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Adsorption Calorimetry on Granulated Catalysts. A Study of Adsorption Processes Relating to Isopropanol Dehydrogenation

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The paper describes a new resistance thermometer calorimeter, suitable for the measurement of heats of adsorption on powdered catalysts. The calorimeter, which is constructed as a single unit, is capable of being outgassed at 500°C and is designed to measure heat liberations down to the order of magnitude of a few millicalories. In this respect it is particularly suited to the measurement of heats of adsorption over small coverage ranges ($\Delta\theta$ from 0.01 to 1%), but it is equally adaptable for conventional studies with large increments.

The calorimeter has been used to measure the heats of adsorption of isopropanol and acetone on a nickel oxide catalyst over a range of ca. 1% coverage at room temperature. The heat of adsorption of isopropanol on an outgassed surface is 16 kcal/mole, independent of coverage. On a surface carrying presorbed oxygen, the heat is again constant, but at a slightly higher value (18 kcal/mole). Although the adsorption under these conditions is primarily physical, hydrogen bonding with oxygen atoms on the surface is invoked to explain the absolute magnitude of the heat and its slight enhancement in the presence of presorbed oxygen. With acetone, the heat of adsorption for the outgassed surface is 11 kcal/mole, but on the oxygenated surface an initial heat of 21 kcal/mole is found, falling to 11 kcal/mole at 0.5% coverage. This result is interpreted as normal physical adsorption for the outgassed surface, but a contribution from dissociative chemisorption is considered as one way to account for the high heats at low coverages on the oxygenated surface. It is suggested that presorbed oxygen may lower the activation energy for the dissociative adsorption and desorption of acetone, and that this may be the mechanism whereby at higher temperatures oxygen enhances the rate of dehydrogenation of isopropanol.

The measurement of small heat effects accompanying chemisorption is a problem of quite general concern in the field of heterogeneous catalysis. Not only is there the fundamental question of exploring as widely as possible the dependence of quasi-differential (incremental) heats of chemisorption as a function of coverage, but there is a growing interest in detecting and studying adsorption on very limited areas of surface, such as, for instance, the metallic surface of a very dilute supported metal catalyst. These studies call for a calorimeter which is capable of measuring heats of the order of magnitude of a few millicalories, yet which is robust, easily recharged, and capable of being outgassed at a high temperature. The precision demanded falls in an intermediate region between that attainable by the familiar Garner (1), Beebe (2), and Beeck (3) types of adsorption calorimeter, on the one hand, and the more elaborate metal de-

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signs, e.g., that of Aston and his co-workers (4), on the other hand. Remembering that many of the gases of interest in catalysis are chemically aggressive, a metal calorimeter is much less desirable than a glass one. We have, therefore, given attention to the problem of adapting the Garner and Beeck designs in order to produce the desired characteristics, and an instrument is described which we believe could be of quite wide application for studies on powdered catalysts.

We illustrate the application of the calorimeter with some experiments at room temperature on the adsorption of isopropanol and acetone on a nickel oxide catalyst. Under these conditions the adsorption of isopropanol may be expected to proceed without dissociation, and there is an interest in seeing how the observed heat compares with that to be expected from purely physical adsorption. The choice of topic was also motivated by the fact that the mechanism of dehydrogenation of alcohols on oxide catalysts is a matter of some controversy (5). A particular aspect which seemed to us worthy of further attention was the observation by Deren *et al.* (6) that oxygen enhances the rate of dehydrogenation, and we have, therefore, looked for an influence of presorbed oxygen on the adsorption of isopropanol and acetone. By making the study at a temperature well below that of the catalysis, we have been able to detect and study a selective interaction and to comment on its implications for the mechanism of dehydrogenation.

Experimental Methods

Apparatus and Procedure

The calorimeter is shown in Fig. 1. It consists essentially of two concentric glass tubes joined at the bottom by a Dewar seal and mounted inside a jacket which can be evacuated to 10^{-6} mm. The concentric glass tubes were constructed of thinned glass, ca. 0.3 mm in thickness, except at the Dewar seal where for practical purposes it was necessary to use thicker glass. The annular space between the tubes was about 2 mm wide. On the outside of the outer tube were interwound two coils of 46

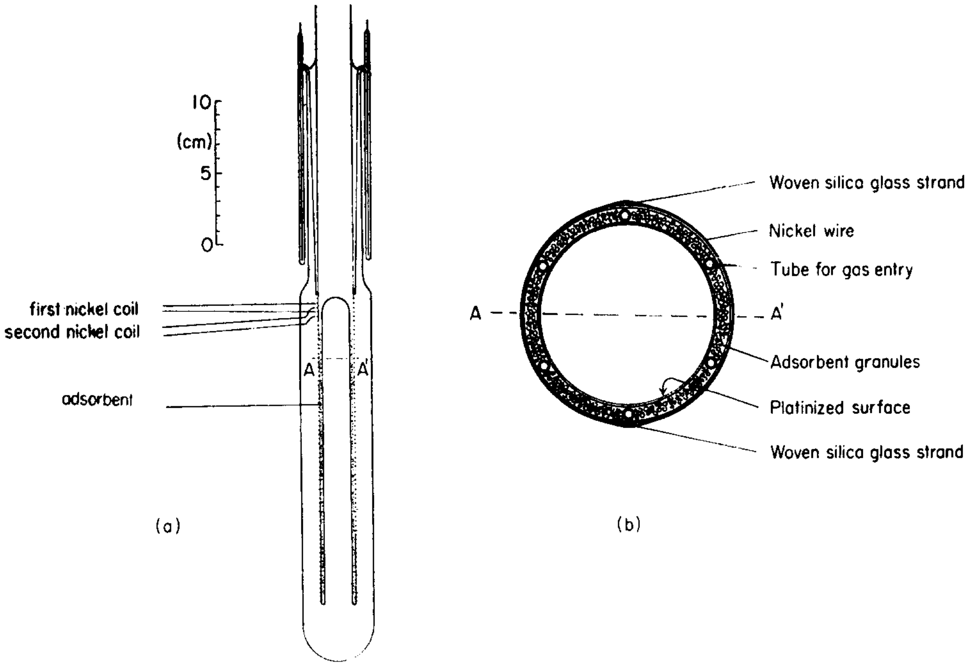

FIG. 1. (a) The calorimeter, as mounted. The lead for evacuating the jacket is not shown. (b) Enlarged cross section of central portion at AA′ (not to scale).

S.W.G. high temperature-coefficient nickel wire, following the pattern of the film calorimeter described by Klemperer and Stone (7). One of these coils of approximately 150 ohms resistance served as a resistance thermometer, and the other was used in the determination of the water equivalent.

Two novel methods have been used to secure the nickel coils. In the first method the calorimeter tube was mounted in the lathe, and the nickel wire was arranged to pass through a solution of sodium silicate immediately before being wound on the tube. The silicate solution formed tiny, discrete beads on the wire. After the winding was completed the tube was heated in a furnace to 500°C and the wire became securely fixed to the tube. The advantage of this method over that in which silicate cement is applied in a layer is that the tube is not rendered opaque. In the second method the windings were applied over two strands of a woven silica glass fiber (Refrasil) laid longitudinally on opposite sides of the tube and lightly cemented in position [Fig. 1(b)]. Contact between the taut coils and the glass tube was only interrupted in a very restricted region on each turn near the woven silica strands. On heating to 500°C the tendency of the coils to lift from the tube (because of expansion) is compensated by the slight lifting of the resilient fiber strands to take up the slack. The coils, therefore, remain taut, displacement is eliminated, and the coils have a longer life than when silica cement is used.

The annular space contained a set of six fine glass tubes placed longitudinally and terminating at different depths. The granulated adsorbent was gently shaken into the remainder of the annular space, care being taken to view through the tube that distribution was uniform. The fine glass tubes, open at both ends, served to distribute incoming gas. A volume of approximately 30 cm^3 was available for the adsorbent. To minimize losses of heat by radiation, the inner surface of the inside concentric tube was coated with a platinum mirror (1). A further refinement adopted from experience with the Garner-Veal calorimeter was the doubling back of the leads at the top of the vacuum jacket to retain a greater length of wire inside the thermostat.

The methods of resistance measurement, water equivalent determination, and calculation of heat of adsorption were as described by Klemperer and Stone (7). Brennan *et al.* (8) have recently raised certain doubts about the refinements of the water equivalent determination as used in that work, but we continue to find it a satisfactory method, and linear Newton cooling plots were obtained with the present instrument provided adsorbent was present to ensure thermal contact between the concentric tubes. Drift was a much less serious problem with the present assembly since it was mounted vertically and was totally immersed in water in a large Dewar vessel of 15 litres capacity.

For the calorimetric experiments described in this paper, the calorimeter was filled with 25 g of nickel oxide catalyst and the water equivalent was 11.7 g. Dosimetry was carried out with gas or vapor at approximately 0.1 mm pressure from a calibrated volume which was 585 cm^3 for large increments and 97 cm^3 for small increments. In view of the possible risk of decomposing isopropanol in a sensitive Pirani gauge, pressure measurements were made throughout with a McLeod gauge. To avoid serious departure from the gas laws, isopropanol and acetone were never compressed in the gauge below level differences of 20 mm and 100 mm respectively. The measurement of the dose size was accordingly the factor which contributed most to the scatter in the heat of adsorption results.

Materials

Nickel oxide was prepared by decomposition of the carbonate according to the method described by Bielanski *et al.* (9). Its surface area was 8 m^2/g.

Special care was necessary in order to avoid any contamination of acetone and isopropanol with water vapor. Acetone was, therefore, purified by crystallization of the

NaI addition compound, decomposition, and distillation in the vacuum system (10). Isopropanol was purified from water by reaction with anhydrous calcium, refractionation, and distillation in the vacuum system (10).

Oxygen was prepared *in situ* by decomposition of potassium permanganate.

RESULTS

Adsorption of Oxygen

The heat of adsorption of oxygen on nickel oxide, previously measured by Dell and Stone (11), was briefly reinvestigated with the present calorimeter. After outgassing the calorimeter at 400°C, the heat of adsorption of oxygen at 23°C was determined for nine successive increments of approximately 0.015 cm^3 each. The tenth admission resulted in a pressure of 9×10^{-2} mm, and no uptake could be detected. The lack of any response from the galvanometer in this case confirmed the absence of spurious heat effects associated merely with the entry of gas into the calorimeter. Over the range of coverage (0.35%) corresponding to the observed total adsorption of the nine increments, the heat of adsorption fell from ca. 40 to 20 kcal/mole, confirming the strong dependence of the heat of adsorption on coverage observed in the earlier study (11). The relatively low initial value of 40 kcal/mole must be taken in conjunction with the low observed limiting uptake of 0.35%.

Adsorption of Isopropanol

The adsorption was first studied on a surface which had been outgassed overnight at 400°C. The heats of adsorption for an accumulation of eight successive increments of approximately 0.1 cm^3 each are shown as curve A in Fig. 2. These results indicate a value of 16 kcal/mole, independent of coverage. Figure 3 shows the response typically obtained from the galvanometer; the curves refer to absolute heat liberations of 0.100 and 0.119 calorie, respectively, correction for cooling having been made by extrapolation of the corresponding Newton law plot. Defining for convenience 100% coverage of isopropanol as 1 molecule per Ni^{2+}/O^{2-} pair in the surface, the range represented in curve A of

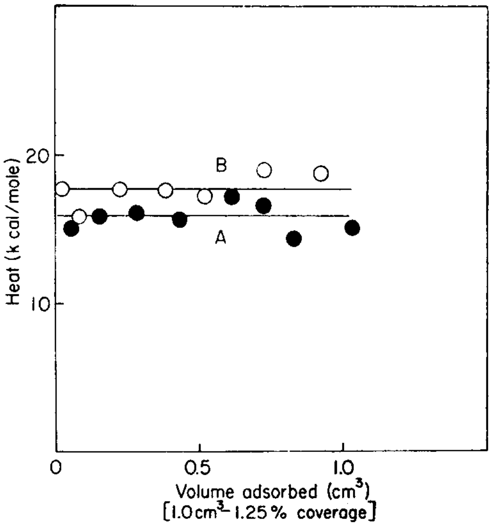

FIG. 2. Heats of adsorption of isopropanol on nickel oxide at 23°C. ● A—Outgassed surface; ○ B—with presorbed oxygen.

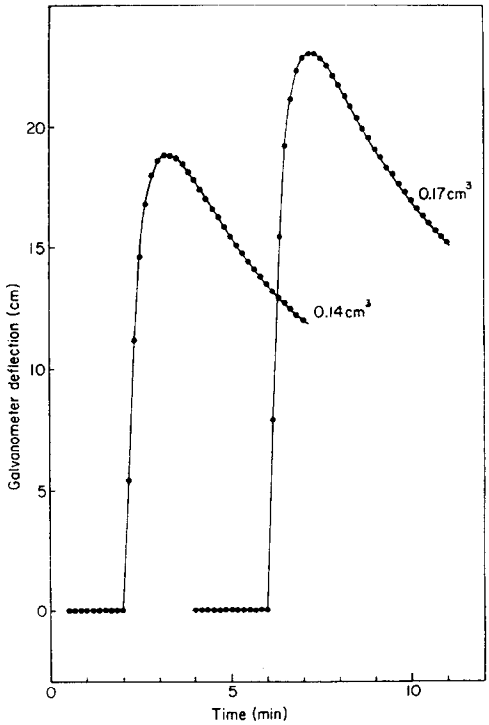

FIG. 3. Liberation of heat during the adsorption of isopropanol (increments 3 and 4).

Fig. 2 is 1.25%. For each of these increments the pressure at equilibrium was below 10^{-5} mm, so the coverage of 1.25% is in no sense to be regarded as a limiting uptake.

In a second series of experiments, oxygen was presorbed at 250°C (yielding a 10% coverage), and the differential heat of adsorption of isopropanol was redetermined over the same range of coverage. This series is shown as curve B in Fig. 2. The heat is again independent of coverage, but the value is significantly greater than that for the outgassed surface.

Adsorption of Acetone

Curve A in Fig. 4 illustrates the relationship between heat of adsorption and coverage for the outgassed surface. The value remains sensibly constant at an average value of 11–12 kcal/mole. As in the case of isopropanol the extent of the curve does not represent the full range of attainable coverage. Curve B in Fig. 4 shows the corresponding series of measurements for a surface oxygenated as before at 250°C. There is a marked enhancement of the heat of adsorption at very small coverages (< 0.5%), but extension of the range of measurements to 2.5% coverage confirmed that the ultimate value of the heat was equal to that for the outgassed surface within the experimental error. It is significant to note that the time lag in reaching the maximum deflection on the galvanometer was about twice as great for the initial increments of curve B as compared with curve A. The release of heat is evidently much slower.

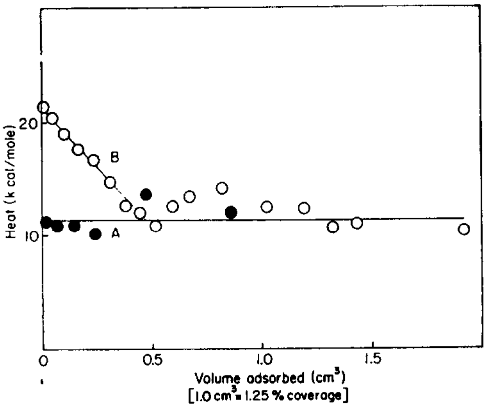

FIG. 4. Heats of adsorption of acetone on nickel oxide at 23°C. ● A—Outgassed surface; ○ B—with presorbed oxygen.

DISCUSSION

Performance of the Calorimeter

The results with isopropanol and acetone amply confirm the value of the instrument for measurements of small heats of adsorption over a narrow range of coverage. Furthermore, having regard to the fact that Fig. 3 relates to a sensitivity five times smaller than the maximum sensitivity of the resistance bridge, it is evident that the responses from increments of one-hundredth the size (~ 0.001 cm^3)‡ could, if necessary, be measured. However, so far as determination of the molar heat of adsorption is concerned, it must frequently happen that the limiting factor (as in the present experiments) will be the accurate determination of the uptake. For gases such as oxygen which adsorb with a high sticking probability, the problem of selective adsorption in successive regions of the adsorbent (12) remains a source of error, but it is less serious in the present design than with the spherical-bulb type of Garner-Veal calorimeter (1). Because of the longer diffusion paths and reduced thermal conductivity of the powdered adsorbent, the response time of 90 sec at the maximum (Fig. 3) is much greater than that of the analogous metal film calorimeter (7), but this is very largely offset by the much lower rate of cooling from the massive sample. To sum up, the principal advantages of the present instrument are its relatively simple all-glass container, its ability to be outgassed at 500°C, and its suitability for exploring heats of adsorption over very small coverage ranges.

The Adsorption of Isopropanol

The low heat of adsorption implies that the dissociative chemisorptions

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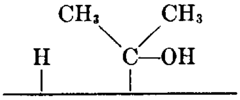
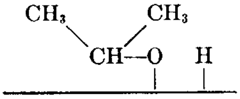
‡ Equivalent to a heat liberation of 1 mcal for a heat of adsorption of 22.4 kcal/mole.


(a)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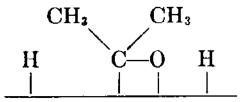
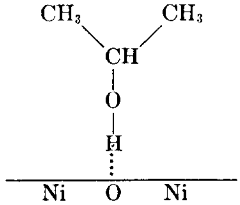

(c)

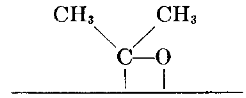
are absent at room temperature, and this conclusion is supported by the observation that the heat is independent of coverage. Comparing the value of 16 kcal/mole for the outgassed surface with q_L, the heat of liquefaction [10.5 kcal/mole for isopropanol (13)], we see that there is a difference of 5.5 kcal/mole. This margin is rather greater than is customary for the first layer of a purely physical adsorption (14), and we attribute the larger heat in the present case to hydrogen bond formation with the oxygen of the surface


(d)

A similar effect has been found by Dry and Beebe (15) for the adsorption of methanol on bone mineral. The slight increase in the heat of adsorption for our oxygenated surface then follows logically from this interpretation.

The Adsorption of Acetone

The low and constant heat of adsorption on the outgassed surface and on the oxygenated surface beyond 1% coverage (Fig. 4) appears to eliminate for these circumstances the concept of a chemisorption


(e)

at room temperature involving opening of the double bond. The observed heat compares favorably with that which might be expected for physical adsorption, since q_L for acetone is 7.3 kcal/mole (13). We may note further that the value obtained isosterically by Schreiner and Kemball (16) for acetone adsorption on the rather chemically inert oxide MgO was 11 kcal/mole, in excellent agreement with our values. Finally, by comparing the result with that for isopropanol, we see that the smaller difference between q_{obs} and q_L in the acetone case, and the fact that at higher coverages the curves for oxygenated and outgassed surfaces coincide, are entirely in line with the fact that for acetone a hydrogen bond interaction with the surface is ruled out.

It remains to discuss the striking rise of up to 10 kcal/mole in the heat of adsorption for the oxygenated surface below 0.5% coverage. It is clear that some chemical interaction has now taken place, and the delay in response time implies that an activated process is present. Moreover, the distinction from the isopropanol case proves that acetone is the more susceptible of the two vapors to the influence of oxygen. This would appear to rule out an explanation based on an exothermic oxidation by chemisorbed oxygen, since on this basis isopropanol, being the more readily oxidized of the two vapors in the normal way, would be expected to show the greater effect.

An alternative explanation which may be tentatively advanced is that this effect of presorbed oxygen is related to the activation of acetone into the chemisorbed form already shown. The conductivity studies of Bielanski *et al.* (17) and the contact potential measurements of Enikeev *et al.* (18) agree in assigning a positive charge to chemisorbed acetone. Negatively charged oxygen in a chemisorbed layer may then be held to activate physically adsorbed acetone molecules either by a direct polarization or by an influence exerted through the positive holes (Ni^{3+} ions) of the oxidized surface (19). A rise in the over-all heat of adsorption may then be expected.

The correctness or otherwise of this view could be checked by conducting heat of adsorption measurements on oxygenated surfaces at progressively higher temperatures. Not only should the initial heat rise further, but the coverage range over which the effect is observable should increase. At high enough temperatures the activation into the (e) form should proceed without the agency of chemisorbed oxygen, and conductivity studies (17) indicate that this is first achieved on nickel oxide at about 100°C. The presence of chemisorbed oxygen might also be expected to influence the formation of the same complex from isopropanol [see structure (c)]. In this case, however, two bonds have to be broken and the activation energy is probably too prohibitive for the process to be feasible at room temperature. We attribute the absence of a similar enhancement of the isopropanol heat to this distinction.

The result with acetone raises an interesting point with regard to the previously mentioned influence of oxygen in enhancing the rate of dehydrogenation of isopropanol (6). In suggesting that oxygen may function by decreasing the activation energy of adsorption (and hence also of desorption) of acetone, the conclusion is in accord with the view (17) that desorption of acetone is the rate-determining step in isopropanol dehydrogenation.

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