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APPLICATION OF ADSORPTION CALORIMETRY TO THE STUDY OF HETEROGENEOUS CATALYSIS REACTIONS *

PIERRE C. GRAVELLE

Institut de Recherches sur la Catalyse, Laboratoire Propre du C.N.R.S. (conventionné à l'Université Claude Bernard, Lyon I), 2 avenue Albert Einstein, 69626 Villeurbanne (France)

ABSTRACT

This survey sets out to show that adsorption calorimeters, and particularly conduction-type calorimeters, can be used to measure catalytic activities and determine (i) rate laws, (ii) probable reaction mechanisms, (iii) the secondary processes which cause catalyst activation or deactivation, and (iv) the site distribution at the catalyst surface. The merits and limitations of the various applications of adsorption calorimetry to the study of heterogeneously catalyzed reactions are critically discussed. Most examples are taken from the author's previous publications.

INTRODUCTION

In the presence of a catalyst, the rate of a reaction is increased and its activation energy is decreased, but neither the equilibrium state nor the thermodynamic quantities that characterize the reaction are modified. Therefore, the enthalpy change of the reaction, whose determination is the cornerstone of classic calorimetry, is indifferent to the presence of a catalyst. It is true that the presence of a heterogeneous catalyst physically modifies the reacting system and compels the experimentalist to design specific calorimeter arrangements. However, these arrangements are no different from those required for the study of gas–solid or liquid–solid interactions. The specific features of adsorption calorimeters and the merits and defects of various instruments have already been reviewed during the present Summer School and elsewhere [1]. These considerations indicate that the interest, if any, of discussing the applications of adsorption calorimetry to the study of heterogeneous catalysis reactions must lie in other topics than reaction heats or instrumentation.

One specific feature of catalyzed reactions has just been mentioned: the catalyst modifies the kinetics of the process by increasing the rate and decreasing the activation energy. This beneficial result is achieved through

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the appearance of a new reaction mechanism that transiently involves the catalyst. This survey attempts to show that calorimetry can help to measure reaction rates and unravel reaction mechanisms. It can also be useful in more complex and, regrettably, common situations, when the catalyst is not totally selective or when it deactivates in the course of its action.

CATALYST ACTIVITY

There are many ways of measuring catalytic-reaction rates and most of them do not involve a calorimeter. This instrument, however, may be useful when (i) a continuous record is needed, (ii) no costly product analysis is required, or (iii) information from other methods is distorted by mass-transfer limitations. The thermal analyser, proposed by Boldyreva and Roiter [2] (Fig. 1), is probably the simplest device for qualitative separation of the catalytic- from the homogeneous-phase fractions of a reaction as the temperature changes. This shows that thermal methods can detect where the reaction is taking place, even though rates cannot actually be measured by means of this instrument. Differential thermal analysers (DTA) [3] and differential scanning calorimeters (DSC) [4] have been used to measure reactions rates and activation energies more quantitatively. They must have arrangements permitting gas flow through the cell and efficient contact between the reactants and the catalyst. Since the DTA or DSC signal is taken as a measure of catalytic activity, the linearity of the instrument response as a function of the heat generated by the reaction must be very precisely checked. Calibration is often a moot point, as there are many paths for the exchange of heat between the sample and its surroundings. In addition, when product analysis is not performed, we must make sure that the selectivity of product formation does not vary during or between runs and that the catalyst does not deactivate. Lastly, when temperature scans are performed to determine activation energies, it must be shown that (i) the reaction reaches stationary state at any temperature, and (ii) the response time of the instrument is rapid compared to the changes in heat production

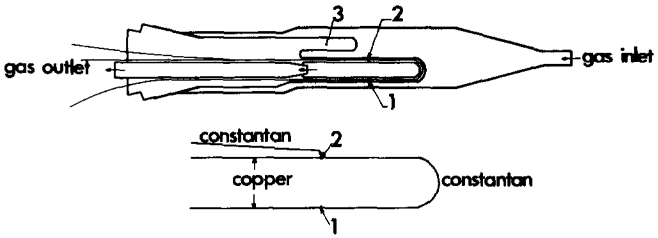

Fig. 1. Reaction vessel for determining the homogeneous and heterogeneous parts of a catalyzed reaction [2]. (1), (2) Differential thermocouple junctions; (3) thermocouple finger for measuring the temperature of the reactor.

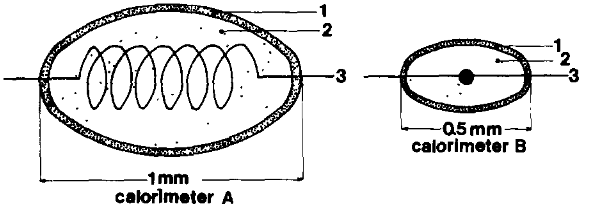

Fig. 2. Reaction calorimeters [5]. Calorimeter A: (1) catalyst; (2) alumina; (3) platinum coil. Calorimeter B: (1) catalyst; (2) alumina; (3) thermocouple junction.

caused by the temperature variation. In most cases when DTAs or DSCs are used, samples are very small and the second condition is reasonably fulfilled.

It is for this very purpose that Firth and Holland [5] have designed their calorimetric beads (Fig. 2): temperature changes caused by the reaction are easily detected and, once calibration is properly carried out, heat leaks can be taken into account and the activity of the catalyst can be reliably measured. However, because of the very small amount of catalyst deposited on the bead, its other properties (specific surface area, porosity, phase composition, etc.) are less easily characterized. This limitation has precluded the development of the calorimetric-bead technique.

RATE LAWS

In principle, rate laws can easily be determined by means of calorimetric experiments, since it is sufficient to compare heats produced for various reactant compositions. This can, for instance, be carried out in Firth-type calorimeters. However, when more common calorimeters requiring larger samples are used, determination of the average sample temperature at any time during the experiment is sometimes inaccurate because of their design (few thermocouple junctions, for instance). In a previous review [6], the author attempted to show that conduction-type calorimeters are particularly convenient for these studies, since (i) all temperature fluctuations at the cell surface are integrated, and (ii) the samples are large enough to be characterized after the calorimetric tests.

Conduction-type calorimeters can be very efficiently combined with a flow-through reactor to study kinetic laws [7]. Preliminary calibration must be carried out to determine the range of linearity of the calorimeter response and its sensitivity. Figure 3 reports such a calibration curve in the case of the reaction of various mixtures of CO, O_2 and helium on an NiO catalyst at 473 K [7]. On this catalyst, changes in the partial pressure of oxygen (or its flow-rate) do not influence the heat production, whereas the heat produced by the reaction is directly proportional to the partial pressure of carbon monoxide in the reaction mixture (Table 1). The conclusion, of course, is that the reaction partial orders are zero with respect to oxygen and one with respect to CO.

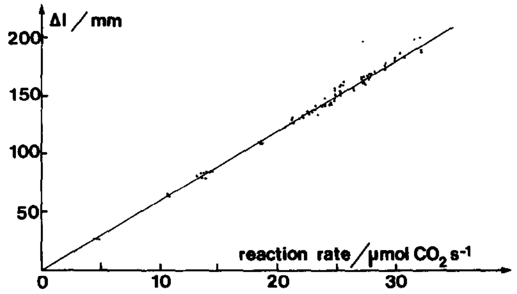

Fig. 3. Plot of the amount of heat produced by the oxidation of carbon monoxide at 473 K and measured by the ordinate of the calorimeter curve, as a function of the quantity of reaction product, detected chromatographically [7].

Conduction-type calorimeters equipped with a constant-volume line can also be utilized for kinetic studies, particularly when a small volume of reaction mixture is required, i.e., to test the activity of a fraction of the active surface during selective poisoning experiments (see later). The reactant pressure continuously decreases during the experiment. A stationary reaction state is never observed, therefore, except for zero-order reactions. The calorimetric curves recorded cannot be directly interpreted in terms of heat production as a function of time, since they are distorted by thermal lags in the calorimeter [8]. "Reconstruction" of the data must be carried out and various techniques have been proposed for this purpose [8]. One must always be careful to select the technique best adapted to the problem at hand, and not to indulge in over-sophistication. Figure 4 shows the linear plot of the heat flux generated by the reaction of various doses of CO–O_2 mixtures on a titanium dioxide catalyst at 773 K as a function of the partial pressure of

TABLE 1

Thermokinetic data for the combustion of carbon monoxide at 473 K [7]

Flow rate (ml min^{-1})			Heat flux (cal s^{-1})
Total (reaction mixture and carrier gas)	Carbon monoxide	Oxygen	
80	2.6	2.4	1.7
80	2.5	5.5	1.6
80	2.6	7.0	1.7
80	2.7	10.5	1.6
36	0.25	3.2	0.37
37	0.76	3.3	0.89
36	0.90	3.3	0.92
38	1.60	3.5	2.06

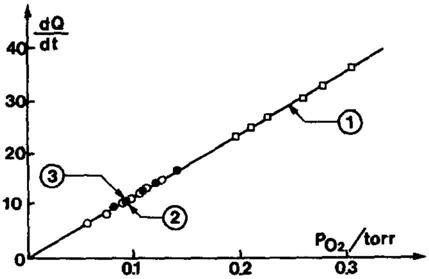

Fig. 4. First-order plot for the combustion at 773 K of carbon monoxide on a CO-activated titanium oxide catalyst [9]. Composition of the reaction mixture: (1) CO + 1/2 CO_2; (2), (3) CO + O_2.

oxygen, independently measured during the reaction. It is clear that the reaction partial order with respect to oxygen is equal to one [9]. In this case, calorimetric data were simply reconstructed by application of the Tian equation [6].

CORRELATIONS BETWEEN ADSORPTION HEAT AND CATALYTIC ACTIVITY

One method often used to cast light on the mechanism of catalytic action is to search for correlations between the catalyst activity or selectivity and some other property of its surface. Since contact catalysis necessarily involves the adsorption of at least one of the reactants as a step of the reaction mechanism, correlation of quantities related to the reactant chemisorption with the catalytic activity has frequently been attempted. The magnitude of the bonds between adsorbate and absorbent is obviously a relevant parameter. For this reason, many attempts have been made to correlate heats of adsorption with activities. Figure 5 shows that these attempts are sometimes successful [10], but some precautions should be taken to avoid artefacts. For instance, it is advisable to study adsorption at the temperature used for the

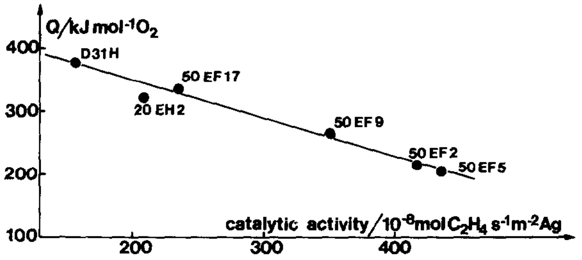

Fig. 5. Average heat of formation of an AgO monolayer at 473 K for a series of silica-supported silver catalysts, as a function of their intrinsic activity for the oxidation of ethylene at the same temperature [10].

catalytic tests. Moreover, in the case of catalysts with an energetically heterogeneous surface, determination, by means of thermochemical cycles if possible (see next section) or otherwise, of the fraction of the surface which actually participates in the reaction and measurements of the adsorption heats on this fraction are recommended. Finally, a direct correlation between activity and the bond energy between the surface and a reactant frequently means that adsorption of the reactant is the rate-limiting step in the reaction mechanism. This ought to be checked by studying the kinetic law.

The preceding remarks indicate that the existence of direct correlations between bond energies and catalytic activities must be cautiously demonstrated. However, their search may be considered an excellent way of improving catalyst design. This should already be sufficient to justify a vigorous development of adsorption calorimetry.

REACTION MECHANISMS

The mechanism of a heterogeneously catalyzed reaction is composed of a series of elementary reactions or "steps". These involve the reactants and the catalyst surface and finally yield the reaction product(s). The basic principle of catalysis, recalled in the introduction, makes it clear that the sum of the heats produced by all these steps must be equal to the enthalpy change of the reaction. Probable reaction steps can be independently studied in the calorimeter by means of successive adsorptions (adsorption sequences), while probable reaction mechanisms, including different series of steps, can be tested in thermochemical cycles. Table 2 reports two such cycles indicating that on the most reactive sites (low coverage) of the NiO catalyst [11] the interaction between adsorbed oxygen species and gaseous carbon monoxide yields adsorbed carbon dioxide, whereas the generated carbon dioxide can desorb from less reactive sites (high surface coverage). Therefore, interactions (1) and (4) are the steps of a reaction mechanism which is thermochemically probable at the surface of NiO. However, the most reactive surface sites will be deactivated by adsorbed carbon dioxide.

Calorimetric data can still yield one more piece of information concerning the reaction mechanism: kinetic analysis of the "reconstructed" calorimetric curves (see Rate Laws section) can indicate (for sites shown to be active) which step is rate-determining. In the case of cycle 2 (Table 2), for instance, interaction (4), occurring at high surface coverages (~ 2 cm^3 g^{-1}), is distinctly slower than interaction (1) and, therefore, limits the rate of the overall process. This conclusion has been confirmed by a more classical study of the same system [11].

The calorimetric method for studying reaction mechanisms outlined here is, in principle, very sound and powerful. It has quantitatively confirmed that only a fraction of the surface sites is active during catalysis, the more

TABLE 2

Thermochemical cycles for the oxidation of carbon monoxide on a nickel oxide catalyst at 303 K [11] [a]

Cycle 1			
(step 1)	$1/2\,O_2(g)+Ni^{2+} \rightarrow O^-(ads)+Ni^{3+}$	+29(0.2)	+11.5(1)
(step 2)	$O^-(ads)+CO(g)+Ni^{3+} \rightarrow CO_2(ads)+Ni^{2+}$	+66(0.4)	+58(2)
(step 3)	$CO_2(ads) \rightarrow CO_2(g)$	−27(0.4)	−26(2)
[(1)+(2)+(3)]	$CO(g)+1/2\,O_2(g) \rightarrow CO_2(g)$	+68	+43.5
Cycle 2			
(step 1)	$1/2\,O_2(g)+Ni^{2+} \rightarrow O^-(ads)+Ni^{3+}$	+29(0.2)	+11.5(1)
(step 4)	$O^-(ads)+CO(g)+Ni^{3+} \rightarrow CO_2(g)+Ni^{2+}$	+66(0.4)	+58(2)
[(1)+(4)]	$CO(g)+1/2\,O_2(g) \rightarrow CO_2(g)$	+95	+69.5

[a] All data are relative to the catalyst denoted NiO (250) in ref. 11; figures not in parentheses refer to the heats of adsorption or interaction in kcal mol^{-1} (1 cal = 4.184 J); figures in parentheses refer to the corresponding surface coverages in $cm^3\ g^{-1}$. The enthalpy change for the homogeneous reaction is 68 kcal mol^{-1}.

reactive sites being inhibited by strongly adsorbed species and the less reactive sites not allowing the formation of active species. It has given information on probable reaction mechanisms and rate-determining steps. However, one should also be aware of its limitations:

(i) adsorption sequences only involve irreversibly adsorbed species, since one reactant in the gas phase is evacuated before the next is introduced;

(ii) mixtures of gases may not behave like individual gases: when a gas mixture comes into contact with a catalyst, induction effects, synergy or inhibition may take place. These are absent when the same gases are successively adsorbed. For these reasons, careful checks should be made to confirm the conclusions derived from thermochemical cycles. These should not be extrapolated to the reaction conditions without discussion. In general, the method is valid for so-called "simple" reactions with permanent gases, which are very selective and involve irreversible adsorption. In other cases, however, although thermochemical cycles will not totally clarify the reaction mechanism, they indicate which interactions are thermochemically probable and thus shed some light on the "chemistry of the process".

The thermal response of an initially quasi-stationary, catalytic system to a perturbation can also be very informative. Figure 6, for instance, reports the calorimetric curve recorded when the decomposition of nitrous oxide into nitrogen and oxygen, catalyzed by nickel oxide at 473 K, was perturbed by freezing-out all the remaining reactant, at regular intervals, in a liquid-nitrogen trap [12]. The very slow endothermic phenomenon, proceeding in the absence of the reactant, was related to the desorption of oxygen from the catalyst surface. Since the desorption heat is equal to the heat of formation of ionic species, $O^-(ads)$, and since desorption of molecular oxygen species,

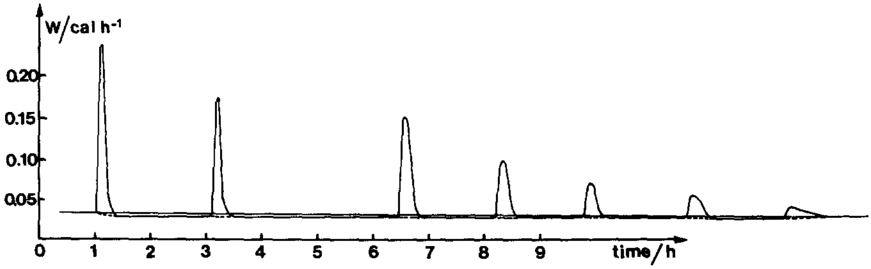

Fig. 6. Calorimetric curve produced by the decomposition at 473 K of a dose of nitrous oxide, catalyzed by nickel oxide, and interrupted, six times, by condensing the reactant at 77 K.

O_2(ads), is rapid, the very slow endothermic phenomenon, which very probably limits the whole catalytic reaction rate, was interpreted [12] as the surface diffusion and recombination of ionic into molecular adspecies

$$2\,O^-(\text{ads}) \overset{\text{slow}}{\rightarrow} O_2(\text{ads})$$

Although interpretation of the transient effects recorded after a perturbation may sometimes cause difficulty, the method frequently yields useful results. It can be applied to any catalytic reaction, the only limitation being the possibility of producing the perturbations.

CATALYST DEACTIVATION

The cycles presented in Table 2 have already shown that the calorimetric study of adsorption sequences may give information on the deactivation of catalysts caused by strongly adsorbed reaction intermediates or products. However, this is not the only phenomenon that can induce catalyst deactivation: coking, pore blocking, sintering and adsorption of poisons in the feed gases are other, frequent causes of activity decrease. Adsorption calorimetry can also contribute to the study of these phenomena.

It must first be mentioned that conduction calorimeters, and DSCs operating at constant temperature, when equipped with a flow system are convenient detectors of all activity fluctuations that may occur during the life of the catalyst. Routine tests can thus be performed with series of catalysts. They require less maintenance and are less costly than usual reactors, since no product analysis is needed.

Adsorption of probe molecules may be carried out on the fresh and used catalyst in order to titrate the decrease in the number of sites and their reactivity. An illustration is presented on Fig. 7, showing the acid-strength distributions of H-mordenite and H-ZSM-5 zeolite before and after their use as catalysts in methanol conversion at 650 K. The distributions were calculated from the differential heats of adsorption of ammonia, measured at 423 K [13]. In both cases, the catalysts used contain much less acid sites than

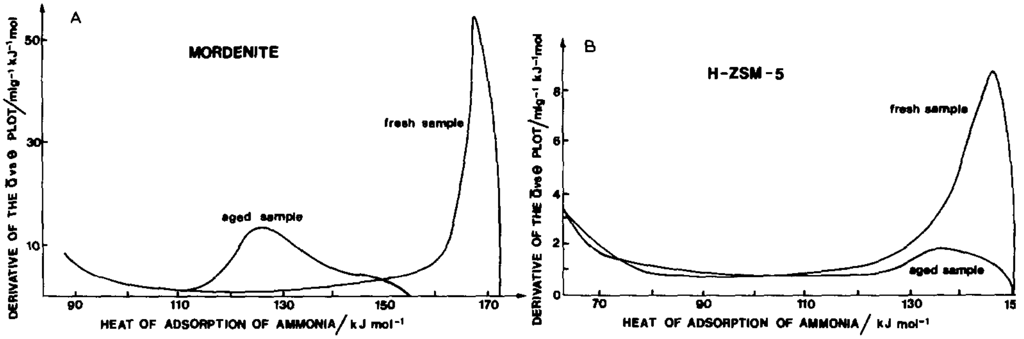

Fig. 7. Acid strength distribution of H-mordenite and H-ZSM-5 zeolite, before and after their use as catalysts in methanol conversion [13]. The spectra were calculated from the differential heats of adsorption of ammonia, measured at 423 K.

the fresh ones (numbers of sites are measured by the area under the curves): deactivation of sites, caused by coking in these experiments, takes place on both catalysts. All the most acidic sites on the mordenite surface are either totally or partially inhibited (partial inhibition of reactive sites is demonstrated by the enhancement of the site population, which adsorbs ammonia with the production of ~ 125 kJ mol^{-1}). Indeed, the catalytic activity of mordenite is reduced by half after a run of 20 min [14]. At the surface of the used ZSM-5 sample, very acid sites are still present and the spectrum of acidity is modified in height, but not in breadth. It is, therefore, not surprising that no activity decrease was observed after a run of 20 min [14]. Two conclusions were deduced from this study: (i) only a fraction of the acid sites titrated by ammonia are really necessary to maintain a high catalytic activity, and (ii) the different behaviour of mordenite and ZSM-5 zeolite during the same catalytic reaction must not be related to a major difference in the acidity distribution of their surface sites, but is very likely explained by their different pore structure [13,14].

Any secondary reaction which changes the selectivity of a catalytic reaction (and catalyst deactivation by products is a secondary reaction) influences the enthalpy change of the system, so that the experimental heats of reaction are different from those expected. Non-selectivity and its common consequence, catalyst deactivation, can therefore easily be detected by classical calorimetric measurements. Figure 8 illustrates the case of oxidation of carbon monoxide over nickel oxide at 303 K [15]. The heat of reaction during the reaction of the first doses of a stoichiometric mixture clearly exceeds 68 kcal mol^{-1}, i.e., the expected value (doses A and B for instance). Some process is causing catalyst deactivation, as kinetic studies have shown. However, production of the expected heat of reaction is observed later (after the successive introduction of all doses up to dose C), and the catalyst then maintains a steady activity. As this example shows, the measurement of experimental heats of reaction is a good test of reaction selectivity; however,

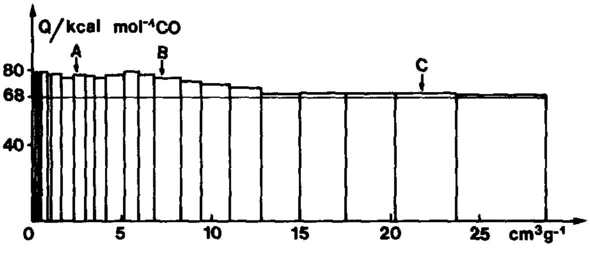

Fig. 8. Differential heats for the combustion of carbon monoxide at 303 K, on a gallium-doped nickel oxide catalyst, as a function of the cumulative volume of reactants consumed [15].

it provides no clue as to the origin of non-selectivity or its relation with activity. This method must, therefore, be supplemented by other, kinetic or spectroscopic, investigations. In the example selected, deactivation and enhanced heats of reaction were explained by the irreversible adsorption of carbon dioxide on the most reactive surface sites (see Table 2).

In some cases, however, thermochemical cycles applied to reaction data can be used to probe deactivation mechanisms. The experimental heats (steps) in Fig. 9 were recorded during the reaction at 473 K of a non-stoichiometric (CO-excess) mixture of carbon monoxide and oxygen (30 : 70% O_2–CO) with a divided nickel oxide catalyst [16]. One mechanism, and only one, correctly reproduced the experimental data (dots on Fig. 9). According to this mechanism, carbon monoxide first reduces the oxide surface to metal, and oxygen then partially reoxidizes it. This is a common redox mechanism. However, the remarkable additional evidence is that, although the heat of reduction corresponds to the reduction of a divided solid, the heat of reoxidation is characteristic for the formation of bulk nickel oxide. It thus appears that the initially divided catalyst is progressively converted into a less divided solid [16]. This "active sintering" explains the rapid ageing observed during catalytic tests under the same conditions.

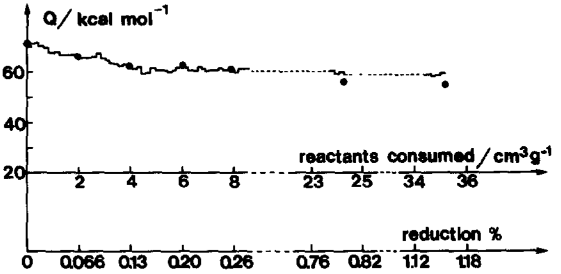

Fig. 9. Differential heats for the reaction of a non-stoichiometric mixture of carbon monoxide (70%) and oxygen (30%), on a nickel catalyst at 473 K (steps: experimental values; dots: calculated values, see text) [16].

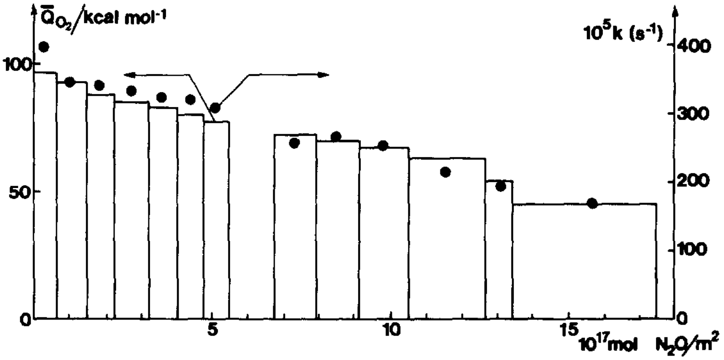

Fig. 10. Catalytic activity spectrum of a nickel oxide catalyst for the decomposition of nitrous oxide at 473 K (dots) and reactivity spectrum of the same catalyst with respect to oxygen at 473 K (steps) [18].

SITE DISTRIBUTION ON A CATALYST SURFACE

The existence of surface heterogeneity leading to a heterogeneous population of active sites at a catalyst surface has been readily accepted, since the pioneer work of Sir Hugh Taylor [17]. It is very often discussed but very seldom taken into account in practical cases, simply because there are very few tools with which to study the heterogeneity of active sites during catalysis. All attempts to do so have been based upon the use of selective poisons. Because of its sensitivity, and the recent development in refined data-reconstruction techniques, adsorption calorimetry could make a significant contribution here, as the results of the (academic) study [18] in Fig. 10 show. Decomposition of nitrous oxide at 473 K on a stoichiometric nickel oxide was selected because the product, oxygen, inhibits the most active surface sites on which it is produced. Therefore, the reaction of small, successive doses of N_2O takes place on different fractions of the catalyst surface. Integration and profile analysis of the calorimetric curves yield the heat of formation of the nickel–oxygen bond at the surface and the activity constant of the reaction. Figure 10 indicates that there is indeed a heterogeneous distribution of active sites at the surface of the NiO sample and that changes in activity are correlated to changes of reactivity with respect to oxygen. The correlation, in this case, is particularly reliable, since both parameters were deduced from the same experiments. It would certainly be a worthwhile task to perform other similar studies in order to determine more firmly the merits of this calorimetric method.

FINAL REMARKS

The various applications of adsorption calorimetry to the study of heterogeneously catalyzed reactions presented in this overview can be separated into two general classes: kinetic studies, on the one hand, and mechanistic studies, on the other.

Kinetic studies generally require simple and, therefore, inexpensive instruments. When no complex chemical analyses are necessary, calorimeters can reliably provide continuous records with very limited maintenance, once calibration has demonstrated the range of linearity and sensitivity of the arrangements. It is, therefore, justified to develop these thermal methods in laboratories where catalysts are routinely tested, and where these methods will yield results equivalent to those of usual reactors at a lower price. Mechanistic studies, by contrast, are frequently time-consuming. They require very sensitive calorimeters and sophisticated data-reconstruction techniques. Their results are sometimes illuminating, but very often it is only after more usual methods have been used and their results exploited that one can take full advantage of the new mechanistic information provided by thermal methods on catalytic systems. For these reasons, the possibility of studying catalytic reaction mechanisms should be considered as an extra bonus provided by the adsorption calorimeter: it should not be presented as the main reason for buying a very expensive machine whose main and essential function remains the study of adsorption at the gas–solid (or liquid–solid) interface.

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