Infrared Radiometry of Thermal Transients on Surfaces. An Approach to the Study of Thermal Effects caused by Gas–Solid Interactions

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THE kinetics and energetics of various gas–solid interactions have been much studied, but because a significant time may elapse between the "start" of a reaction and the first measurement, there is little direct information dealing with the initiation and early stages of most reactions. Such information would be useful, as rapid changes in temperature would certainly effect the kinetics,[1] or might affect the solid such as to exert some influence on the later stages of reaction. Extrapolation to initial conditions could thus be misleading. Measurements of temperature-transients during the early stages of gas-solid interactions are capable, in principle, of giving useful information about such processes. Some temperature effects caused by the rapid adsorption of water on bentonite have been reported[2] but the procedures were obscure and the treatment of data uncertain. We have now examined radiometrically the sorption of gases on supported metals and describe some preliminary results for the sorption of oxygen on nickel to illustrate the techniques involved.

Adsorbents containing 1, 5, and 10 atom-% Ni were prepared[3] by impregnating Cab-O-Sil silica, which was compressed into 1 in. diameter discs mounted on a movable quartz carriage in a high-vacuum cell fitted with a NaCl window. Samples were reduced at 400° with Pd-filtered H_2 for 12 hr., degassed at 10^{-6} torr, and then cooled to room temperature *in vacuo*. Oxygen was then introduced at a pre-determined pressure, and the radiation was monitored by a Kodak Ektron PbS detector connected in a bridge network to an oscilloscope. The radiometer was calibrated with a standard black body emitter similar to that described by Smith and his co-workers,[4] and the emissivity of the sample was taken to be unity.[5]

The maximum temperature rise above ambient temperature, ΔT_m, was obtained after 8 to 12 sec. had elapsed, and, as with the H_2O–bentonite system,[2] the data could be described by the Weibull equation,[6]

$$\Delta T = \Delta T_m[1 - \exp(-wt^n)] \qquad (1)$$

where ΔT is the temperature rise above ambient at t milliseconds, w and n are constants in any one experiment, and ΔT and ΔT_m are given in °C (Figure 1). Some cooling curves were also measured. The decrease in temperature after ΔT_m had been reached could be expressed by the empirical relation,

$$\Delta T = \Delta T_m \exp[- k(t - u^m] \qquad (2)$$

where k, u, and m are constants, and u is the value of t when ΔT_m is reached.

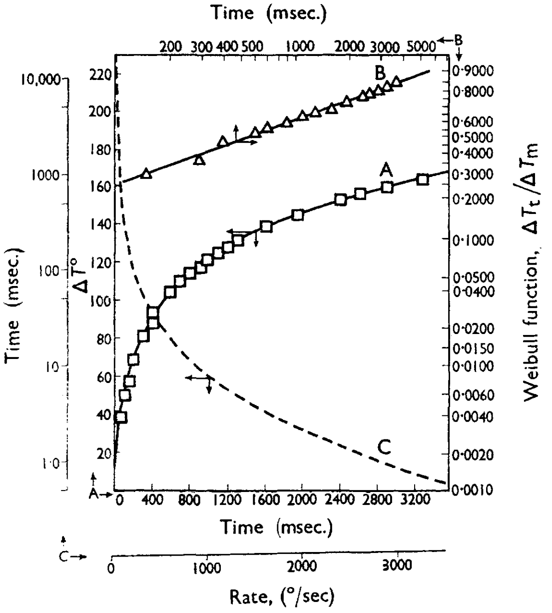

FIGURE 1. *Oxygen sorption on* Ni-SiO_2.

A: ΔT–t *plot, initial* O_2 *pressure* 1·60 *torr*.
The open circles are observed values and were taken from an oscillogram. The solid line was calculated using equation (1) and the values $\Delta T_m = 200°$, $w = 0·0298$, $n = 0·05$, derived from a Weibull plot.

B: *Weibull plot of the data of plot* A.

C: *Rate of temperature rise calculated using the data of plots* A *and* B *and equation* (1).

Equation (1) described the data over long intervals (Figure 1), but deviations frequently occurred, giving abrupt changes in the slopes of Weibull plots, and were ascribed to changes in the values of w and n. Such changes indicate changes in mechanism of the sorption process, by analogy with Elovich plots.[7] The deviations depended on the surface pretreatment.

Changes in Ni particle size may be responsible for other variations in ΔT–t plots, which frequently showed an inflection or "break", *e.g.* Figure 2, much as if an individual plot resulted from the superposition of two thermal processes; interaction of oxygen with the degassed Ni and the formation of a NiO surface, and oxygen chemisorption on NiO and incorporation of oxygen into the NiO. This would explain the occurrence of the break at lower ΔT and t values when the experiment was repeated under conditions where sintering would be expected (Figure 2): if the metal area were reduced, the first process would be less extensive and of shorter duration.

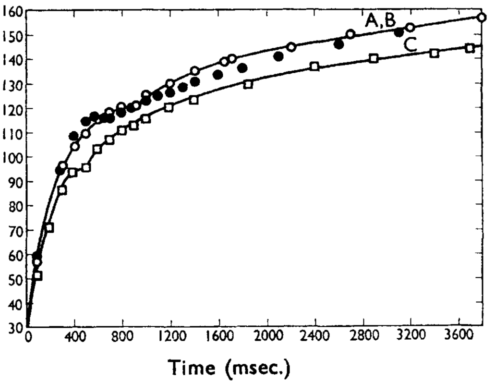

FIGURE 2. *Repetition of sorption experiment.*

The three sets of data shown resulted from sorptions carried out under the same conditions (initial O_2 pressure of 5 torr). Fresh samples prepared under identical conditions were used for A (open circles) and B (filled circles), but C was obtained with the same sample used for B.

Thermal data such as those of Figures 1 and 2 may be used to estimate rates of absorption, sticking probabilities, theoretical ΔT_m, and the like. The validity and application of derived quantities to the mechanism of nickel oxidation will be taken up elsewhere.

Improving the simple device used in these preliminary studies by means of more sensitive and faster detectors should permit the study of more rapid and/or less energetic reactions. The technique would appear to offer a potentially valuable avenue of approach to the study of temperature rises produced on catalysts at the onset of a catalyzed conversion or the burn-off of catalytic "coke."

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