO and the steam that also takes place during gasification which is referred to as the water-gas shift reaction. This reaction produces CO_2 and additional H_2.

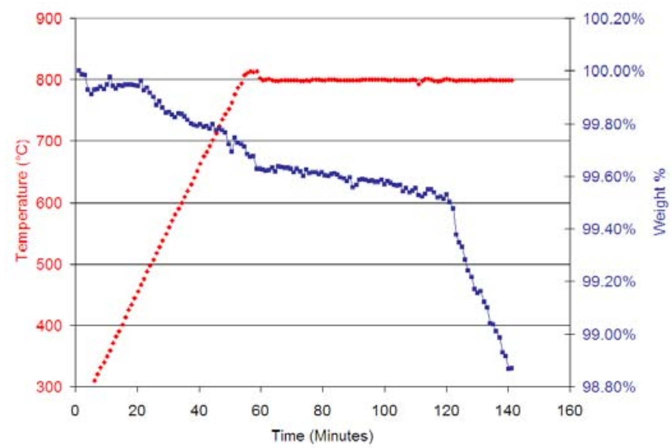

Fig. 1 Gasification of a BPL activated carbon sample at 800°C and 15 bar pressure.

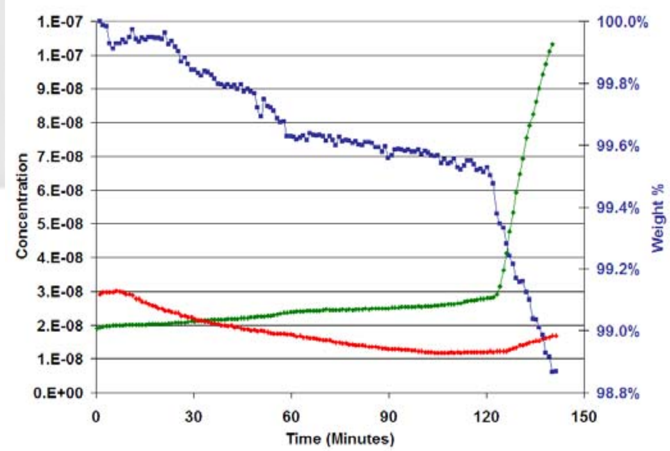

Fig. 2 Addition of mass spectrometer data indicating the onset of the gasification process at 120 minutes, by the production of hydrogen and carbon dioxide gas.

The desire to use hydrogen as an energy source has increased dramatically in the past decade. One of the main issues related to its use is its storage. Storing enough hydrogen onboard a vehicle to obtain a driving range of 300 miles is a significant challenge[3]. At this time, there does not exist a material that can store significant amounts of hydrogen, easily release it for use, and then be used for storage again, all in a timely manner. Therefore a tremendous amount of research is occurring in the study of novel materials for the storage of hydrogen. Many of these materials are studied by high pressure TGA since the storage capacity of hydrogen can be increased with pressure. Thus the adsorption capabilities of the materials in storing hydrogen are studied under various pressure and temperature conditions. When carbon nanotubes were first discovered, it was highly anticipated that these materials would store copious amounts of hydrogen[4]. This has turned out not to be true[5]. Figure 3 illustrates an experiment in which the storage capacity of carbon nanotubes was studied at room temperature from atmospheric pressure up to 80 bars in a TGA-HP150. The data show a mass change due to the uptake of hydrogen of less than 0.5%. Note how the gravimetric adsorption is quantified over a wide pressure range, from sub-atmospheric to nearly 80 bars.

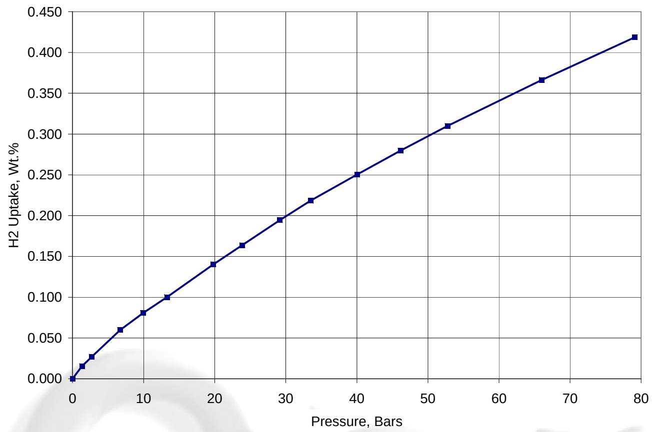

Fig. 3 TGA-HP data showing the quantitative adsorption of hydrogen gas onto an activated carbon matrix.

Finally, the desire to capture greenhouse gases, termed sequestration, has also prompted the investigation of many new and novel materials including nanocarbon[6]. Figure 4 shows the adsorption and desorption of carbon dioxide onto nanocarbon material at two different temperatures: 35 and 200°C. The data is collected from vacuum levels to over 11000 torr (~15 bar) and emphasizes that these instruments work not only at high pressure, but high vacuum too. As would be expected, the ability of the carbon to adsorb decreases at higher temperature due to the increase in the kinetic energy of the gas. The fact that the desorption curves overlay exactly the adsorption curves indicate that the gas is easily removed from the carbon for more permanent storage in a different manner.

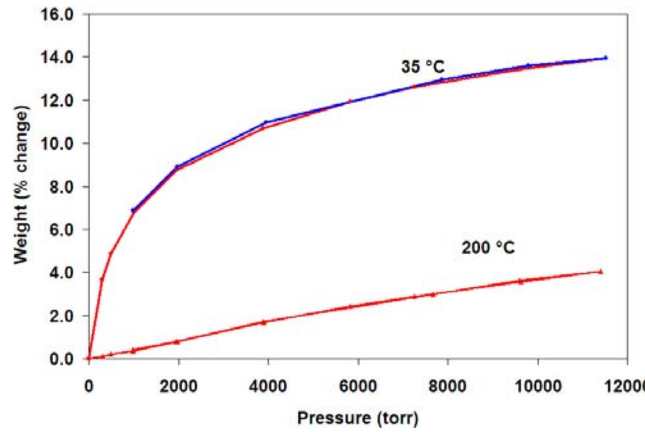

Fig. 4 Adsorption / desorption plots at 35 and 200°C of carbon dioxide on carbon nanotubes.

Conclusions

High pressure thermogravimetric instruments have found significant application in the study of carbon materials. From the study of gasification to the adsorption of hydrogen and carbon dioxide, these instruments have provided valuable data.

References

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