Use of the DSC and TG-DSC techniques for the investigations of gas interaction on zeolites

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INTRODUCTION

The investigation of gas adsorption on zeolites requires a very good interaction between the reactive gas and the powder. The Calvet-type DSC offers the main advantage to work with an open tube detection. This configuration allows the adaptation of different types of experimental crucibles, especially with the possibility of introduction of various types of gas under normal or high pressure. The silica tube reactor is one option for the applications on zeolites. It makes possible the simulation of the use of a plug-flow fixed bed reactor in heterogeneous catalysis. The gas can be introduced with a continuous flow, but more generally a gas injection loop is used to produce pulses of known volume of reactive gas. As a silica tube is used, any type of reactive gas, even corrosive, can be used.

THE SILICA TUBE REACTOR

The silica tube (Figure 1) is introduced in the Calvet type DSC, set in the vertical position. A sintered silica glass frit is located in the middle of the tube to receive the powdered sample in order to be surrounded by the calorimetric detector. Tight connections are adjusted at both ends of the tubes for the gas inlet and outlet. With such an experimental design, the reactive gas goes through the powdered sample.
The gas can be introduced with a continuous flow, but more generally a gas injection loop is used to produce pulses of known volume of reactive gas. As a silica tube is used, any type of reactive gas, even corrosive, can be used. The connection with a gas analyzer (GC, MS, FTIR) is very easy to perform

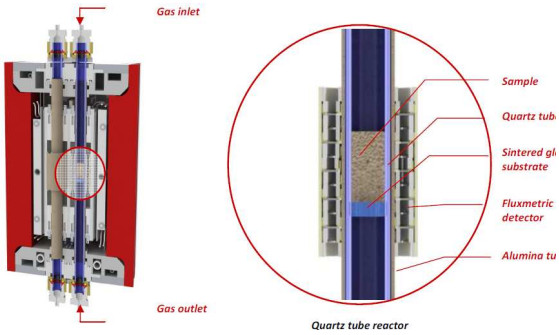

Figure 1 – Calvet type DSC cross section in the vertical mode with the quartz tube reactor

APPLICATIONS OF THE QUARTZ TUBE REACTOR

Such a quartz tube reactor has been used for different applications in the field of solid adsorbents with different EGA combinations (1,2,3,4,5)
An example is given with the interaction of CO on a Cu-zeolite (from 5). CO is introduced at 25°C on the zeolite via the pulse mode (injection loop of 0.2 ml) (figure 2).The calorimeter is connected to a mass spectrometer. If the MS does not detect any CO amu signal, it is a clear indication that the injected CO volume is fully adsorbed on the zeolite. In the same way, when a CO amu signal is detected, the amount of CO that has effectively adsorbed on the zeolite is calculated. From these DSC and MS data, the variation of the heat of adsorption of CO on the zeolite according to the surface coverage is obtained (Figure 3)

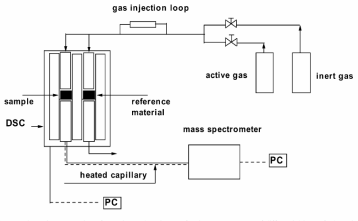

Figure 2 – Schematic representation of the Calvet type DSC with the injection loop and the MS coupling

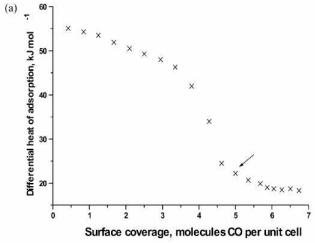

Figure 3 – Differential heats of adsorption of CO on CuY as a function of surface coverage

THE SILICA FINGER REACTOR

For investigations of adsorption/desorption in the static mode, Setaram has developed a silica glass finger, adapted to the Sensys DSC to work under normal pressure or vacuum. This vessel is also designed for the coupling between the Sensys DSC and a volumetric equipment in order to get a simultaneous measurement of the adsorbed volume and the corresponding heat of adsorption. A metallic pressure version (200 bar) is also available for investigations up to 800°C.

Figure 4 – Silica glass finger and the adaptation to Sensys DSC

THE TG-DSC INVESTIGATION

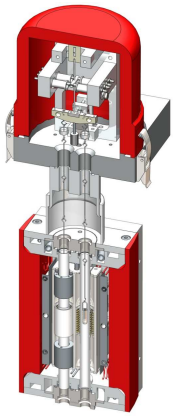

Figure 5 – Sensys TG-DSC cross-section

The Sensys TG-DSC uses the DSC detector in the vertical position. On top of the DSC, is adjusted a symmetrical balance (Figure 5). The crucibles containing the sample and the inert material are hung on each side of the balance and introduced in the calorimetric zone of the DSC without touching the walls.
This technique is very powerful for the investigation of gas interaction on solid or liquid sample, such as adsorption, adsorption, desorption, catalytic reaction under various types of gas (inert, oxidative, reducing, corrosive, humid).
An example is given with the adsorption/desorption of NH_3 on a zeolite at 120°C. The TG and DSC curves provide the amount of gas adsorbed by the zeolite and the corresponding enthalpy. The desorption process under helium shows that all NH_3 is not removed from the zeolite at this temperature (Figure 6).

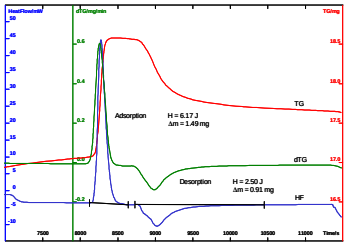

Figure 6 – Adsorption and desorption of NH_3 on a zeolite at 120°C (silica crucible)

CONCLUSION

The adaptation of different silica reactors on the Calvet DSC opens a large range of applications for zeolites and solid adsorbents with various types of gas in the dry state but also in the humid state. It gives also the possibility to follow a heterogeneous catalytic reaction with on-line analysis of the products that are obtained from the reaction. The TG-DSC combination is another option to associate gravimetric and enthalpic data.

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