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A Microcalorimetric Determination of the Distribution of Active Sites at a Catalyst Surface

The existence of a heterogeneous distribution of active sites at a catalyst surface is an old concept in heterogeneous catalysis, but one which is more often assumed than actually verified. This situation is unfortunate for obvious practical and fundamental reasons but is not surprising since the experimental determination of the "activity spectrum" of a catalyst, with respect to a given catalytic reaction, is difficult. In the studies on the detailed quantitative treatment of inhibition of catalytic reactions, e.g., Ref. (*1*), the change of the *average* activity of the catalyst surface sites is followed as a function of inhibitor content. This method gives access albeit indirectly to the activity of the different sets of surface sites. A more straightforward determination of the activity spectrum of a catalyst requires not only the choice of a selective reaction inhibitor to cover progressively the different sets of sites but also the use of a very sensitive technique to study the reaction kinetics on the most active sites which remain in the surface fraction still not inhibited and to determine their activity.

It has been postulated earlier that heat-flow microcalorimetry can be used for this purpose, provided that the calorimeter response has been corrected from the instrumental distortion due to thermal lags (*2*). In the present Note, an application of this method to the determination of the activity spectrum of a nickel oxide catalyst for the decomposition of nitrous oxide is presented. The choice of this reaction is justified by the fact that, at the surface of a nearly stoichiometric nickel oxide, the decomposition of a limited amount of nitrous oxide produces exclusively gaseous nitrogen and adsorbed oxygen which inhibits the active surface. By introducing, onto the catalyst surface, successive doses of nitrous oxide whose volume is small compared to the number of surface sites on the catalyst sample, placed in the calorimeter, it is therefore possible (i) to determine the average activity of those sites involved in the reaction of each dose and (ii) to simultaneously inhibit them for the reaction of further doses.

Nearly stoichiometric nickel oxide was prepared by the vacuum (10^{-6} Torr) (*3*) dehydration of nickel hydroxide at 473 K (*4*). Nitrous oxide was purified by successive freezing (77 K)–pumping (10^{-6} Torr)–sublimation cycles. The Calvet-type calorimeter, operating at 473 K, the volumetric line and the data amplification–acquisition line have been previously described (*5*). A procedure, based on the state-function theory, has been used for the correction of the experimental calorimeter response (*6*). This procedure is an improved and simplified version of the general deconvolution method proposed earlier (*7*). Identification of the linear system, i.e., the calorimeter, is achieved by means of thermal steps generated in an electrical heater (*8*).

Figure 1 represents the experimental and corrected calorimetric curves produced by the reaction, at 473 K, of a dose of nitrous oxide (9.79×10^{17} molecules) on a 80.3 mg sample of nickel oxide (160 m^2/g). Pressure measurements and mass spectrometric analyses of the gas phase after reaction con-

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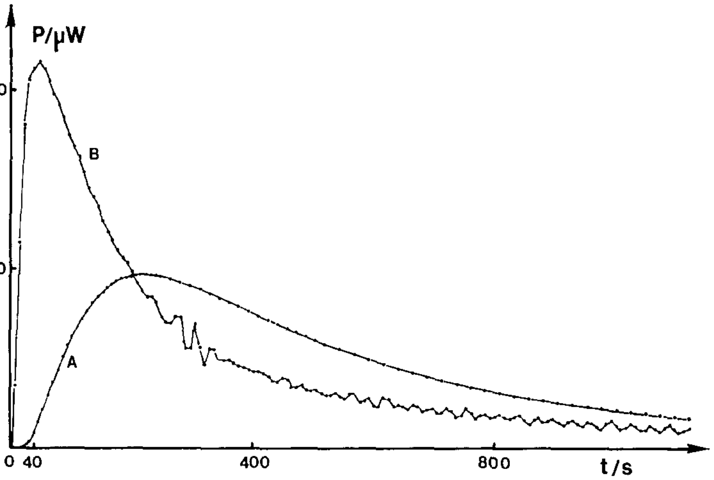

Fig. 1. Experimental (A) and corrected (B) calorimetric curves produced by the decomposition of nitrous oxide on nickel oxide at 473 K.

firm that nitrogen only is evolved, all the generated oxygen being retained by the solid. After the reaction of a dose, nitrogen is evacuated, the catalyst being maintained at 473 K, and, when the residual pressure is down to $\simeq 10^{-6}$ Torr, i.e. after ~ 2 hr pumping, another dose of nitrous oxide, of similar volume, is introduced, the complete reaction of which produces another calorimetric curve. The experiments were discontinued when oxygen appeared in the gas phase. The quantity of oxygen, then irreversibly adsorbed on the catalyst surface, corresponds to $\sim 16\%$ of the available surface sites, assuming as is usually done (*9*) that the number of exposed nickel ions per unit (m^2) area is equal to 1.1×10^{19} and that each surface nickel ion adsorbs one oxygen atom. When the experiment was discontinued, the catalyst surface still contained a population of sites, active in the nitrous oxide decomposition. However, oxygen is not irreversibly adsorbed on these sites and desorbs to the gas phase (*10*).

It is generally assumed, but not spectroscopically confirmed in the case of nickel oxide, that the decomposition of nitrous oxide produces adsorbed atomic oxygen species. If this is indeed the case, the reaction of all doses should follow first-order kinetics. This can be ascertained in the following manner:

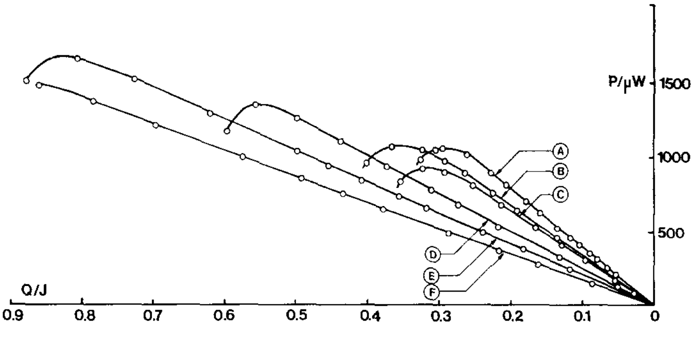

Fig. 2. First-order transforms of the calorimetric data recorded during the reaction of doses (A) to (F) of nitrous oxide on nickel oxide at 473 K.

The ordinate of the corrected calorimetric curve, i.e., the thermal flux produced by the reaction, is, at any time, proportional to the reaction rate. The proportionality coefficient is the change of enthalpy produced by the reaction. It remains constant during the reaction of a dose if the heat of adsorption of oxygen is constant for all the surface sites involved in the reaction of this particular dose. The limited volume of each dose being considered, this assumption is reasonable.

The reaction of all reactant remaining in the system, at time *t*, produces an amount of heat which can be calculated by integration, from time *t* to infinity, of the corrected calorimetric curve.

Finally, a first-order transform of the calorimetric data is obtained by plotting, for any time, the ordinate of the corrected calorimetric curve as a function of the area of the calorimetric curve, integrated from time *t* to infinity. Such plots for some doses of nitrous oxide are presented in Fig. 2.

It appears that the plots are indeed linear, as preliminary experiments had already indicated (*2*). This result, *a posteriori*, confirms that the decomposition of nitrous oxide on nickel oxide into nitrogen and adsorbed oxygen is a monomolecular process and that the different surface sites which participate in the reaction of each successive dose are energetically homogeneous with respect to oxygen. The first-order relation is not, however, obeyed during the first instants (20–40 s) of the reaction (curves A to F in Fig. 2) which correspond to the ascending branch of the corrected calorimetric curve (Fig. 1). The time lag which separates the beginning of the experiment from the maximum heat flux (Fig. 1) is explained by an imperfect reconstruction of the data. Similar ascending branches and similar time lags have been also observed, after correction, on the calorimetric curves corresponding to thermal steps generated during the electrical calibration of the calorimeter (*6*). A perfect reconstruction of the data is difficult when the heat flux changes rapidly with time, e.g. at the beginning of the reaction of a dose. However, simulated experiments have demonstrated that progressive changes of heat flux are satisfactorily reconstructed (*6*, *7*). The descending branches of the corrected calorimetric curves (Fig. 2), which contain the kinetically significant information, are much less affected by residual distortion than the ascending branches. Moreover, the descending branches of all the calorimetric curves being similar, the residual distortion, if there is any, is the same for all of them. The comparison of the first-order plots (Fig. 2), deduced from the different calorimetric curves, is therefore justified.

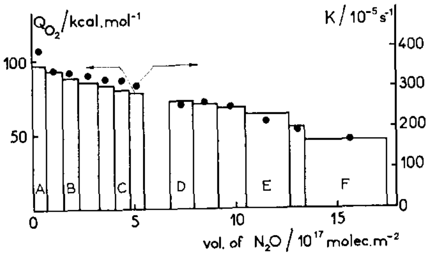

FIG. 3. Variations of the first-order activity constant [the "activity spectrum" (●)] and of the differential heats of adsorption of oxygen (steps) as a function of the cumulated number of molecules of nitrous oxide decomposed per unit catalyst area at 473 K. This number is equal to the number of surface sites (activity constants for doses (A) to (F) were calculated from the slopes of the linear transforms in Fig. 2).

The slope of the straight lines, which measures the first-order activity constant, changes for the successive doses. It is presented as a function of the cumulated volume of the doses in Fig. 3. A twofold regular decrease of activity is thus demonstrated from the most to the least active surface sites.

The same calorimetric data can be used to calculate the heat of adsorption of oxygen produced by the reaction. This is simply achieved by comparing the experimental heats of reaction to the known change of enthalpy produced by the gas phase decomposition of nitrous oxide into nitrogen and molecular oxygen. The heats calculated for the dissociative adsorption of oxygen:

$$O_{2(g)} \rightarrow 2\ O_{(ads)},$$

are presented as steps on Fig. 3. They are in excellent agreement with previously published data (*10*).

It is concluded from these results that:

i. Heat-flow calorimetry can be utilized not only to determine the distribution of heats of adsorption at an adsorbent surface but also the "activity spectrum" of a catalyst. Application of the method, however, requires the correction of the calorimetric data from the distortion due to thermal lags and is limited to systems in which the catalyst surface sites may be selectively inhibited.

ii. The decomposition of nitrous oxide over stoichiometric nickel oxide at 473 K is a monomolecular process, thereby producing oxygen adatoms.

iii. It has been concluded, from earlier studies, that the variation, with surface coverage, of the differential heat of adsorption of oxygen is a consequence of the heterogeneous distribution of lattice imperfections (vacancies, steps, etc. . . .) which exists at the surface of nickel oxide, especially when it is prepared at a low temperature (*11*, *12*). The close parallelism between the changes in activity for the decomposition of nitrous oxide, into gaseous nitrogen and adsorbed oxygen, and the variation of the heat of adsorption of oygen, which appears from the results represented in Fig. 3, indicate therefore that the catalytic activity of nickel oxide for this reaction is also related to the structure of the catalyst surface. A similar conclusion has already been proposed in the case of the room-temperature oxidation of carbon monoxide on similarly prepared nickel oxide catalysts, increasing activity being then associated with decreasing heats of adsorption of oxygen (*12*).

iv. A correlation between catalytic activity with respect to a given reaction and another property of the catalyst is generally established with data obtained for a series of catalysts and not for different sets of sites at the same catalyst surface, as in the present study. By means of the existing data on the catalytic decomposition of nitrous oxide on semiconducting oxides, Vijh (*13*) has correlated the catalytic activity, measured by the temperature at which the reaction first becomes appreciable on a given oxide, with the heat of formation per equivalent of the oxide and with the heat of atomization per equivalent of the oxide catalyst. Heat of formation and heat of atomization may be considered as estimates of the S–O bond energy, S–O being the solid (catalyst)-oxygen complex formed at the surface as an adsorbed intermediate in the overall reaction. The differential heats of adsorption of oxygen, calculated from calorimetric data and represented in Fig. 3, are more closely related to the S–O bond energy than the thermochemical quantities cited by Vijh. It is worth noting then that, in both correlations proposed by Vijh (*13*), nickel oxide is located on that branch of the plots for which the catalytic activity *decreases* as the S–O bond energy increases, whereas Fig. 3 shows that, in the present case, the catalytic activity *increases* as the S–O bond energy increases. According to Vijh's interpretation (*13*), the latter correlation (this work) indicates that the rate determining step (rds) of the decomposition of nitrous oxide into nitrogen and *adsorbed* oxygen species involves the *formation* of S–O bonds. The former correlations indicate that the rds for the overall reaction (the production of nitrogen and *gaseous* oxygen) involves the *rupture* of S–O bonds. The overall reaction rate would thus be limited by the rate of desorption of oxygen, in accord with some previous studies (*10*, *14*).

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