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SCTA AND ADSORBENTS

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Abstract

Sample controlled thermal analysis (SCTA) can be used in several manners with respect to adsorbents. Almost 70% of adsorbent synthesis procedures involve a thermal step that can be adapted to a sample controlled method. In this respect, SCTA has been used for the preparation of activated alumina, calcination of zeolites and activation of carbons. The thermodesorption of adsorbed molecules can also be carried out using a sample controlled method. Here, both the surface area and pore volume of adsorbents can be assessed. Finally, SCTA can be highly beneficial in the thermal pretreatment of adsorbents prior to adsorption.

Keywords: adsorbents, SCTA, thermodesorption

Introduction

Quite often, the problems raised by the thermal preparation of materials become more critical with the preparation of adsorbents, whose texture and surface properties highly depend on this thermal step. Indeed, sample controlled thermal analysis (SCTA) can be used in several manners with respect to adsorbents. The following paragraphs show the use of SCTA in adsorbent preparation, characterisation and outgassing.

SCTA and adsorbent preparation or activation

A thermal step is indeed used in the preparation of almost 70% of adsorbent powders. This thermal step is critical with respect to adsorbent activity and above all to structure degradation. Sample controlled methods have already aided the optimisation of industrial adsorbent preparations however to the authors' knowledge SCTA has not been directly used to prepare adsorbents. Nevertheless, the direct use of SCTA is interesting from several aspects. The ability to apply a method in which it is possible to limit at will the pressure and temperature gradients within the adsorbent grains proffers not only sample homogeneity, but also helps to avoid secondary reactions and structural degradation.

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SCTA is more often used as a tool to understand the modifications that occur during heat treatment. In such cases, it is possible to provide information to model furnace processes in taking into account, for example, various partial pressures within the furnace.

Several studies show the possibilities to apply SCTA to tailor make adsorbents with specific pore sizes and surface properties. Of these it is interesting to note the use of SCTA for the preparation of activated alumina [1], zeolite [2, 3] and MCM-41 [4, 5] calcination as well as in carbon activation [6, 7].

SCTA and adsorbent characterisation

The control that can be attained using SCTA methods can be used for the characterisation of adsorbents. Whilst the thermodesorption of chemisorbed species using SCTA is used to characterise catalysts, it is also possible to thermodesorb physisorbed molecules. In such cases, one can glean information about surface area and pore size.

Indeed if one preadsorbs at a partial pressure in which a monolayer is adsorbed, it is possible to desorb under SCTA conditions allowing to fix the desorption pressure and to determine the amount desorbed. This is of interest when the surface area under investigation is low. This can be the case where a thin, porous oxide layer is formed during the corrosion of metals. In such cases, the resolution of 2 cm^2 that can be attained using sample controlled thermodesorption is of great interest [8].

In other cases, if one chooses to preadorb at relatively high partial pressures (e.g. $p/p°$=0.95), it is possible to obtain information on the desorption of the preadsorbed species from the pores. It is thus possible to relate the desorption temperature to the pore size via the Kelvin equation [8], instead of relating the pore size to the desorption pressure, as is usually done in the isothermal Barrett, Joyner and Halenda method.

SCTA and adsorbent outgassing

The aim of adsorbent outgassing is to prepare a well-defined, reproducible intermediate state before any adsorption experiment; this state is not that of a perfectly clean surface, but it must be meaningful with respect to the application envisaged for the adsorbent. Thus the elimination of species adsorbed during storage (H_2O, CO_2) should be carried out without any appreciable modifications of the nature of the surface (ageing, sintering or modification of surface functional groups). One is thus left with a sample which will withstand the initial vacuum for adsorption equipment without further modifications. These aims can be easily achieved using SCTA.

One of the initial uses of SCTA in the 1960's was the preparation of samples prior to adsorption experiments. Indeed a conventional outgassing procedure could lead to several problems. In addition to the problems of sample reproducibility and structural degradation, the problem of sample 'bumping' or sputtering had to be overcome. Indeed, the gas flow that can be created during the loss of physisorbed species, is enough to induce the evacuation of the powder itself. Thus the possibility to control the gas flow rate generated by the sample (as automatically done by controlled rate thermal analysis, CRTA) during this pretreatment is advantageous.

Conclusions

The present communication has shown the interest of SCTA, especially in the form of CRTA in thermal treatments involving adsorbents. We can even consider this approach as the most suited, today, for the thermal preparation of adsorbents to be used as reference materials.

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