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ADSORPTION CALORIMETRY : AN OVERVIEW OF ITS PRACTICE AND APPLICATIONS

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ABSTRACT :

Chemisorptions and catalyzed reactions, like any chemical reaction, are associated with changes of enthalpy and can therefore be studied by means of calorimeters. Many calorimeters, operating on different principles, have indeed been used for this purpose, as it will be attempted to show in a brief review (ref. 1). In our opinion, however, heat-flow calorimeters are particularly convenient for these studies (ref. 2). They offer a number of advantages which will be illustrated by means of selected examples.

Heat-flow calorimetry, preferably in association with other physico-chemical or physical techniques, may be used to describe the surface properties of a solid. It will be shown that, for instance, differential heats of adsorption of ammonia may serve to quantitatively describe surface acidity in small-pore zeolite, e.g. H-ZSM5, and thus to complement the information provided by i.r. spectroscopy (ref. 3).

Information on the bonds energy, deduced from calorimetric data, is needed to achieve a theoretical description of the adsorbate-adsorbent bond. It will be shown, for instance, that, in the case of the adsorption of hydrogen on nickel-copper alloys, a correlation between heats of adsorption and surface magnetic properties can be demonstrated. The correlation indicates that the energy of the bond between adsorbed hydrogen and nickel atoms is regulated by the electron density of states, near the Fermi level, for the metal surface (ref. 4).

Adsorption of one, at least, of the reagents is a necessary step in all heterogeneously catalyzed reactions. Calorimetric investigations of the adsorptions of the pure reagents on the catalysts may therefore provide some information on the catalytic reaction itself. It appears, for instance, that there exists an inverse linear correlation between the activity of silver catalysts for the epoxidation of ethylene and the bonding energy of oxygen at their surface (ref. 5).

The change of enthalpy associated with the reaction is, of course, not modified by the presence of the catalyst. Therefore, thermochemical cycles, based on experimentally determined heats of adsorption of interaction of reagents, introduced successively at the catalyst surface, may give indication on the most proba-

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ble reaction mechanism, in the case of "simple" catalytic reactions. The recorded heat of reaction, however, may differ from the expected one when secondary reactions, eventually leading to the catalyst activation or deactivation, take place. The calorimetric study of the catalytic reaction, when a steady state of activity is not yet established, may therefore give information on the catalysts evolution or even on the reaction mechanism. These applications of calorimetry will be illustrated by various studies of the combustion of carbon monoxide on divided nickel oxide catalysts at 300 and 473 K (ref. 6).

Heat-flow calorimeters are also used for kinetic studies. Several examples will be presented to show how reaction orders, kinetic laws and, in favourable cases, activity spectra of the catalysts surface can be determined (ref. 1). In the case of fast processes, deconvolution of the calorimetric data must be achieved (ref. 7).

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