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Review

Adsorption/reaction energetics measured by microcalorimetry and correlated with reactivity on supported catalysts: A review

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ABSTRACT

The formations and transformations of the chemical bonds of reactants and intermediates on catalyst surfaces occur in conjunction with the evolution of heat during catalytic reactions. Measurement of this evolved heat is helpful in terms of understanding the nature of the interactions between the catalyst and the adsorbed species, and provides insights into the reactivity of the catalyst. Although various techniques have previously been applied to assessments of evolved heat, direct measurements using a Tian-Calvet microcalorimeter are currently the most reliable method for this purpose. In this review, we summarize the relationship between the adsorption/reaction energetics determined by microcalorimetry and the reactivities of supported catalysts, and examine the important role of microcalorimetry in understanding catalytic performance from the energetic point of view.

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1. Introduction

During the reactions of molecules over a catalyst, there are significant interactions between these molecules and the catalyst surface. The reactivity of a catalyst is therefore highly dependent on the strength of such interactions. According to the Sabatier principle, the ideal catalyst will bind reaction intermediates with sufficient strength to activate the reactants but not so strongly that desorption of the products is inhibited [1]. Thus, investigations of the binding of reactive molecules with catalyst surfaces can provide important insights into the reactivity of the catalyst.

A heterogeneous catalytic reaction is initiated by the formation of bonds between the reactant and the solid catalyst surface, accompanied by the release of heat. The evolved heat,

defined as adsorption heat, is related to the bonding strength, and therefore to the reactivity of the catalyst. Adsorption heat can be obtained indirectly by methods such as temperature-programmed desorption (TPD) and isothermal adsorption [2]. However, in many cases, adsorbed species will decompose rather than undergo desorption when using these methods. Furthermore, the application of heat during the desorption process can also induce structural changes or even the decomposition of the catalyst before the adsorbed species desorb. In addition, these techniques only provide the isosteric heat of adsorption, which does not give any information regarding the surface energy heterogeneity [3]. These shortcomings therefore limit the applications of such methods to the measurement of adsorption heat.

With the development of commercial calorimeters, the as-

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assessment of adsorption heats using microcalorimeters based on the Tian-Calvet principle has become the most reliable method for this purpose [3–5]. Through the judicious choice of gas phase probe molecules, analogies between the adsorption energetics of these probe molecules and the properties of the active sites on catalysts can be established. As an example, the adsorption energetics of basic compounds such as ammonia and pyridine on zeolites and metal oxides provide a better understanding of the acidic sites on such materials [6,7]. As well, the adsorption heats of CO on metal catalysts can be related to the metal-carbon bond strengths in hydrocarbon reactions [8].

Microcalorimetry has, in fact, been employed for surface science and catalysis studies since the 1930s, and some excellent reviews regarding fine wire and single-crystal model systems [9–11] and analyses of supported catalysts [6,7,12–14] have been published. Nevertheless, an overview of the direct relationship between adsorption/reaction energetics and reactivity on supported catalysts is still lacking. In this review, we firstly introduce the various microcalorimetric techniques used for measurements of adsorption/reaction energetics. Following this, we summarize the applications of microcalorimetry to determining the adsorption/reaction energetics on supported catalysts, and discuss the relationships between reactivity and the quantities and strengths of active sites, the binding strengths of reactants, intermediates and products, and the reaction energetics. Finally, conclusions and future microcalorimetric applications in catalysis research are presented.

2. Instrumentation

2.1. Adsorption microcalorimetry

Adsorption microcalorimetry is the most widely used calorimetric method for the measurement of heats of adsorption on supported catalysts, and various instrumental setups have been reported [15–21]. A schematic diagram showing a typical adsorption microcalorimetry apparatus is shown in Fig. 1. The instrumentation usually consists of a microcalorimeter, based on the Tian-Calvet or heat-flow principle, capable of operating over a wide temperature range. This microcalorimeter is attached, by way of various types of calorimeter cells made from glass or stainless steel, to a volumetric system.

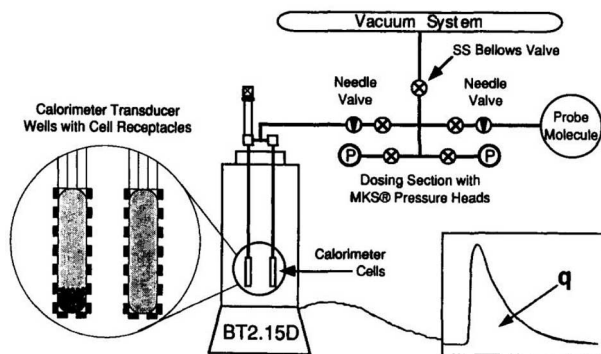


Fig. 1. Schematic diagram of a typical adsorption microcalorimetry apparatus [16].

apparatus includes a high vacuum system, various probe molecule reservoirs, and a calibrated dosing volume with MKS pressure heads. In a microcalorimetric experiment, small doses of gaseous probe molecules are successively introduced onto the surface of the catalyst. The evolved heat and corresponding adsorption amount at each dose are measured by the microcalorimeter and the volumetric system, respectively. The resulting plot of adsorption heat as a function of probe molecule uptake provides information concerning the distribution of interaction strengths over the catalyst surface. In addition, the saturation uptakes obtained from adsorption measurements can be interpreted to obtain data regarding the quantity of accessible surface sites.

The amount of the probe compound that is adsorbed is usually determined based on a volumetric method. For this reason, it is possible to obtain an inaccurate value for the amount adsorbed when reactions of the probe compound occur rather than simple adsorption, leading to artifacts in the differential plot of heat as a function of surface coverage [22]. This possibility limits the accuracy of such measurements in those cases in which reactions do take place, and various alternative microcalorimetric setups have been developed to address this issue [23–27].

2.2. Gas flow-through microcalorimetry

A commercial MICROSCAL FMC gas flow-through microcalorimeter is one alternative approach to measure the energetics of a catalyst, working in the flow mode [23,24]. In this method, the sample is placed in a calorimetric cell that is subsequently purged with high purity He until thermal equilibrium is reached. At this point, the He stream is replaced by a reactant molecule flow and the adsorption/reaction experiment is initiated. The experiment is ended when the heat evolution is observed to plateau, indicating no further adsorption/reaction of the probe molecules. In a final step, desorption is performed by switching the probe flow back to a He purge. The flow rates of the helium and the probe are tightly controlled during the entire process, typically at values in the range of 3–7 cm³/min. A thermal conductivity detector (TCD) can be used to measure the amount of the probe compound that is adsorbed or desorbed, and this method makes it possible to determine both the reaction and adsorption energetics. Nevertheless, flow-through microcalorimetry often allows one to determine only the average heat output of the adsorption process.

2.3. In situ pulse microcalorimetry

Differential adsorption/reaction energetics can also be obtained by *in situ* microcalorimetry, working in the pulse mode [25,26]. In contrast to gas flow-through microcalorimetry, *in situ* pulse microcalorimetry introduces a series of successive small pulses of probe molecules to the catalyst surface until saturation is achieved. This technique employs a Tian-Calvet microcalorimeter coupled with a pulse microreactor system, as shown in Fig. 2. In this apparatus, a specially designed calorimetric cell, in which samples are pretreated *in situ*, is connect-

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