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THERMOKINETIC STUDIES IN ADSORPTION AND HETEROGENEOUS CATALYSIS

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ABSTRACT

One feature common to many thermal methods is that they allow a continuous record of the evolution of the system under study, as a function of time or temperature. Thus, not only is information collected on the equilibrium states of the system but also on the transitions between equilibrium states. Thermal methods can therefore be used for the kinetic study of chemical or physical processes (ref.1). Thermokinetic techniques are commonly used in some fields, biology for instance. They are still little known in heterogeneous catalysis although, in this field, they sometimes surpass, with regard to the convenience or the quality of the information, more common techniques, as it will be attempted to show by means of selected examples (ref.2).

Thermokinetic measurements are based upon two assumptions :

i) the change of evolved heat with time is proportional to the reaction rate. The proportionality coefficient is the reaction change of enthalpy, in the case of a simple process. In all cases where selectivity changes or where the catalyst is activated or deactivated during the reaction, the coefficient does not remain constant.

ii) it is assumed that the amount of heat detected by the sensing element of the instrument is, at any time, a measure of the total amount of heat generated, at the same time, by the reaction under study. Because of thermal lags in the heat-measuring device, the second assumption is generally not valid. "Reconstruction" of the data is often necessary.

When the reaction, taking place into the calorimeter cell, can be maintained at stationary state, e.g. by the continuous introduction of a constant flow of reaction mixture, all problems caused by thermal lags are solved. Simple instruments can then be used in order to test the activity of series of catalysts (catalyst screening) .The difference between the homogeneous and heterogeneous contributions to the rate of a given reaction can be, for instance, detected by means of the calorimeter device proposed by Boldyreva and Roiter (ref.3).

Papadatos and Shelstad (ref.4) have used a differential thermal analyzer (DTA) to test the activity of a series of cobalt-metal oxide catalysts in the complete oxidation of toluene. These methods are faster than more classical ones when no time-consuming product analysis is necessary.

However, for more quantitative studies a more detailed control of heat exchange between the catalyst sample, the calorimeter heat-sink, gases entering and leaving the cell is required : DTA instruments should then be replaced by calorimeters, preferably of the heat-conduction type (ref.2), and by differential scanning calorimeters (DSC). The advantages and limitations of DSC in catalysis investigations may be, for instance, illustrated by a study of the influence of carbon deposition on the methanation rate over nickel catalysts published by Beecroft, Miller and Ross (ref.5).

Specialized calorimeters have been constructed to measure the rate of catalytic reactions. Firth et al (ref.6) have described for instance, a calorimetric system which consists of a small platinum thermometer embedded in a bead of alumina upon which the catalyst is deposited. When the calorimetric bead, placed in a thermostated glass vessel, contacts the reaction mixture, the changes in resistance of the thermometer with time and temperature enable the rate and the activation energy of the catalytic reaction to be measured.

More classical calorimeters can also be used provided that heat and mass transfer limitations through the catalyst, or adsorbent, bed are carefully avoided. The association of a dynamic reactor with a Calvet-type calorimeter has been, for instance, described (ref.7). The method rapidly yields information on kinetic laws, and catalyst activation or deactivation.

When information other than that connected with a stationary regime is required, flow methods must be abandoned and one must then contact the catalyst sample, placed in the calorimeter cell, with successive doses of reactants in order to study their interaction with different fractions of the catalyst surface. Calorimetric curves are then successively recorded, the analysis of which yields kinetic data. In the case of slow phenomena, the calorimetric curves may be used without any reconstruction for a qualitative determination of reaction rates. However, when the rates of different surface processes are to be compared, even in a qualitative manner, an elementary 1st-order analysis of the corresponding calorimetric curves, by means of Tian equation (ref.1), is necessary. This method can be illustrated by the results of a study on the determination of the rate limiting step for the oxidation of carbon monoxide over a nickel-oxide catalyst (ref.8).

The accurate reconstruction of kinetic data requires the use of sophisticated methods. Most of the methods presently developed are based on the hypothesis that the calorimeter, considered as a "black box", behaves as a linear system.

Fourier transforms analysis, state function theory, dynamic optimalization or recursion methods have been used for the thermokinetic data reconstruction as well as RC circuits and electronic or digital inverse filters. Several methods have been jointly tested during an international comparison programme (ref.9). Before making use of any method, the amount of noise in the data, the linearity of the calorimeter response and the quality of the transfer function, used in the deconvolution procedure, should be carefully determined (ref.10).

Sensitive calorimeters together with data-reconstruction techniques are needed when the activity of a small number of active sites at a catalyst surface is to be studied. The distribution of activity on a catalytically active surface, i.e. the study of the "activity spectrum" of a catalyst, therefore requires the use of sophisticated techniques for the data reconstruction. This may be illustrated by a study of the activity spectrum of a nickel oxide catalyst for the decomposition of nitrousoxide (ref.11).

Finally, the removal of instrumental distortion from the thermokinetic data recorded by means of a temperature-scanning calorimeter requires the determination of the instrument transfer function and of its changes in the course of the experiments. It has been shown that pseudo-random binary sequences of thermal pulses, generated by a computer system on-line with the calorimeter, can be conveniently used for this purpose (ref.12).

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